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by

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ABSTRACT

THE EFFECT OF D-ELECTRON CORRELATION ON THE MIXED-VALENCE PHASE OF SAMARIUM SULFIDE

By

Glenn Fletcher

We present the results of calculations made on the two-band Hubbard model. Unlike previous investigators we have included electron correlation in both bands. We have used various approximation schemes to investigate the ground state of the model, in which we calculated the Green function by using the equation of motion decoupling technique of Zubarev.

We have applied the two-band Hubbard model to the problem of mixed-valent systems, in particular to SmS. Schweitzer showed that the Falicov-Kimball model could account for the first-order transition to a mixed-valence phase observed in SmS. We find that including conduction-electron correaltion as an intrasite interaction between electrons of opposite spin (Hubbard model) does not qualitatively change the results of Schweitzer. The critical values of the parameters are changed in a way that should give a better agreement of Schweitzer's results with the experimental values.

DEDICATION

To Maurine, with love.

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I. INTRODUCTION

This thesis contains an analysis of the general problem of two interacting, correlated bands of electrons. Specifically, this model is applied to the description of the mixed-valence compound Samarium Sulfide (SmS).

The problem of electron correlation in narrow bands arises in many areas of solid state physics. For example, the experimental data on the magnetic properties of transition metals seem to require at the same time a localized electron model and an itinerant electron, or band, model for a satisfactory explanation. The observation of non-half-integral atomic moments is difficult to explain with a simple atomic or localized electron picture, while spin waves are usually explained in terms of localized spins. It is believed that correlation effects in the narrow d bands can account for the atomic behavior and therefore for the simultaneous localized and itinerant pictures. Thus, the addition of correlation effects may radically change the expected behavior of a band model of a physical system.

Mixed-valence materials are usually described in terms of the presence, near the Fermi energy, of both f electrons and d electrons, and their interaction. Usually, the f electrons are treated as a highly correlated band with zero bandwidth; i.e., in the atomic limit. The d electrons, on the other hand, are assumed to be in a wide band and correlation effects are ignored. However, the estimated values of the correlation energies of the d electrons are comparable to the interband interaction energies in SmS. This indicates that the effect of the d-electron correlation probably cannot be ignored.

We have started with a model which successfully predicts mixed valence and have added a two-particle interaction between the d electrons. Thus, we are dealing with a two-band model which contains interband and intraband interactions. This model is solved using various approximations and the resulting change in the ground-state properties is investigated.

A. Physical Properties of SmS

Samarium Sulfide (SmS) is one of a large number of materials which exhibits the property of intermediate valence.[1] At atmospheric pressure, SmS is a semiconductor with Sm^{2+} and S^{2-} ions in a NaCl lattice. At a pressure of 6.5 kbar[2], a first order semiconductor-metal transition takes place with a volume decrease of about 10-12% and an increase in conductivity. In addition, experiments indicate that the valence of the Sm ions in the collapsed phase is intermediate between Sm^{2+} and Sm^{3+}.

The samarium atom has the electronic structure $Xe+4f^6 5d^0 6s^2$ and sulfur has $Ne+3s^2 3p^4$. When Sm forms a compound with S, the two outer 6s electrons are given up by the Sm atom. The 5d band broadens due to the crystal

field effects and hybridizes with the 6s band, forming the 5d-6s conduction band. The 4f electrons are relatively unaffected by their surroundings (except for a constant energy shift) since they are highly localized.

At room temperature and pressure, SmS is a semiconductor with a gap of approximately .1 eV between the 4f levels and the conduction band. If we now increase the pressure, the d-band (which is split by the crystal field) broadens and moves closer to the f-levels. Before the gap closes, a first-order insulator-metal transition takes place. During this transition, the volume decreases by about 13%, the conductivity increases, the color changes from black to gold, but the crystal structure remains the same. The volume of SmS vs. pressure is plotted in Figure 1.

Because the volume decreases suddenly and especially because the conductivity increases, the obvious explanation would be that one f-electron per Sm ion has been promoted to the conduction band, leaving behind Sm^{3+} ions. Since Sm^{3+} has a smaller volume than Sm^{2+}, this would account for the volume decrease. In addition, the conduction band would then be occupied, thereby increasing the conductivity. However, other experiments have yielded results which cannot be explained by such a simple model.

The results of the volume measurements (see Figure 1) show that in the collapsed phase the lattice parameter is 30% larger than it should be if all the sites were Sm^{3+}.

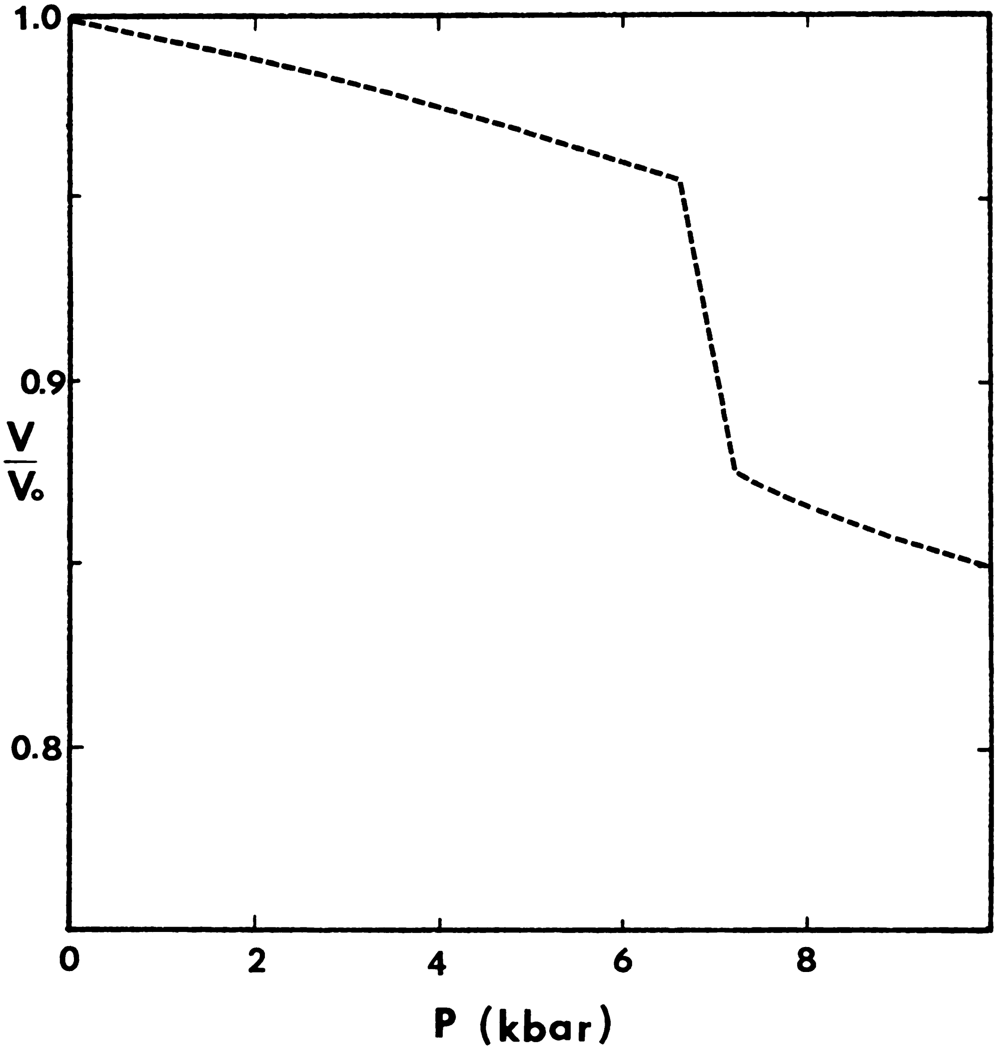


Figure 1. SmS during insulator-metal transition.

Chatterjee et al.[3] have deduced from the lattice data that for SmS the valence is 2.8, which is intermediate between +2, for all sites Sm^{2+}, and +3, for all sites Sm^{3+}. This is the origin of the term "intermediate valence". Another experiment which gives the valence of SmS is that of Campagna et al.[4] Their XPS (x-ray photoemission spectra) data from SmS in the collapsed phase show two peaks which correspond to emission of an f electron from Sm^{2+} and Sm^{3+} ions. This experiment gives a valence which agrees to within 20% of the lattice constant determinations.

From the fact that the valence is not +3, we could infer that not all of the Sm ions lose an f electron to the conduction band. A possible description would be a spatially inhomogeneous distribution of Sm^{2+} and Sm^{3+} ions. However, experiments using the Mossbauer effect to determine the valence in the collapsed phase have also been done[5], with surprising results. Mossbauer experiments provide a measure of the density of the 5s electrons at the nucleus. This density will be different for the Sm^{2+} and Sm^{3+} ions, since the 5s electrons in the latter are screened from the nucleus to a lesser degree. In the collapsed phase, the Mossbauer line is found to be intermediate between the lines expected from the Sm^{2+} and Sm^{3+} ions alone. If the two kinds of ions were simultaneously present at fixed sites, we would expect to see two separate lines.

The physical picture that emerges which includes the experimental results outlined above is as follows: each Sm site is equivalent, with an f electron hopping back and forth between the f level and the conduction band. The lifetime of an f electron at a given site can be determined to within a range of from 10^{-16} sec to 10^{-9} sec. The upper limit is determined from the Mossbauer data. Since only one line is seen, the hopping time must be less than the resolution of the experiment, which is estimated to be 10^{-9} sec. The lower limit is due to the XPS experiments which are estimated to have a time resolution on the order of 10^{-16} sec. This picture of an f electron hopping between the f level and the conduction band is the source of the term "fluctuating valence".

Theoretical models must therefore explain at least the following properties of SmS:

i) A pressure-induced first-order phase transition from a semiconductor to a conductor.

ii) Intermediate or fluctuating valence in the collapsed phase.

iii) A homogeneous distribution of Sm ions with intermediate valence.

B. Theoretical Models

In discussing the various theoretical models which have been suggested to explain the pressure-induced phase transition in SmS, we follow Robinson[1] and separate the theories into two broad categories. The first category consists of those theories which emphasize the Coulomb interaction between the f electrons and the conduction electrons as the principal cause of the transition. These theories are usually based on the model proposed by Falicov and Kimball.[6] The second category of theoretical models includes those in which the electron-lattice interaction is primarily responsible for the transition. We shall compare the two categories briefly and then discuss the electronic models in detail, since these are the theories of interest in this presentation.

Hirst[7] showed that a first-order pressure-induced phase transition may occur if one considers only the volume dependence of the energies of the lattice and the electrons. Physically, his "compression-shift" model proposes that a decrease in the volume of the lattice shifts the energy of the f electrons upward relative to the conduction band and thereby causes them to delocalize. This promotion of the f electrons further compresses the lattice, since the ionic size decreases after losing an f electron. Then the parameters can be adjusted to produce a first-order phase transition. In order to prevent the collapse from proceeding all the way to +3 valence (in which one electron/site is promoted to the conduction band), Hirst considered a volume dependent bulk modulus which increases with compression.

Others have considered models which rely on the electron-lattice interaction. Varma and Heine[8] proposed a model very similar to that of Hirst, in which the elastic energy depends on the different ionic volumes. The stability of their model depends on a nonlinear lattice contraction with volume change. The nonlinearity is treated as an adjustable parameter and they are able to achieve agreement to within 20% of the experimental results. Their model neglects all Coulomb correlations.

Coqblin and Blandin[9] presented a model in which the compression-shift mechanism is responsible for the first-order phase transition. However, they use the virtual bound states of Friedel-Anderson[10] to broaden the f level and allow for the possibility of non-integral valence.

Others have used the periodic Anderson[10] model,using electron-phonon interactions to bring about the phase transition. For example, Entel, Leder, and Grewe[11] use the periodic Anderson model, which consists of an Anderson local impurity at each site which can exchange electrons with the conduction band. They claimed that within the Hartree-Fock approximation it is not possible to have a discontinuous transition with a periodic array of Anderson impurities alone. They included the interaction of 4f electrons with the longitudinal optical phonons which can shift the 4f electron energies and can induce 4f-5d interband transitions, thereby renormalizing the explicit hybridization and bringing about a discontinuous change in the number of f electrons.

The models considered so far have assumed that the f electrons are delocalized through promotion into the conduction band. However, Hall coefficient measurements[12] on $Sm_{.75}Y_{.25}S$, which is an example of chemically collapsed SmS by the introduction of Y atoms, suggest that the extra electron doesn't go into the conduction band. In addition, optical experiments[13] done on SmS in the semiconducting phase show rather narrow peaks in the d band. This experimental evidence, along with the difficulty in explaining the magnetic properties of SmS in the collapsed phase, led Kaplan and Mahanti[14] to propose an excitonic or "essentially localized" model in which all but a few (about .1 electron/ion) of the electrons are localized. So for SmS the transition is predominantly f^6 to f^5d_l, where d_l stands for a localized d electron. Since the one-electron mixing interaction between $l=2$ and $l=3$ orbitals on the same site vanishes by inversion symmetry, Kaplan and Mahanti suggested that two Sm sites simultaneously mix f and d electrons. This avoids the symmetry difficulty. In order to explain the phase transition, Mahanti et al.[15] added the elastic energy of the lattice and were able to predict a discontinuous valence change by the compression-shift mechanism.

In the lattice model, the compression-shift mechanism gives a sharp transition and the stiffness of the lattice halts the valence change at a non-integral value. In the electronic models, which we now consider, the volume change is treated as an effect rather than as the cause of

the transition, with the f electron-conduction electron Coulomb interaction being the cause.

When a Samarium ion gives up an f electron to the conduction band, there is a residual interaction between the conduction electron and the "f hole" left behind. This interaction is usually attractive, even when screening is taken into account. This attractive force lowers the energy of the conduction band, so that as more f electrons are promoted to the conduction band, it lowers further, allowing more f electrons to enter it, and so on. This is the mechanism for the insulator-metal transition suggested by Ramirez, Falicov, and Kimball[6]. This model has been studied by many authors[16] and will be discussed in detail in Section II.

The model proposed by Ramirez, Falicov, and Kimball was solved by them in the mean-field approximation. They found that for different values of G, the electron-hole interaction strength, they could predict either a first-order or a continuous phase transition. However, the discontinuous phase transition is always to a state in which all ions are Sm^{3+}; i.e., each Sm ion has given up an f electron and intermediate valence is precluded.

In order to predict a first-order transition to an intermediate valence state, many authors[17] have added a hybridization term to the Falicov-Kimball Hamiltonian which mixes the localized and itinerant electrons. This gives the f level a finite width by giving the f electrons a finite lifetime. It is then possible to have the Fermi energy pinned inside the f band, producing intermediate valence. This also accounts for the large density of states at the Fermi energy which is indicated by the large electronic specific heat.[18]

Khomskii and Kocharjan[19] attempted to obtain an intermediate valence state without an explicit hybridization term in the Hamiltonian. They started with the Falicov-Kimball model (for a single impurity) and made a mean-field approximation in which they retained terms which represent the quantum mechanical admixture of f electrons and conduction electrons. Therefore, in their solution, the f electron-conduction electron mixing arises from the Coulomb interaction, G. With this approximation scheme they found first-order phase transitions to intermediate valence states. However, hewson and Riseborough[20] showed that this problem is exactly soluble and that the first-order transition found by Khomskii and Kocharjan is probably due to their approximation.

Although it is likely that mixing terms, either one- or two-particle, are necessary to explain the ground-state and low lying excitation properties (susceptibility, neutron form factor, etc.) of mixed-valence systems, it was shown by Schweitzer[21] that these terms may not be necessary to account for the phase transition to mixed valence. He derived an approximate solution to the Falicov-Kimball model in which a first-order transition to a state with

intermediate valence is possible. However, since he did not include a mixing term, his solution must be an inhomogeneous distribution of Sm^{2+} and Sm^{3+} ions. Presumably, a small mixing term would give a homogeneous mixed-valence ground state without affecting his results. His approximation included exciton-like correlations between f electrons and conduction electrons. Schweitzer's work will be discussed in Section II.

C. d Electron Correlation

The conduction electrons in the collapsed phase of SmS move in a band made up from 5d and 6s bands. These electrons will be referred to as d electrons. In all of the previous models for the phase transition of SmS, the Coulomb interaction between d electrons has been neglected. Schweitzer's approximation includes exciton-type correlations which tend to localize d electrons around f holes. However, localization can also take place due to the mutual repulsion of the d electrons. A calculation[22] of the Coulomb correlation energy in transition metals gives values of U/W between .3 and .8, where U is the Coulomb correlation and W is the bandwidth. No such calculation exists at present for the 5d band in the rare earths. However, rough estimates can be made which predict values of U/W on the order of .5 eV. Since this is the range of values for the f-d interaction, G/W, it is not obvious that the d-electron Coulomb repulsion can be excluded without affecting the phase transition.

The model we consider here is essentially a two-band Hubbard[23] model with correlation in both bands. This model is interesting in its own right. In addition we believe that it has an important application in the area of intermediate valence systems. We shall refer to this model as the "two-band model" in the remainder of this thesis.

In Section II we discuss the Falicov-Kimball model and the approximate solutions due to Ramirez, Falicov, and Kimball and due to Schweitzer. In Section III we discuss electron correlation in narrow bands and the Hubbard model. Section IV contains a description of the model being considered here, along with two approximate solutions, in which the d-electron correlation is treated in a mean-field approximation. The two-band model is exactly soluble in the infinitely-narrow-bandwidth limit and the solution is discussed in Section V. An intermediate solution is discussed in Section VI, in which the Hubbard decoupling scheme is applied to the two-band model, using the exact solution of section V. An improved approximate decoupling scheme is derived in Section VII along with the results of calculations made using this approximation. A summary and conclusions are presented in Section VIII.

II. THE FALICOV-KIMBALL MODEL

In order to explain the metal-insulator transitions observed in various materials, Falicov and Kimball[6] proposed a model in which both localized and itinerant quasiparticle states exist simultaneously. The interaction responsible for the electronically driven phase transition is taken to be the intra-atomic Coulomb repulsion between the two kinds of quasiparticles.

This model was applied to the α-δ phase transition in metallic Ce by Ramirez and Falicov. They assumed that there are two different types of electron states: (a) an extended, uncorrelated band, obtained from hybridized s- and d-like Bloch states and (b) a set of localized, highly correlated f-like states. The mechanism for the phase transition is the short-range Coulomb interaction matrix element between f-states and conduction-band states.

The Hamiltonian first introduced by Falicov and Kimball can be written

$$H = \sum_{\vec{k}\sigma} \varepsilon(k) a^{+}_{\vec{k}\sigma} a_{\vec{k}\sigma} + \sum_{i\sigma} E b^{+}_{i\sigma} b_{i\sigma} - G \sum_{i\sigma\sigma'} b^{+}_{i\sigma} a^{+}_{i\sigma'} a_{i\sigma'} b_{i\sigma} , \qquad (1)$$

where $a^{+}_{\vec{k}\sigma}$ ($a_{\vec{k}\sigma}$) creates (destroys) an electron in state k with spin σ and energy $\varepsilon(k)$, $b^{+}_{i\sigma}$ creates a hole with spin σ at site i with energy E, and

$$a^{+}_{i\sigma'} = \frac{1}{\sqrt{N}} \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{R}_i} \, a^{+}_{\vec{q}\sigma'} \quad . \tag{2}$$

They assumed the interaction strength, G, is positive, corresponding to an attractive electron-hole force.

A. The Ramirez, Falicov, and Kimball Approximation

The Falicov-Kimball model was solved for the case of a finite bandwidth by Ramirez, Falicov, and Kimball[6] in the Hartree (or mean-field) approximation. The last term in the Hamiltonian, which represents the interaction between itinerant and localized quasiparticles at the same site, can be written as

$$- G \sum_{i\sigma\sigma'} b^{+}_{i\sigma} a^{+}_{i\sigma'} a_{i\sigma'} b_{i\sigma} \rightarrow - G \sum_{\sigma} \langle b^{+}_{\sigma} b_{\sigma} \rangle \sum_{i\sigma'} a^{+}_{i\sigma'} a_{i\sigma}$$

$$= -Gn_c \int_{-\infty}^{\infty} \rho(\varepsilon) f(\varepsilon) d\varepsilon \quad , \tag{3}$$

where n_c is the number of conduction electrons/site, which equals the number of f-holes/site; $f(\varepsilon)$ is the Fermi function and $\rho(\varepsilon)$ is the density of states for electrons with both spins in the conduction band. Since for a non-interacting band

$$\sum_{\vec{k}\sigma} \varepsilon(\vec{k}) \, \langle a^{+}_{k\sigma} a_{k\sigma} \rangle = \int_{-\infty}^{\infty} \rho(\varepsilon) f(\varepsilon) d\varepsilon \quad , \tag{4}$$

if we set E = 0, we obtain for the total energy

$$E = \int_{-\infty}^{\infty} (\varepsilon - n_c\ G)\rho(\varepsilon)f(\varepsilon)d\varepsilon \ . \qquad (5)$$

For the ground state, T →0 and $f(\varepsilon) \rightarrow \theta(\mu-\varepsilon)$, where

$$\theta(x) = \begin{cases} 1 & x>0 \\ 0 & x<0 \end{cases} \qquad (6)$$

and μ is the chemical potential or Fermi energy. Then at zero temperature

$$E = \int_{-\infty}^{\mu} (\varepsilon - n_c\ G)\rho(\varepsilon)d\varepsilon \ . \qquad (7)$$

The chemical potential is determined from the constraint equation

$$n_cN = \int_{-\infty}^{\mu} \rho(\varepsilon)d\varepsilon \ . \qquad (8)$$

The density of states, $\rho(\varepsilon)$, is derived from the Green function for the itinerant electrons. In the mean-field approximation the Green function is easily found, since the first equation of motion is exactly soluble. (See Appendix A) If we define the Fourier transform of the double-time Green function by

$$G^{\sigma}(k,\omega) = \langle\langle a_{\vec{k}\sigma};\ a^{+}_{\vec{k}\sigma}\rangle\rangle_{\omega} \ , \qquad (9)$$

it satisfies the equation of motion

$$\omega\langle\langle a_{\vec{k}\sigma};a^{+}_{\vec{k}\sigma}\rangle\rangle_{\omega} = \langle\ a_{\vec{k}\sigma},a^{+}_{\vec{k}\sigma}\ \rangle + \langle\langle\ a_{\vec{k}\sigma},H\ ;a^{+}_{\vec{k}\sigma}\rangle\rangle \ . \qquad (10)$$

Using the Hamiltonian (1) we have

$$a_{\vec{k}\sigma}, H = \varepsilon(k) a_{\vec{k}\sigma} - 2Gn_c a_{\vec{k}\sigma} \qquad (11)$$

and, using the fact that $a_{\vec{k}\sigma}, a^{+}_{\vec{k}\sigma} = 1$, we find

$$\omega << a_{\vec{k}\sigma}; a^{+}_{\vec{k}\sigma} >> = 1 + \{\varepsilon(\vec{k}) + 2Gn_c\} << a_{\vec{k}\sigma}; a^{+}_{\vec{k}\sigma} >> \qquad (12)$$

or

$$G^{\sigma}(\vec{k},\omega) = \{\omega - \varepsilon(\vec{k}) - 2n_c G\}^{-1} . \qquad (13)$$

The density of states is given by

$$\rho(\omega) = \frac{1}{\pi} \operatorname{Im} \sum_{\vec{k}\sigma} G^{\sigma}(\vec{k}, \omega - i0^{+}) \qquad (14)$$

and we get $\rho(\omega) = \rho_0 \ (\omega - 2n_c G)$, (15)

where $\rho_o \ (\omega)$ is the unperturbed density of states.

So, the unperturbed density of states is rigidly shifted by $2n_c G$. Ramirez, Falicov, and Kimball used for their unperturbed density of states an approximation to a simple-cubic lattice. In order to compare their results with the approximation due to Schweitzer (to be discussed later), we shall use the semi-elliptic density of states given by

$$\rho_0(\omega) = \frac{8}{\pi W^2} \sqrt{W^2/4 - \varepsilon^2} \ , \qquad (16)$$

where W is the bandwidth. This is plotted in Figure 2, along with the effect of the interaction in the mean-field approximation, Eq. (15).

The occupation of the conduction band at zero temperature is obtained by finding the absolute minimum of the total energy with respect to n_c, the number of con-

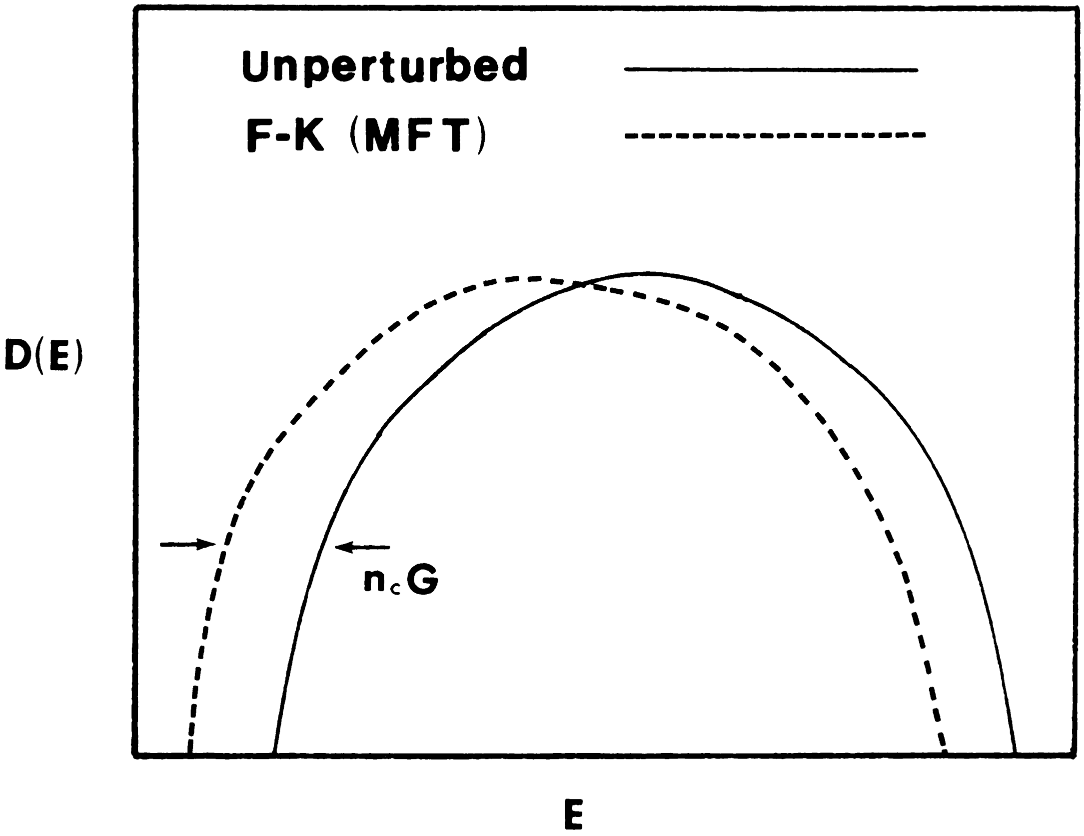


Figure 2. Density of states in Falicov-Kimball approx.

duction electrons. This was done for various values of G and Δ, the gap energy, which is the energy difference between the localized levels and the bottom of the conduction band. The results are shown in Figure 3. Whether the transition is first order or sicond order depends on the value of G.

In Figure 4 we plot a phase diagram in which the parameters are G and . As was shown above, there are first and second order transitions possible where n_c goes from 0 to 1. However, there is no region of intermediate valence that can be reached by a first order transition.

As we discussed in the introduction, there have been many attempts[17] to modify the Ramirez, Falicov, and Kimball model in order to explain intermediate valence. However, we will describe in the next section an approximate solution of the Falicov-Kimball model due to Schweitzer which goes beyond the mean-field approximation and is able to predict intermediate valence states.

B. The Schweitzer Approximation

Schweitzer[21] assumed for the Falicov-Kimball Hamiltonian the idealized model

$$H = \sum_{i\sigma} (\varepsilon_f n^f_{i\sigma} + \frac{U^{ff}}{2} n^f_{i\sigma} n^f_{i\sigma}) + \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) n^d_{\vec{k}\sigma}$$

$$+ \frac{G}{N} \sum_{i\sigma\sigma'} n^f_{i\sigma'} n^d_{i\sigma} \quad , \qquad (17)$$

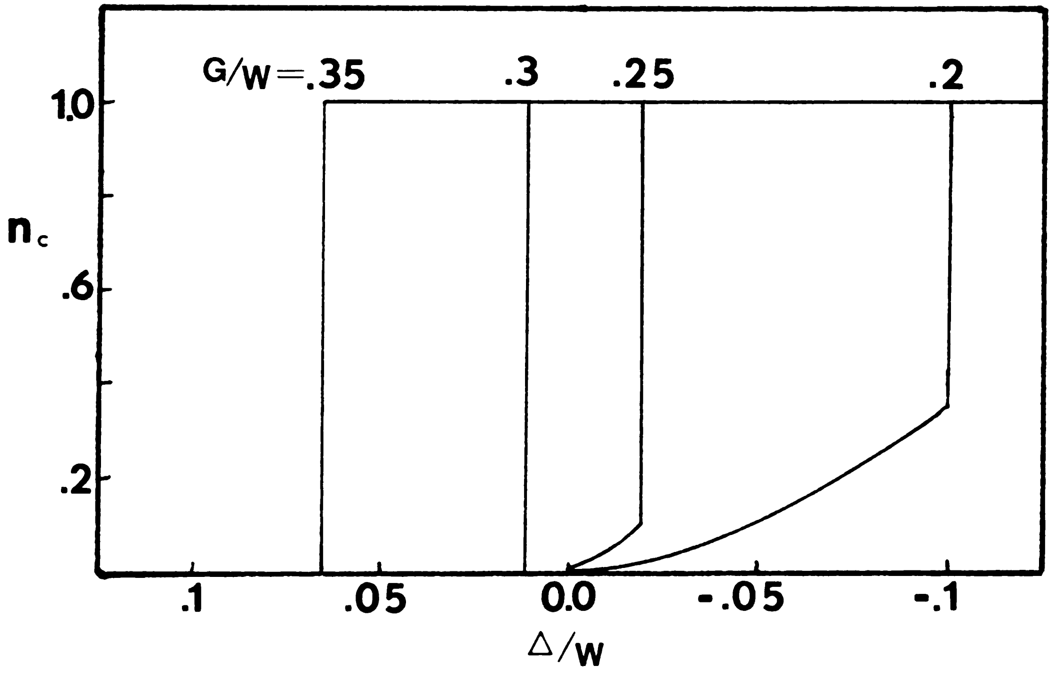


Figure 3. n_c vs. band gap in Falicov-Kimball approx.

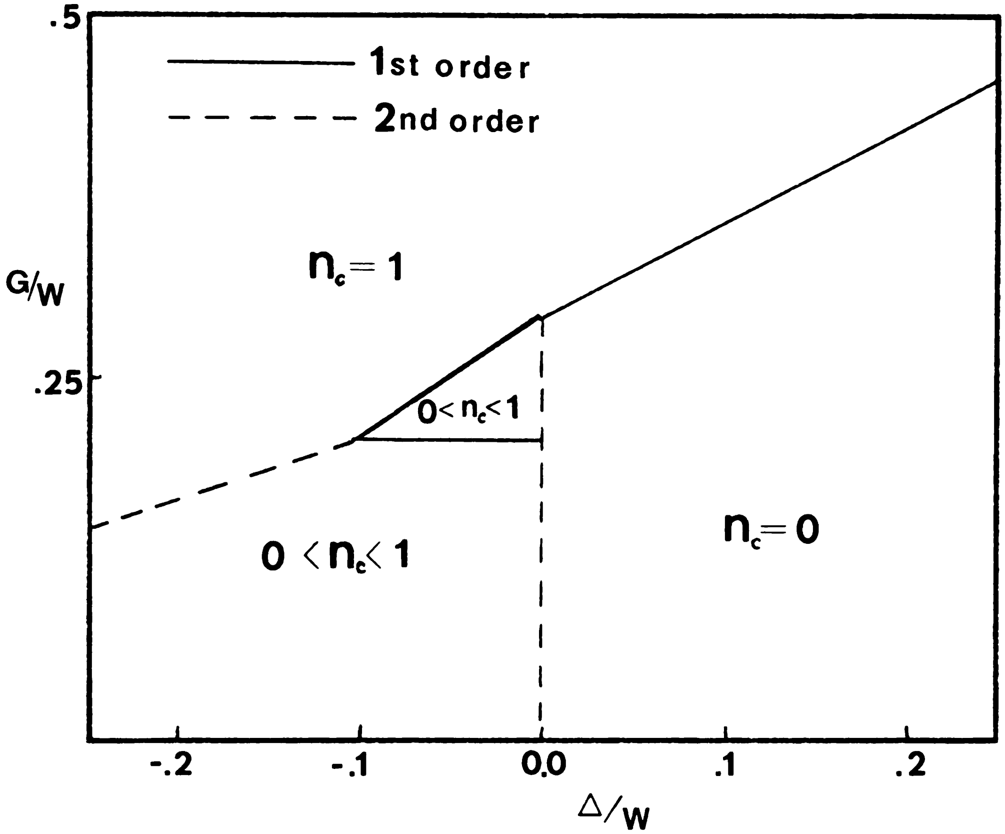


Figure 4. Phase diagram for Falicov-Kimball approx.

where $n^f_{i\sigma}$ is the number operator which counts the number of localized electrons with spin $-\sigma$ and energy ε_f at site i, $n^d_{\vec{k}\sigma}$ counts the number of itinerant electrons with spin σ and energy $\varepsilon(\vec{k})$, and

$$n^d_{i\sigma} = \frac{1}{N} \sum_{\vec{k}\vec{k}'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_i} c^+_{\vec{k}'\sigma} c_{\vec{k}\sigma} . \tag{18}$$

U^{ff} is the intra-atomic Coulomb correlation energy of a localozed electron and G is the f-d interaction.

For the case of SmS, the localized states correspond to the 4f levels of Sm. The state with two "f-electrons" corresponds to the $4f^6$ configuration and the state with one "f-electron" corresponds to the $4f^5$ configuration. The state with zero "f-electrons" is projected out due to the large U^{ff}; i.e.,

$$<(1 - n^f_{i\sigma})(1 - n^f_{i\sigma})> = <\bar{n}^f_{i\sigma}\ \bar{n}^f_{i\sigma}> = 0 , \tag{19}$$

where $\bar{n}^f_{i\sigma}$ counts the number of holes at site i with spin σ.

It should be pointed out here that since the f electron number operator, $n^f_{i\sigma}$, commutes with the Hamiltonian, Eq. (17), the number of f electrons at site i is a good quantum number and therefore a homogeneous mixed-valence ground state is ruled out. However, a small hybridization or f-d mixing term should be included in order to give a homogeneous mixed-valence state without affecting the phase transition.

The total energy is completely determined as a function of n_c by the conduction electron Green function. It can be shown that, since the conduction band is non-interacting,

$$\varepsilon(n_c)/N = (2\varepsilon_f + U^{ff}) - (\varepsilon_f + U^{ff})n_c + 2\int_{-\infty}^{\infty} \varepsilon\rho^{\sigma}(\varepsilon)f(\varepsilon)d\varepsilon \ , \qquad (20)$$

where

$$\rho^{\sigma}(\varepsilon) = -\frac{1}{\pi N} \ \mathrm{Im} \sum_{\vec{k}} G_c^{\sigma} \ (k,\varepsilon+i0^{+}) \ . \qquad (21)$$

We define the gap parameter Δ to be the energy required to excite an electron out of the localized state into a state at the bottom of the band, ignoring excitonic correlations. Then

$$\Delta = (\varepsilon_f + 2G + \varepsilon_d - W/2) - (2\varepsilon_f + U^{ff}) \ . \qquad (22)$$

Ignoring the constant first term in (20), we can write the energy per particle as

$$\varepsilon(n_c)/N = (\Delta - \varepsilon_d + W/2 - 2G)n_c + 2\int_{\infty}^{\infty} \varepsilon\rho^{\sigma}(\varepsilon)f(\varepsilon)d\varepsilon \ . \qquad (23)$$

In order to derive the Green function in Schweitzer's approximation, we again use the equation of motion method. Since Schweitzer did not make the Hartree approximation, the decoupling of the equations of motion was made by using the following approximation:

$$\sum_{\sigma\sigma'} \langle\langle \bar{n}^{f}_{i\sigma'} \bar{n}^{f}_{j\sigma''} c_{i\sigma};c^{+}_{\vec{k}\sigma}\rangle\rangle \simeq n_c \sum_{\sigma'} \langle\langle \bar{n}^{f}_{i\sigma'} c_{i\sigma};c^{+}_{\vec{k}\sigma}\rangle\rangle$$

$$+ n_c \sum_{\sigma'} \langle\langle \bar{n}^{f}_{i\sigma'} c_{j\sigma}; c_{\vec{k}\sigma}\rangle\rangle - n_c^2 \langle\langle c_{i\sigma};c^{+}_{\vec{k}\sigma}\rangle\rangle . \qquad (24)$$

This approximation terminates the hierarchy of equations of motion by writing three-particle Green functions in terns of two-particle Green functions. The third term in (24) is necessary to avoid double-counting. Phisically, this approximation corresponds to two particles "propagating" in the presence of the "mean field" of the third particle. The two-particle Green function can be thought of as representing a particle in the d band and a hole in the f band propagating together and for this reason , Schweitzer refers to these terms as "exciton-like correlations".

Using the above approximation and Eq. (10), Schweitzer obtained the following Green function:

$$G^{\sigma}(\vec{k},\omega) = \{\omega - \varepsilon(\vec{k}) - \Sigma(\omega)\}^{-1} , \qquad (25)$$

where

$$\Sigma(\omega) = (2 - n_c)G + \frac{n_c(1-n_c)G^2F\{\omega-(2-n_c)G\}}{1+(1-2n_c)GF\{\omega-(2-n_c)G\}} \qquad (26)$$

and

$$F(\omega) = \frac{1}{N} \sum_{\vec{k}} \frac{1}{\omega-\varepsilon(\vec{k})} \quad . \qquad (27)$$

We can obtain the perturbed density of states from the imaginary part of the Green function, as in Eq. (21). (See Figure 5.) At zero temperature, the number n_c of conduction electrons/site is determined from the absolute minimum of the total energy. We have plotted the results for various values of the parameters in Figure 6. In addition, the phase diagram is plotted in Figure 7. It

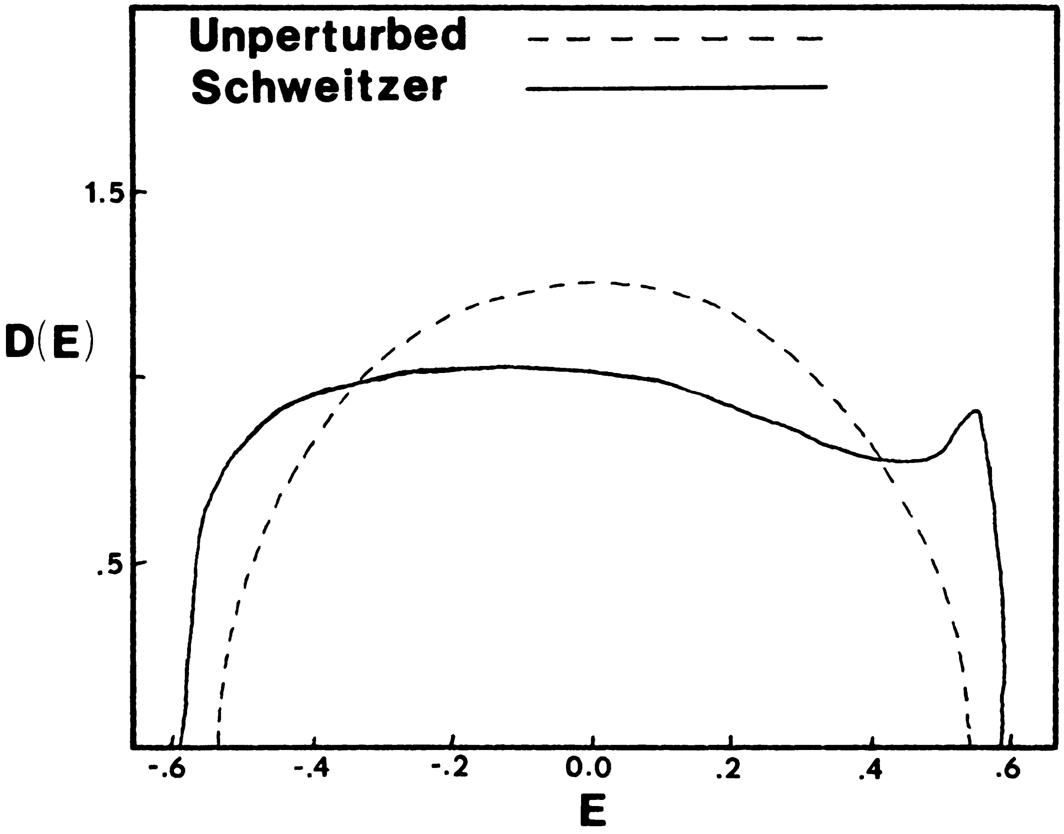


Figure 5. Density of states in Schweitzer approx.

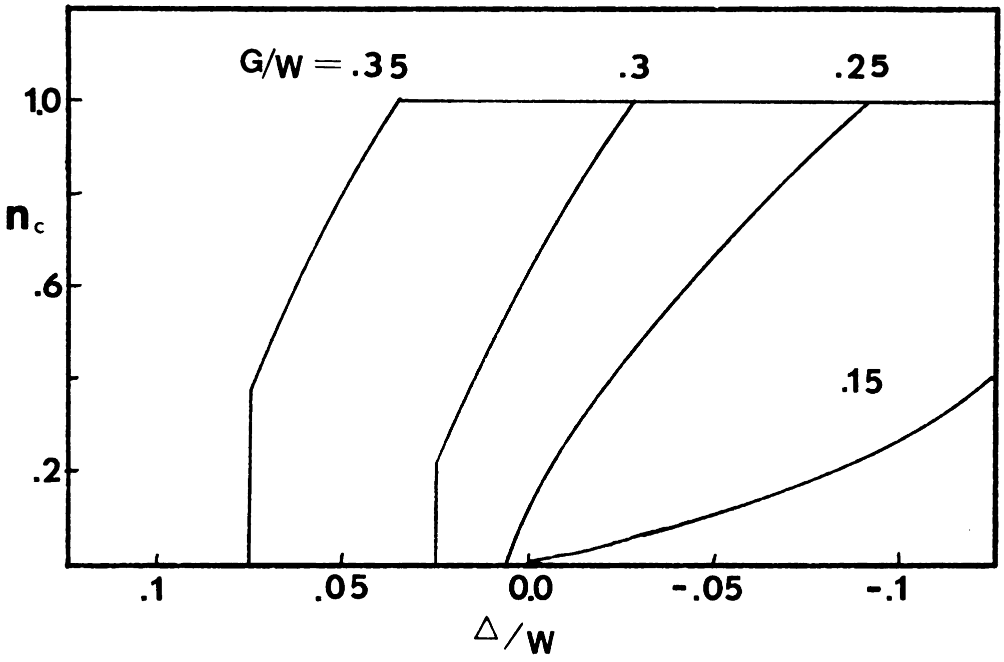


Figure 6. n_C vs. band gap in Schweitzer approx.

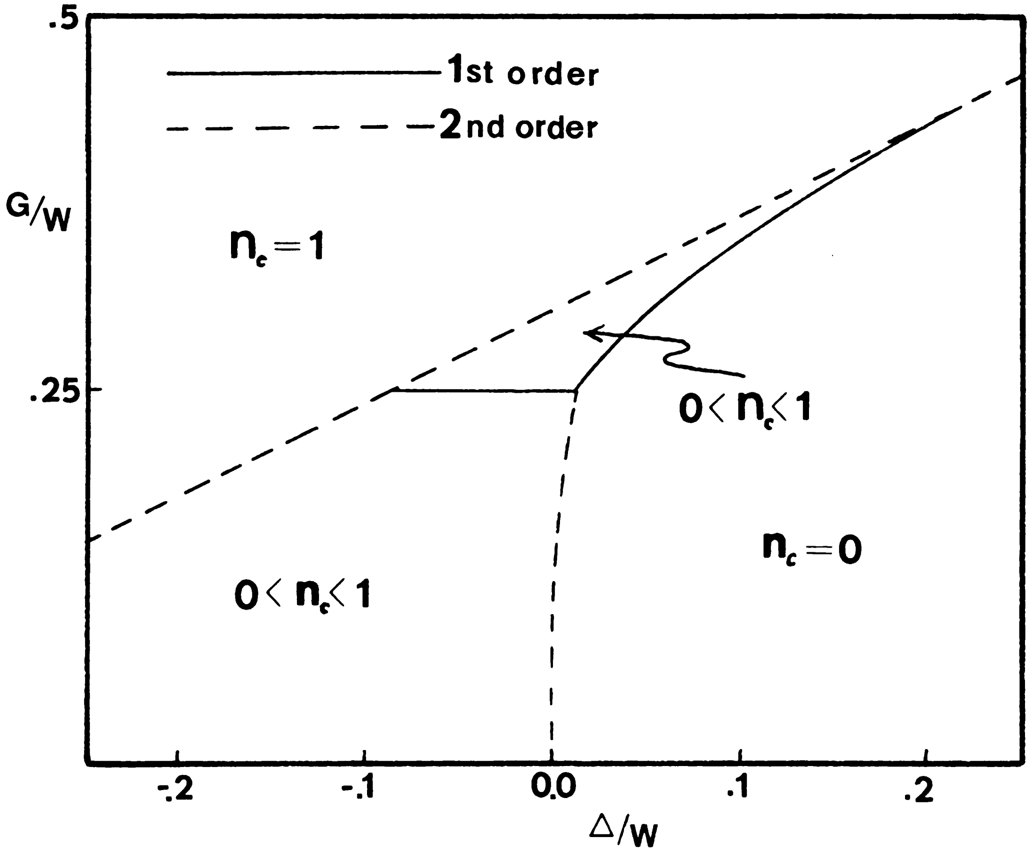


Figure 7. Phase diagram for Schweitzer approx.

is clear from Figure 7 that there is a region in which there is intermediate valence and which can be reached by a first order transition.

Schweitzer's approximate solution of the Falicov-Kimball model is able to produce a first order transition to an intermediate valence state. However, the Falicov-Kimball model neglects correlation in the conduction band. In Section IV we present a model which extends the Falicov-Kimball model to include d-electron correlation. Section III contains a summary of the Hubbard[23] model and the Hubbard approximation, which forms the basis for our treatment of the d-electron correlation.

III. THE HUBBARD MODEL FOR ELECTRON CORRELATION

In this section we introduce d-electron correlation and discuss how it will be treated within the Green function technique. We discuss the Hubbard[23] model of correlation in narrow bands and the Hubbard I[24] approximation. Hubbard considered a single narrow band, built from Bloch functions, in which electrons interact when two electrons are in Wannier orbitals on the same atom. Thus, Hubbard only considered intra-atomic interactions among electrons in the band. The Hubbard Hamiltonian is given by

$$H = \sum_{ij\sigma} \varepsilon_{ij} c^{+}_{i\sigma} c_{j\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}} , \qquad (1)$$

where $c^{+}_{i\sigma}$ creates an electron at site i with spin σ and $n_{i\sigma}$ is the corresponding number operator; $n_{i\bar{\sigma}} = c^{+}_{i\bar{\sigma}} c_{i\bar{\sigma}}$.

A. The Atomic Limit

Hubbard first considered the limiting case of zero bandwidth, which corresponds to negligible overlap of the d-electron wavefunctions on different atoms. This reduces the problem to a system of isolated atoms and atomic theory gives the exact solution. The method of Green functions also gives the exact results, as we now show.

Following Hubbard we use the mithod of double-time Green functions (see Appendix A). We define the center of the band by

$$T_0 = \frac{1}{N} \sum_{\vec{k}} \varepsilon(\vec{k}) \quad . \qquad (2)$$

In the limit of zero bandwidth, $\varepsilon(\vec{k}) \to T_o$, so that

$$\varepsilon_{ij} = \frac{1}{N} \sum_{\vec{k}} \varepsilon_{\vec{k}} e^{i\vec{k}\cdot(\vec{k}_i - \vec{k}_j)} \to T_o \delta_{ij}. \tag{3}$$

The Hamiltonian of Eq. (1) now becomes

$$H = T_o \sum_{i\sigma} n_{i\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i\bar{\sigma}}. \tag{4}$$

The Green function is defined as

$$G^{\sigma}_{ij}(E) = \langle\langle C_{i\sigma}; C^{+}_{j\sigma} \rangle\rangle_E. \tag{5}$$

The equation of motion for this Green function is given by

$$E \langle\langle C_{i\sigma}; C^{+}_{j\sigma} \rangle\rangle = \langle [C_{i\sigma}, C^{+}_{j\sigma}]_{+} \rangle + \langle\langle [C_{i\sigma}, H]; C^{+}_{j\sigma} \rangle\rangle. \tag{6}$$

Using (4),

$$[C_i, H] = T_o C_i + U n_{i\sigma} C_{i\sigma} \tag{7}$$

and since $[C_{i\sigma}, C^{+}_{j\sigma}] = \delta_{ij}$, we get

$$E G^{\sigma}_{ij}(E) = \delta_{ij} + T_o G^{\sigma}_{ij}(E) + U \Gamma^{\sigma}_{ij}(E) \tag{8}$$

where

$$\Gamma^{\sigma}_{ij}(E) = \langle\langle n_{i\sigma} C_{i\sigma}; C^{+}_{j\sigma} \rangle\rangle . \tag{9}$$

If we now write the equation of motion for $\Gamma^{\sigma}_{ij}(E)$, we get a term proportional to

$$\langle\langle n^2_{i\sigma} C_{i\sigma}; C^{+}_{j\sigma} \rangle\rangle.$$

Since $n^2_{i\bar{\sigma}} = n_{i\bar{\sigma}}$ for fermions, the sequence of equations of motion is terminated and we get

$$\Gamma^{\sigma}_{ij}(E) = \frac{\delta_{ij} < n_{i\bar{\sigma}}>}{E - T_o - U} \, . \tag{10}$$

$n_{i\bar{\sigma}}$ is independent of i and σ (paramagnetic limit) so that $n_{i\bar{\sigma}} = n/2$. Finally we obtain

$$G^{\sigma}_{ij}(E) = \delta_{ij} \left[\frac{1 - n/2}{E - T_o} + \frac{n/2}{E - T_o - U} \right] . \tag{11}$$

The density of states is given by

$$\rho^{\sigma}(E) = \frac{1}{2\pi i} \sum_j \left[G^{\sigma}_{ij}(E - io^+) - G^{\sigma}_{ij}(E + io^+) \right]$$

$$= (1 - n/2)\, \delta(E - T_o) + n/2\, \delta(E - T_o - U) . \tag{12}$$

B. Finite Bandwidth

Hubbard next considered the case of finite bandwidth, which involved additional terms requiring approximations. In order to terminate the hierarchy of equations of motion, he used the following approximations:

$$<<n_{i\bar{\sigma}} c_{k\sigma}; c^+_{j\sigma}>> \simeq <n_{i\bar{\sigma}}> <<c_{k\sigma}; c^+_{j\sigma}>>$$

$$<<c^+_{i\bar{\sigma}} c_{k\bar{\sigma}} c_{i\sigma}; c^+_{j\sigma}>> \simeq <c^+_{i\bar{\sigma}} c_{k\bar{\sigma}}> <<c_{i\sigma}; c^+_{j\sigma}>> \tag{13}$$

$$<<c^+_{k\bar{\sigma}} c_{i\bar{\sigma}} c_{i\sigma}; c^+_{j\bar{\sigma}}>> \simeq <c^+_{k\sigma} c_{i\bar{\sigma}}> <<c_{i\sigma}; c^+_{j\sigma}>> \, .$$

The condition that Hubbard set is that the resulting Green function reduce to the correct zero-bandwidth result.

Instead of reproducing Hubbard's derivation of the finite-bandwidth problem, we present here an alternate derivation introduced by Doniach.[25] This method will be used later on the two-band Hubbard model being considered in this thesis.

Doniach observed that for the usual tight-binding model of band theory, where

$$H_{TB} = \sum_{ij\sigma} \varepsilon_{ij} C^{+}_{i\sigma} C_{j\sigma} = \sum_{i\sigma} T_o n_{i\sigma} + \sum_{\substack{i\neq j\\ \sigma}} \varepsilon_{ij} C^{+}_{i\sigma} C_{j\sigma}, \tag{14}$$

the Green function defined by

$$G^{\sigma}_{ij}(E) = \langle\langle C_{i\sigma}; C^{+}_{j\sigma}\rangle\rangle \tag{15}$$

satisfies the equation of motion

$$(E - T_o) G^{\sigma}_{ij}(E) = \delta_{ij} + \sum_{\ell\neq i} \varepsilon_{i\ell} G^{\sigma}_{\ell j}(E). \tag{16}$$

If we Fourier transform the Green function we get

$$G^{\sigma}(\vec{k},E) = \frac{1}{E-\varepsilon(\vec{k})+io^{+}} \quad . \tag{17}$$

Equation (16) can be written as a perturbation series by iterating $G^{\sigma}_{ij}(E)$:

$$\begin{aligned} G^{\sigma}_{ij} &= G_{empty} + G_{empty}\varepsilon_{ij}G_{empty} \\ &\quad + G_{empty} \sum_{\ell}{}' \varepsilon_{i\ell}\, G_{empty}\, \varepsilon_{\ell j} G_{empty} + ---- \end{aligned} \tag{18}$$

where

$$G_{\text{empty}} = \frac{1}{E-T_o+io^+} \tag{19}$$

is the propagator for the empty atom.

Hubbard's decoupling procedure is equivalent to a generalization of (18) in which G_{empty} is replaced by the atomic-limit solution, equation (11). Thus,

$$G^{\sigma}_{ij}(E) = G^{\sigma}_{\text{atomic}}\delta_{ij} + G^{\sigma}_{\text{atomic}} \sum_{\ell} \varepsilon_{i\ell}G^{\sigma}_{\ell j}(E). \tag{20}$$

Taking the Fourier transform yields

$$G^{\sigma}(\vec{k},E) = \frac{1}{\left[G^{\sigma}_{\text{atomic}}\right]^{-1} - \varepsilon(\vec{k}) + T_o}$$

$$= \frac{1}{(E-T_o)\dfrac{E-T_o-U}{E-T_o-U(1-\frac{n}{2})} + T_o - \varepsilon(\vec{k})} \tag{21}$$

which is the same as that derived by Hubbard.

So, physically, Hubbard's decoupling scheme is equivalent to starting with the exact isolated-atom limit and then turning on the "hopping" term and letting the electrons propagate to nearest neighbors with a probability given by ε_{ij}.

Since the Hubbard model is concerned with a band of interacting electrons, the total ground-state energy is given by (see Appendix B)

$$E = \sum_{\vec{k}\sigma} \int_{-\infty}^{\mu} \frac{[\varepsilon(\vec{k})+\omega]}{2} A^{\sigma}(\vec{k},\omega)d\omega, \tag{22}$$

where μ is obtained from the constraint

$$n_c N = \sum_{\vec{k}\sigma} \int_{-\infty}^{\mu} A^{\sigma}(\vec{k},\omega)\,d\omega \tag{23}$$

and

$$A^{\sigma}(\vec{k},\omega) = \frac{1}{2\pi i}\left[G^{\sigma}(\vec{k},\omega-i0^{+}) - G^{\sigma}(\vec{k},\omega+i0^{+})\right] \tag{24}$$

is the single particle spectral weight function.

IV. THE TWO-BAND MODEL WITH MEAN-FIELD SOLUTIONS

The model which we present in this section is that of Falicov and Kimball[6] plus the addition of the d-electron correlation. The interaction between the electrons in the conduction band is included as an intrasite interaction, as in the Hubbard model (see Section III). The Hamiltonian is

$$H = \sum_{i\sigma} \left(\varepsilon_f n^f_{i\sigma} + \frac{U^{ff}}{2} n^f_{i\sigma} n^f_{i\bar{\sigma}}\right) + \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) n^d_{\vec{k}\sigma}$$

$$+ G \sum_{i\sigma\sigma'} n^f_{i\sigma'} n^d_{i\sigma} + \frac{U}{2} \sum_{i\sigma} n^d_{i\sigma} n^d_{i\bar{\sigma}} \quad . \qquad (1)$$

In this section we present two approximate solutions of the Hamiltonian in (1), both of which are mean-field treatments of the d-electron correlation. The first approximation consists of adding to the total energy in Schweitzer's approximation (see Section II) a mean-field energy term. The second solution consists of calculating a new d-electron Green function with the d-electron correlation treated in the mean-field approximation and using this Green function to obtain the total energy.

A. Mean-Field Energy Approximation.[26]

The model Hamiltonian Eq. (1) can be written as

$$H = H_{FK} + \frac{U}{2} \sum_{i\sigma} n^d_{i\sigma} n^d_{i\bar{\sigma}} \quad , \qquad (2)$$

where H_{FK} is the Falicov-Kimball Hamiltonian, eqn (II.1).

We can calculate the total energy by using

$$E = \langle H \rangle = \langle H_{FK} \rangle + \frac{U}{2} \sum_{i\sigma} \langle n^d_{i\sigma} n^d_{i\bar{\sigma}} \rangle \quad . \tag{3}$$

If we apply a mean-field approximation to the d-electron correlation term, we get

$$\frac{U}{2} \sum_{i\sigma} \langle n^d_{i\sigma} n^d_{i\bar{\sigma}} \rangle \to \frac{U}{2} \sum_{i\sigma} \langle n^d_{i\sigma} n^d_{i\bar{\sigma}} \rangle = \frac{U}{2} \sum_{i\sigma} \frac{n_c^2}{4} = N \frac{Un_c^2}{4}, \tag{4}$$

where $n_c = \sum_{\sigma} \langle n^d_{i\sigma} \rangle$.

As a first approximation to the total energy we calculate $\langle H_{FK} \rangle$ using Schweitzer's approximation. Then the total energy is just the sum of the energy calculated in Schweitzer's approximation and the d-electron interaction term;

$$E_T(n_c) = E_{sch}(n_c) + \frac{Un_c^2}{4} \quad . \tag{5}$$

It should be emphasized that $E_{sch}(n_c)$ contains no contribution from the d-electron correlation. The ground state then corresponds to the value of the conduction band occupation number, n_c, which gives the absolute minimum of the total energy.

B. Mean-Field Green Function Approximation.

The Hamiltonian Eq. (1) with the d-electron interaction treated in the mean-field approximation is given by

$$H = H_{FK} + \frac{U}{2}\sum_{i\sigma} \quad \langle n^{d}_{i\sigma}\rangle n^{d}_{i\bar{\sigma}} + \langle n^{d}_{i\bar{\sigma}}\rangle n^{d}_{i\sigma} - \langle n^{d}_{i\sigma}\rangle\langle n^{d}_{i\bar{\sigma}}\rangle$$

$$= H_{FK} + \frac{Un_c}{2}\sum_{i\sigma} n^{d}_{i\sigma} - \frac{Un_c^{2}}{4} \quad .$$

The last term is a constant and drops out when the Green function is derived. H_{FK} contains a term

$$\sum_{\vec{k}\sigma} \varepsilon(\vec{k}) n^{d}_{\vec{k}\sigma}$$

ans, since $\sum_{i\sigma} n^{d}_{i\sigma} = \sum_{\vec{k}\sigma} n^{d}_{\vec{k}\sigma}$,

the effect of the d-electron correlation can be accounted for by defining

$$\tilde{\varepsilon}(\vec{k}) = \varepsilon(\vec{k}) + \frac{Un_c}{2} \quad ,$$

in which case the Hamiltonian reduces to the Falicov-Kimball Hamiltonian with $\varepsilon(\vec{k})$ replaced by $\tilde{\varepsilon}(\vec{k})$. Then, within the Schweitzer approximation,

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{\omega - \tilde{\varepsilon}(\vec{k}) - \Sigma(\omega)} \quad ,$$

where $\Sigma(\omega)$ is given by Eq. (II.26).

Since we have an interacting system, we can no longer calculate the total energy as was done in the Schweitzer calculation. The derivation of the correct ground-state energy equation is given in appendix B, Eq. (B.13), with $\tilde{\varepsilon}(\vec{k})$ replacing $\varepsilon(\vec{k})$:

$$\sum_{\vec{k}\sigma} \tilde{\varepsilon}(\vec{k})\langle n^{d}_{\vec{k}\sigma}\rangle + G \sum_{i\sigma\sigma'} \langle n^{f}_{i\sigma'}, n^{d}_{i\sigma}\rangle$$

$$= \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} \omega \tilde{A}^{\sigma}(\vec{k},\omega) f(\omega) d\omega .$$

Therefore,

$$\sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} \omega \tilde{A}^{\sigma}(\vec{k},\omega) f(\omega) d\omega = \sum_{\vec{k}\sigma} \varepsilon(\vec{k})\langle n^{d}_{\vec{k}\sigma}\rangle$$

$$+ G \sum_{i\sigma\sigma'} \langle n^{f}_{i\sigma'}, n^{d}_{i\sigma}\rangle + \frac{Un_c}{2} \sum_{\vec{k}\sigma} \langle n^{d}_{\vec{k}\sigma}\rangle$$

$$= \sum_{\vec{k}\sigma} \varepsilon(\vec{k})\langle n^{d}_{\vec{k}\sigma}\rangle + G \sum_{i\sigma\sigma'} \langle n^{f}_{i\sigma'}, n^{d}_{i\bar{\sigma}}\rangle$$

$$+ \frac{NUn_c^{\,2}}{2} .$$

But,

$$E_T = \langle H\rangle = \sum_{\vec{k}\sigma} \varepsilon(\vec{k})\langle n^{d}_{\vec{k}\sigma}\rangle + G \sum_{i\sigma\sigma'} \langle n^{f}_{i\sigma'}, n^{d}_{i\sigma}\rangle$$

$$+ \frac{U}{2} \sum_{i\sigma} \langle n^{d}_{i\bar{\sigma}}\rangle\langle n^{d}_{i\sigma}\rangle .$$

So,

$$E_T = \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} \omega \tilde{A}^{\sigma}(\vec{k},\omega) f(\omega) d\omega - N\frac{Un_c^{\,2}}{4} .$$

In this equation, $\tilde{A}^{\sigma}(\vec{k},\omega)$ is calculated from the Green function which contains the d-electron correlation in the mean-field approximation. The last term is subtracted from the expression to compensate for double-counting the interaction.

C. Mean-Field Results.

The approximations described in Sections A and B were used to find the ground state of the two-band model. The results are presented in this section.

In order to find the conduction band occupation in the ground state, we used the procedure outlined in Appendix C. This procedure yields the value of n_c, the number of conduction electrons, which minimizes the total energy for different values of the parameters G/W and U/W, where W is the conduction band width.

Phase diagrams for the mean-field energy approximation (Section A) are plotted in Figures 8 and 9 for U/W = .1 and U/W = .3, respectively. These phase diagrams show possible first-order (solid lines) and second-order (dashed lines) phase transitions as the gap parameter, Δ, changes with pressure. A comparison with Figure 7, which is the phase diagram for Schweitzer's approximation (U=0), shows that the mixed-valence region in phase space accessible by a first-order phase transition has increased in area due to the addition of d-electron correlation. The reason for this can be found by looking at Figure 10. Figure 10 is a plot of the value of n_c on the mixed-valence side of the first-order transition for G/W = .35. As U is turned on, three changes become apparent. First, the value of the gap parameter, Δ, at which the phase transition takes place shifts to a smaller value. Second, the value of n_c, after the first-order

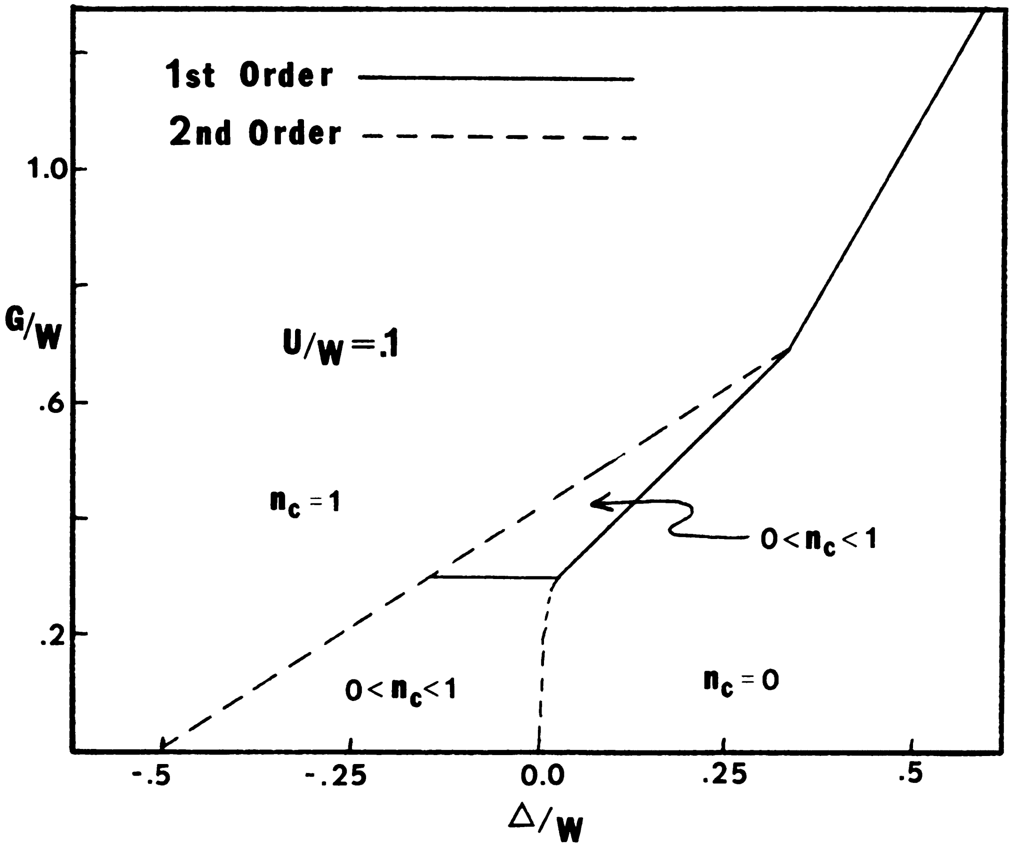


Figure 8. Phase diagram with U/W = .1 (mean-field).

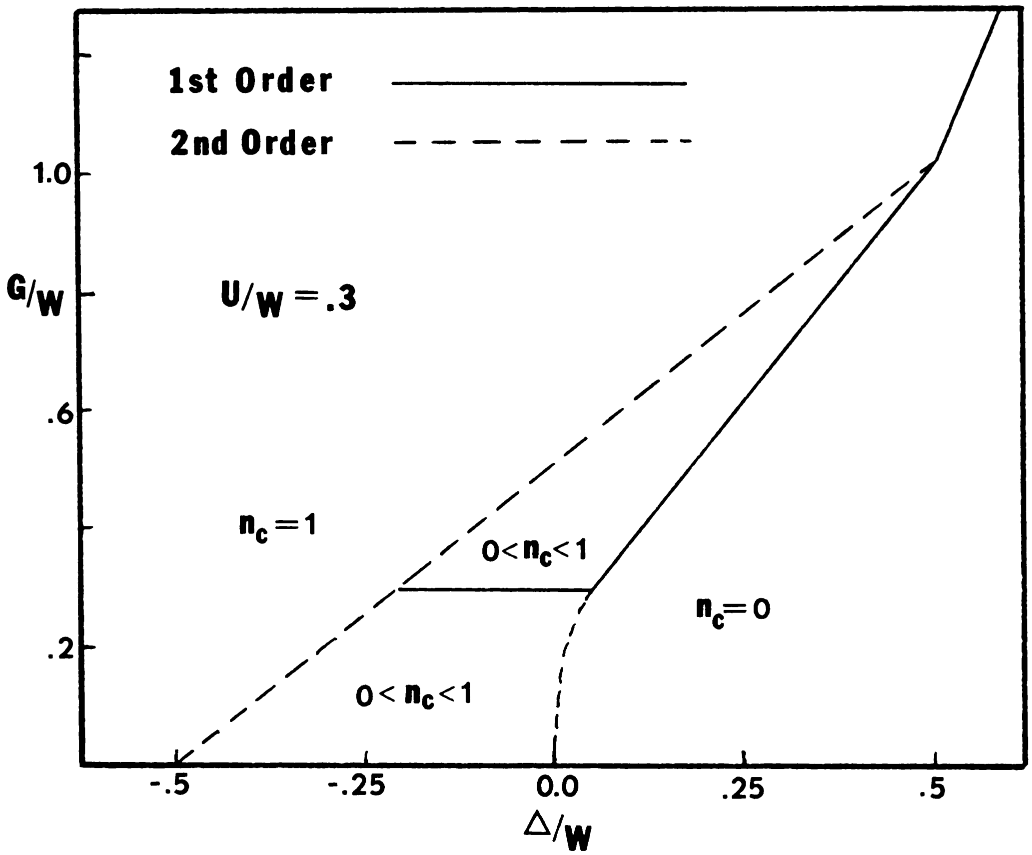


Figure 9. Phase diagram with U/W = .3 (mean-field).

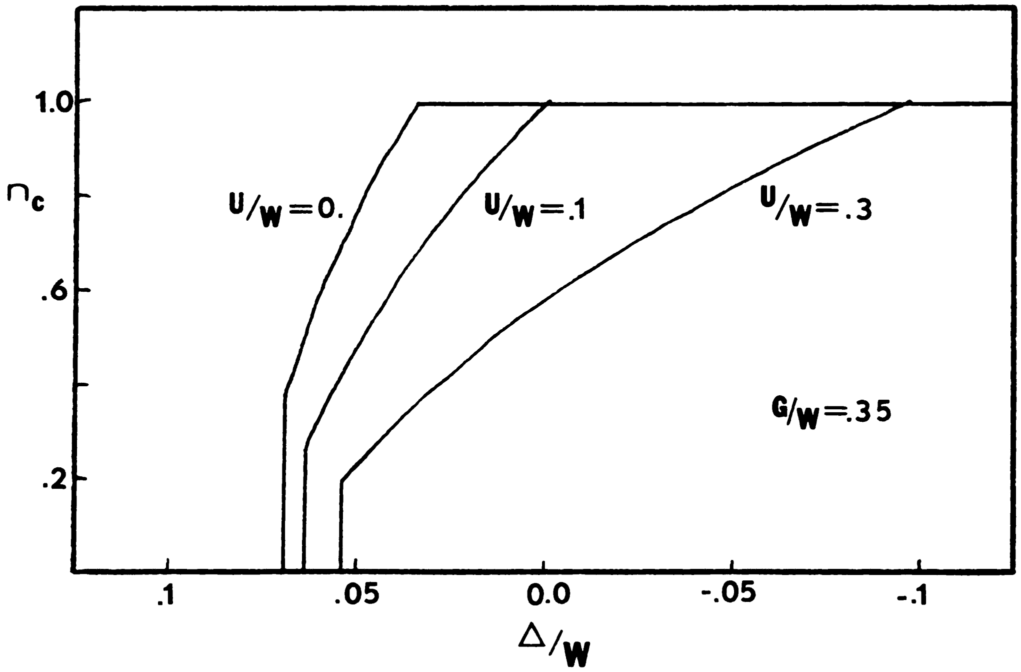


Figure 10. n_c vs. band gap with $U \neq 0$. (mean-field).

transition, is lowered. Third, the rate at which the conduction band fills up as the gap closes (i.e., the slope of the line as Δ decreases) decreases. Therefore, when $U \neq 0$, a smaller gap is required to obtain the same n_c as when $U=0$ so that the mixed-valence region increases in size.

Figures 11 and 12 are phase diagrams for the mean-field Green function approximation (Section B). The effect of d-electron correlation is seen to be qualitatively the same as in the previous mean-field approximation. Figure 13 shows more clearly that there are quantitative between the two approximations. The value of Δ at which the discontinuous transition takes place does not shift as dramatically as in Figure 10. However, the occupancy of the conduction band at the transition is lower in Figure 13 and the slope is smaller in this approximation.

Both approximations yield the same qualitative results which can be summarized as follows. The Coulomb repulsion between conduction-band electrons opposes the promotion of f electrons into the conduction band, thereby increasing the critical pressure (or decreasing the critical gap parameter, Δ) and decreasing the value of n_c at the transition for a particular value of the f-d interaction strength, G.

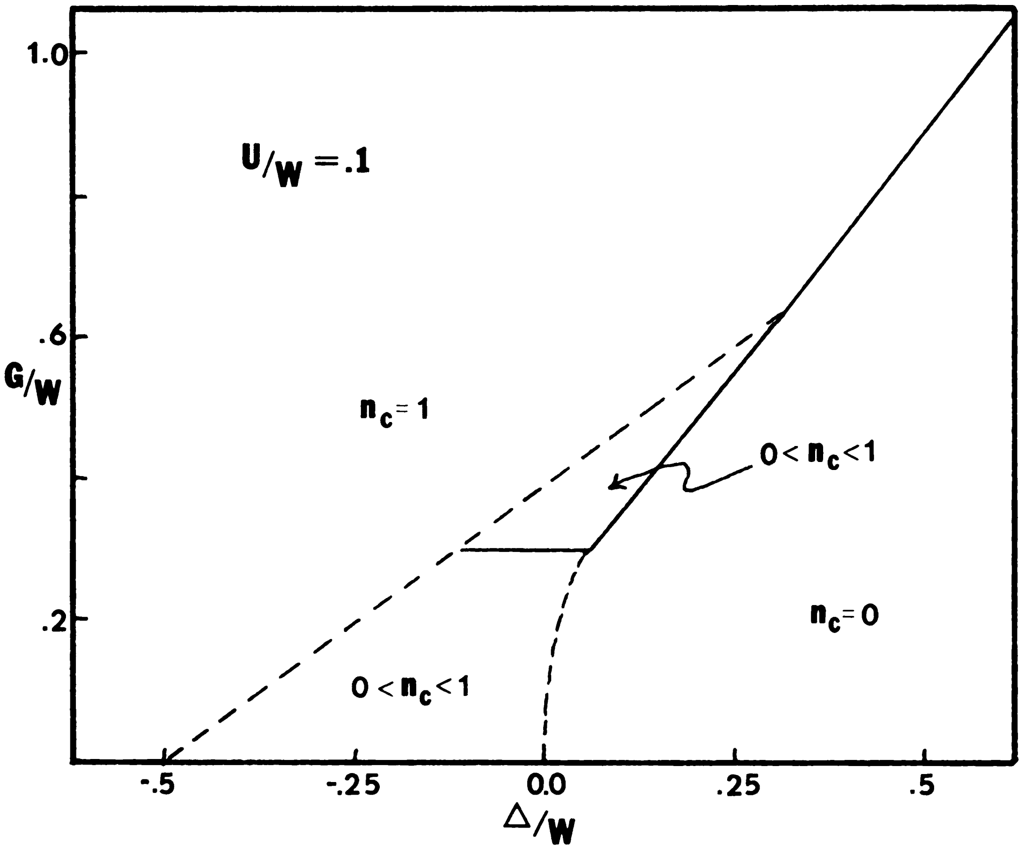


Figure 11. Phase diagram with U/W = .1 (mean-field).

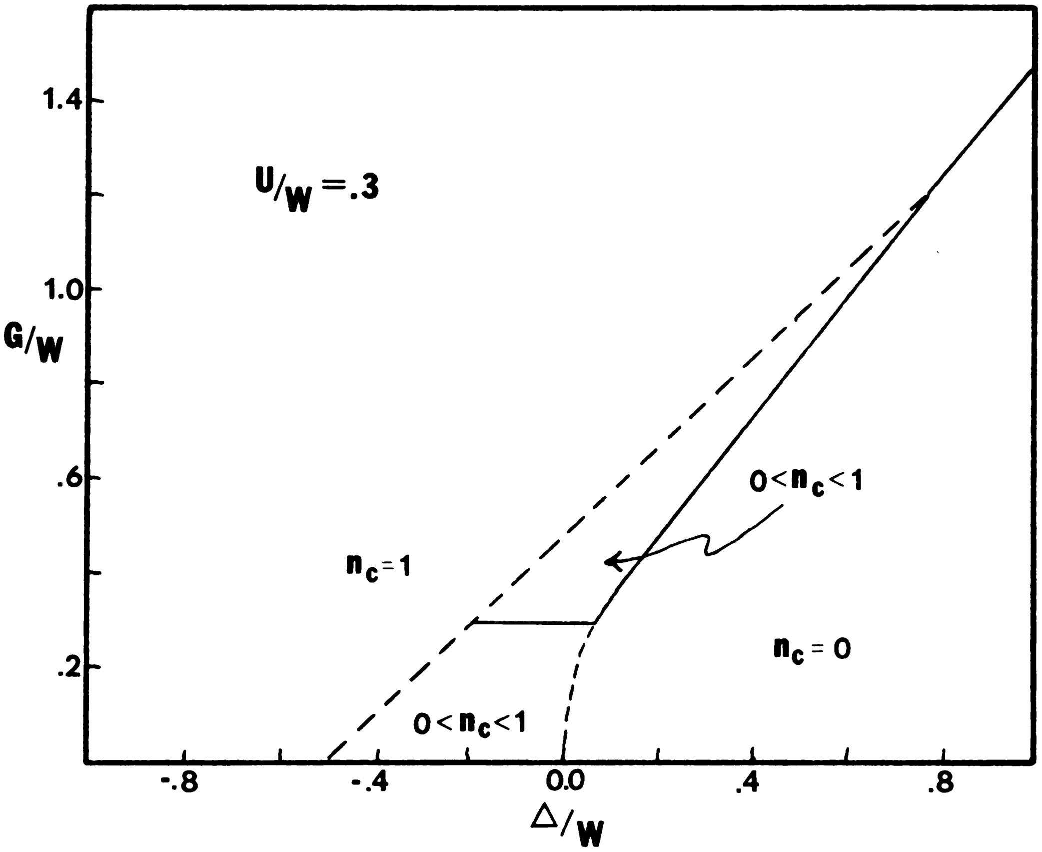


Figure 12. Phase diagram with U/W = .3 (mean-field).

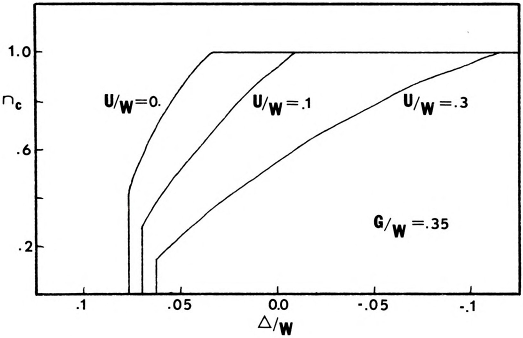


Figure 13. n_c vs. band gap with $U \neq 0$. (mean-field).

V. THE TWO-BAND MODEL IN THE ATOMIC LIMIT

A. The Green Function

In this section we present a derivation of the d-electron Green function for the two-band model in the atomic limit. Although this Green function can be found exactly, we are interested in the case where the f-electron correlation energy, U^{ff}, is so large as to preclude the simultaneous excitation of two f electrons into the conduction band. Therefore, we project out the state with two f holes. The required Green function is derived using the equation of motion method and is found to be exact due to the termination of the hierarchy of equations of motion.

In the atomic limit, each atom is isolated and the model reduces to N independent atoms. Therefore, the Hamiltonian can be written as

$$H = \sum_i H_i = \sum_i (H_i^f + H_i^d + H_i^{fd} + H_i^{dd})$$

$$= \sum_i (H_i^f + \varepsilon d \sum_\sigma n_\sigma^n + G \sum_{\sigma\sigma'} n_{\sigma'}^f n_\sigma^d + \frac{U}{2} \sum_\sigma n_{-\sigma}^d n_\sigma^d) . \quad (1)$$

We have left H_i^f as it is since both n_σ^f and n_σ^d commute with it and it therefore doesn't enter into the equations of motion for the Green function. In addition, we set $\varepsilon_d=0$ and define $\bar{n}_\sigma^f = 1-n_\sigma^f$, so that the Hamiltonian can be rewritten as

$$H = H^{f} + 2G \sum_{\sigma} n^{d}_{\sigma} + \frac{U}{2} \sum_{\sigma} n^{d}_{\bar{\sigma}} n^{d}_{\sigma} = G \sum_{\sigma\sigma'} \bar{n}^{f}_{\sigma'} n^{d}_{\sigma} , \qquad (2)$$

where we have dropped the site index, i.

The Green function for the d-electrons is defined by

$$G^{\sigma}(\omega) = \langle\langle c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle \quad . \qquad (3)$$

The equation of motion for $G^{\sigma}(\omega)$ is

$$\omega \langle\langle c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle = 1 + \langle\langle [c_{\sigma}, H] ; c^{+}_{\sigma} \rangle\rangle \qquad (4)$$

Using (2), we get

$$[c_{\sigma}, H] = 2Gc_{\sigma} + U n^{d}_{\bar{\sigma}} c_{\sigma} - G \sum_{\sigma'} \bar{n}^{f}_{\sigma'} c_{\sigma} . \qquad (5)$$

Therefore,

$$(\omega - 2G) \langle\langle c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle = 1 + U \langle\langle n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle - G \sum_{\sigma'} \langle\langle \bar{n}^{f}_{\sigma'} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle . \qquad (6)$$

We now write equations of motion for the two-particle Green functions that were generated. For the d-d Green function,

$$(\omega - 2G) \langle\langle n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle = \langle n^{d}_{\bar{\sigma}} \rangle + U \langle\langle n^{d}_{\bar{\sigma}} n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle - G \sum_{\sigma} \langle\langle \bar{n}^{f}_{\sigma''} n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle$$

where we have used $\left[n^{d}_{\bar{\sigma}}, H \right] = 0$. Since for Fermions, $n^{d}_{\bar{\sigma}} n^{d}_{\bar{\sigma}} = n^{d}_{\bar{\sigma}}$, we have

$$(\omega - U - 2G) \langle\langle n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle = \langle n^{d}_{\bar{\sigma}} \rangle - G \sum_{\sigma''} \langle\langle \bar{n}^{f}_{\sigma''} n^{d}_{\bar{\sigma}} c_{\sigma} ; c^{+}_{\sigma} \rangle\rangle . \qquad (8)$$

Likewise, for the f-d Green function we obtain

$$(\omega-G)\langle\langle \bar{n}^f_{\sigma'}, c_\sigma ; c^+_\sigma \rangle\rangle = \sum_\tau \langle \bar{n}^f_\tau \rangle + U \sum_{\sigma''} \langle\langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle . \tag{9}$$

The equation of motion for the three-particle f-d-d Green function is

$$\begin{aligned}(\omega-U-2G)\langle\langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle &= \langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} \rangle \\ &- G \sum_\tau \langle\langle \bar{n}^f_\tau \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle . \end{aligned} \tag{10}$$

Since $\bar{n}^f_{\sigma''} \bar{n}^f_{\sigma''} = \bar{n}^f_{\sigma''}$ and since, following Falicov-Kimball[6], we have chosen U^{ff} and ε_f such that

$$\langle \bar{n}^f_\sigma \bar{n}^f_{\bar{\sigma}} \rangle = 0, \tag{11}$$

$$\sum_\tau \langle\langle \bar{n}^f_\tau n^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle = \langle\langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle . \tag{12}$$

Therefore, (10) becomes

$$(\omega-U-G)\langle\langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} c_\sigma ; c^+_\sigma \rangle\rangle = \langle \bar{n}^f_{\sigma''} n^d_{\bar{\sigma}} \rangle . \tag{13}$$

Substituting (13) into (8) and (9), and substituting the result into (6) gives

$$\begin{aligned}(\omega-2G)\langle\langle c_\sigma ; c^+_\sigma \rangle\rangle &= 1 + \frac{U\langle n^d_{\bar{\sigma}} \rangle}{\omega-U-2G} - \frac{G \sum_{\sigma'} \langle \bar{n}^f_{\sigma'} \rangle}{\omega-G} \\ &-UG \sum_{\sigma'} \langle \bar{n}^f_{\sigma'} , n^d_{\bar{\sigma}} \rangle \left[\frac{1}{(\omega-U-G)(\omega-U-2G)} \right. \\ &\left. + \frac{1}{(\omega-G)(\omega-U-G)} \right] . \end{aligned} \tag{14}$$

If we define $n_c = \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} \rangle = \sum_{\sigma} \langle n^{d}_{\bar{\sigma}} \rangle$, we can rewrite (14) as

$$G^{\sigma}(\omega) = \frac{n_c - \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega - G} + \frac{1 - \frac{3n_c}{2} + \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega - 2G}$$

$$+ \frac{\sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega - U - G} + \frac{n_c/2 - \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega - U - 2G} . \qquad (15)$$

The Green function just derived can be written in the form

$$G^{\sigma}(\omega) = \sum_{j} \frac{A^{\sigma}_{j}(\omega)}{\omega - \omega_{i}} \qquad (16)$$

where the ω_j are the excitation energies and the $A^{\sigma}_{j}(\omega)$ are the spectral weights. A condition which must be satisfied by the spectral weights is

$$\sum_{j} A^{\sigma}_{j}(\omega) = 1. \qquad (17)$$

It can be shown that this sum rule is satisfied in the present case.

B. Derivation of the f-d Correlation Function Using the Partition Function.

The correlation function, $\sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle$, which appears in the atomic-limit Green function could be derived using the fd Green function and Eq. (A,8). However, since the energies are known for all possible states, the partition function, and therefore the correlation function, is easy to find.

The possible states of the system along with their energies and degeneracies are listed in Table (1). The correlation function is given by

$$\sum_{\sigma'} \langle \bar{n}^f_{\sigma'} , n^d_{\bar{\sigma}} \rangle = \frac{1}{Z} \, \mathrm{Tr} \, e^{-\beta(H-\mu N)} \left(\sum_{\sigma'} \bar{n}^f_{\sigma'} , n^d_{\bar{\sigma}} \right) , \qquad (18)$$

where μ is the chemical potential, $\beta=1/kT$, N is the total number operator, and

$$A = \mathrm{Tr} \, e^{-\beta(H-\mu N)} . \qquad (19)$$

In order to facilitate the following expressions, we define the variables

$$s = e^{\beta\mu} \qquad x = e^{-\beta U^{ff}}$$

$$t = e^{-\beta(\varepsilon_f - \mu)} \qquad y = e^{-\beta U} , \qquad (20)$$

$$v = e^{-\beta(G-\mu)}$$

Then the partition function can be written

$$Z = 2t + 4tv = 2tv^2y + t^2x + 2t^2v^2sx + t^2v^4xys^2 . \qquad (21)$$

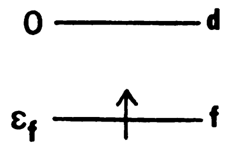
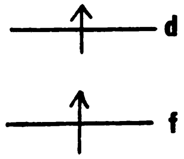
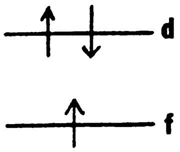
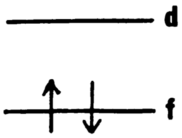
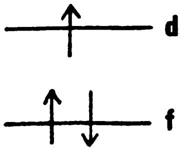
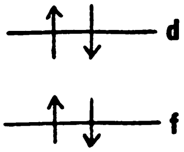
The correlation function is

$$\sum_{\sigma'} \langle \bar{n}^f_{\sigma'} , n^d_{\bar{\sigma}} \rangle = \frac{1}{Z} \left(2tv + 2tv^2y \right) . \qquad (22)$$

We can eliminate the partition function Z by using the fact that

$$\langle \bar{n}^f_{\sigma} \rangle = n_c/2 = 1/Z \left(t + 2tv + tv^2y \right) . \qquad (23)$$

Table 1. Possible states in the atomic limit.

STATE	$E-\mu N$	Degeneracy
	$\varepsilon_f - \mu$	2
	$\varepsilon_f + G - 2\mu$	4
	$\varepsilon_f + 2G + U - 3\mu$	2
	$2\varepsilon_f + U^{ff} - 2\mu$	1
	$2\varepsilon_f + U^{ff} + 2G - 3\mu$	2
	$2\varepsilon_f + U^{ff} + 4G + U - 4\mu$	1

Then

$$\sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle = \frac{f(G)}{1 - f(U+G) + f(G)} , \tag{24}$$

where $f(x) = \dfrac{1}{e^{\beta(x-\mu)}+1}$ is the Fermi function which, at zero temperature, goes to $\theta(\mu - x)$, the step function.

To summarize, we have derived the atomic-limit Green function for the two-band model. This Green function is exact in the case being considered here; i.e., the intra-atomic Coulomb interaction between two f electrons, U^{ff}, is so large that the possibility of exciting two f electrons into the d level from the same site is zero. The Green function is given by

$$G^{\sigma}(\omega) = \frac{n_c - C_F}{\omega - G} + \frac{1 - \frac{3}{2} n_c + C_F}{\omega - 2G} + \frac{C_F}{\omega - U - G} + \frac{n_c/2 - C_F}{\omega - U - 2G} , \tag{25}$$

where $C_F = \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle$ (26)

and is given by Eq. (24). This Green function will be used in the next section in an "intermediate solution" calculation based on Hubbard's[23] approximation.

VI. HUBBARD APPROXIMATION OF THE TWO-BAND MODEL

Recently, Mazzaferro and Ceva[27] applied the Hubbard I[23] approximation to the Falicov-Kimball model (no d-electron correlation). They referred to their calculation as an "intermediate solution", since Hubbard I is thought to be an improvement over mean-field approximations but not as good an approximation as CPA (Coherent Potential Approximation).[28] They were concerned with the possibility of a phase transition as a function of temperature and found no first-order transition.

Schweitzer's[21] approximation goes beyond mean-field to include excitonic correlations. However, this approximation is also an improvement over the Hubbard I decoupling scheme, since (see Section III) the approximations are made on the three-particle instead of the two-particle Green functions. It is interesting to compare Schweitzer's approximation with the CPA method. In a later paper[29] Schweitzer presented the results of a CPA calculation on chemically induced intermediate valence in SmS. He started with the Falicov-Kimball Hamiltonian and generalized it for the case of the ternary alloy $Sm_{1-x}R_xS$, where R denotes any rare-earth element that is trivalent in the monosulfides. His results included the case where x=0, which corresponds to SmS. Although we were unable to show a mathematical equivalence between the self-energy derived in ref. 21 and 29, the numerical results of the two calculations are nearly identical.

Therefore, Schweitzer's improved approximation of the Falicov-Kimball model is very similar to CPA, and the calculation of Mezzaferro and Ceva is intermediate between the mean-field approximation and Schweitzer's approximation.

In this section we present a calculation using the Hubbard I approximation to the two-band model. When the d-electron correlation is turned off (U=0), we recover the results of Mezzaferro and Ceva. However, since we are interested in the possibility of a pressure-induced transition, our calculation is done at a fixed temperature (T=0) as a function of the gap parameter, Δ. We find that a first-order transition to an intermediate valence phase is possible even in this simpler approximation. The two-band model is also solved with $U \neq 0$ in order to find the effect of the d-electron correlation on the phase transition.

A. The Green Function

Mazzaferro and Ceva[27] used Hubbard's[23] decoupling scheme (see Section III), which is equivalent to starting with the atomic-limit Green function and allowing hopping to nearest-neighbor sites. Therefore, for the Falicov-Kimball model,

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{\left[G_A^{\sigma}(\omega)\right]^{-1} - \varepsilon(\vec{k})} , \qquad (1)$$

where $G_A^{\sigma}(\omega)$ is the exact atomic-limit Green function for the Falicov-Kimball Hamiltonian; we have chosen the atomic level to be $T_o=0$. We can obtain this Green function by letting U=0 in the atomic-limit solution of the two-band model derived in Section V. We then have

$$G_A^\sigma(\omega) = \frac{n_c}{\omega - G} + \frac{1 - n_c}{\omega - 2G} \quad . \tag{2}$$

Using this equation in (1), we obtain for the Hubbard I approximation to the Falicov-Kimball model

$$G^\sigma(\vec{k},\omega) = \left[\frac{(\omega-G)(\omega-2G)}{\omega-(1+n_c)G} - \varepsilon(\vec{k})\right]^{-1} \quad . \tag{3}$$

This is equivalent to the Green function derived in ref. 27.

The intermediate solution for the two-band model can be constructed in a similar way. From Section V we have for the exact atomic-limit Green function

$$G_A^\sigma(\omega) = \frac{n_c-C_F}{\omega-G} + \frac{1-\frac{3}{2}n_c+C_F}{\omega-2G} + \frac{C_F}{\omega-U-G} + \frac{n_c/2-C_F}{\omega-U-2G} \quad , \tag{4}$$

where C_F is the $\bar{f}$-d correlation function,

$$C_F = \sum_{\sigma'} \langle n_{\sigma'}^{\bar{f}} n_\sigma^d \rangle \quad . \tag{5}$$

The finite-bandwidth solution using the Hubbard decoupling scheme is then given by

$$G^\sigma(\vec{k},\omega) = \frac{1}{\left[G_A^\sigma(\omega)\right]^{-1} - \varepsilon(\vec{k})} \quad . \tag{6}$$

We now derive the perturbed density of states

$$\sum_{\vec{k}} A^{\sigma}(\vec{k},\omega) \tag{7}$$

along with

$$\sum_{\vec{k}} \varepsilon(\vec{k}) A^{\sigma}(\vec{k},\omega) , \tag{8}$$

both of which are required for the total energy.

If we define the poles and the spectral weights of the atomic-limit Green function as

$$\begin{array}{ll} \omega_1 = G & A_1 = n_c - C_F \\ \omega_2 = 2G & A_2 = 1 - \frac{3}{2} n_c + C_F \\ \omega_2 = U + G & A_3 = C_F \\ \omega_4 = U + 2G & A_4 = n_c/2 - C_F , \end{array} \tag{9}$$

then

$$G_A^{\sigma}(\omega) = \sum_{i=1}^{4} \frac{A_i}{\omega - \omega_i} . \tag{10}$$

The finite-bandwidth Green function is then given by

$$G^{\sigma}(\vec{k},\omega) = \frac{1}{\left[\sum\limits_{i=1}^{4} \frac{A_i}{\omega-\omega_i}\right]^{-1} - \varepsilon(\vec{k})} \tag{11}$$

The spectral weight function for this Green function is

$$A^{\sigma}(\vec{k},\omega) = \frac{1}{2\pi i} \left[G^{\sigma}(\vec{k},\omega - i\eta) - G^{\sigma}(\vec{k},\omega + i\eta) \right] , \tag{12}$$

or

$$A^{\sigma}(\vec{k},\omega) = \delta\left[S(\omega) - \varepsilon(\vec{k})\right] , \tag{13}$$

where

$$S(\omega) = \left[\sum_{i=1}^{4} \frac{A_i}{\omega-\omega_i}\right]^{-1} . \tag{14}$$

Then

$$\sum_{\vec{k}} A^{\sigma}(\vec{k},\omega) = \rho_o\left[S(\omega)\right] \tag{15}$$

and

$$\sum_{\vec{k}} \varepsilon(\vec{k})A^{\sigma}(\vec{k},\omega) = S(\omega)\rho_o\left[S(\omega)\right] . \tag{16}$$

B. The Total Energy

The total energy is found by using an equation similar to one derived in Appendix B. However, the following difficulty arises. If we use Eq. (B.19), we have the following equation for the total energy:

$$E = \sum_{\vec{k}\sigma} \int_{-\infty}^{\mu} \left[\frac{\varepsilon(\vec{k})+\omega}{2}\right] A^{\sigma}(\vec{k},\omega)d\omega + \frac{NG}{2} \sum_{\sigma\sigma'} \langle \bar{n}^{f}_{\sigma}, n^{d}_{\bar{\sigma}} \rangle \tag{17}$$

When G=0, the $\bar{f}$-d correlation term drops out and the expression reduces to the Galitskii-Migdal expression, Eq. (B.8). When G≠0, we must evaluate the $\bar{f}$-d correlation function. However, if we use the atomic-limit correlation function, which was derived in Section V Eq. (V.24) , we do not recover the correct energy expression when U=0.

Therefore, we will use Eq. (B.17),

$$E = \int_{-\infty}^{\mu} \omega \sum_{\vec{k}\sigma} A^{\sigma}(\vec{k},\omega)\,d\omega - \frac{UN}{2} \sum_{\sigma} \langle n^d_{\sigma} n^d_{-\sigma} \rangle \,, \tag{18}$$

and we will evaluate the d-d correlation function in such a way that (18) gives the Galitskii-Migdal expression when G=0.

In order to derive the d-d correlation function which gives the correct energy when G=0, we first derive a similar expression for the Hubbard model (G=0) and show that the total energy using this expression is equivalent to the energy obtained by using the exact expression, Eq. (B.8). Then $\langle n^d_{\sigma} n^d_{-\sigma} \rangle$, the d-d correlation function for the present model, is approximated in such a way as to give the Hubbard value for the total energy when G=0.

In Hubbard's approximate solution to his Hamiltonian, the d-d Green function, Γ^{dd}, is never explicitly derived. However, we find from his derivation that

$$\begin{aligned} \sum_i \Gamma^{dd} &= \sum_i \langle\langle n^d_{i\bar{\sigma}} c_{i\sigma}; c^+_{i\sigma} \rangle\rangle \\ &= \frac{n_c/2}{\omega - U} \; N + \sum_{\vec{k}} \varepsilon(\vec{k}) \langle\langle c_{\vec{k}\sigma}; c^+_{\vec{k}\sigma} \rangle\rangle \quad . \end{aligned}$$

From Eq. (A.8) we find

$$\sum_i \langle n^d_{i\sigma} n^d_{i-\sigma} \rangle = \frac{n_c}{2} \sum_{\vec{k}} \varepsilon(\vec{k}) \int_{-\infty}^{\infty} \frac{A^{\sigma}(\vec{k},\omega) f(\omega)\, d\omega}{\omega - U} \tag{20}$$

Then, using (18) we obtain for the total energy

$$E = \int_{-\infty}^{\infty} \omega f(\omega) \sum_{\vec{k}\sigma} A^{\sigma}(\vec{k},\omega)d\omega - \frac{U}{2}\sum_{i} \langle n^{d}_{i\sigma} n^{d}_{i\bar{\sigma}}\rangle$$

$$= \int_{-\infty}^{\infty} \omega \sum_{\vec{k}\sigma} A^{\sigma}(\vec{k},\omega) f(\omega)d\omega$$

$$- \frac{Un_c}{4} \int_{-\infty}^{\infty} \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) \frac{A^{\sigma}(\vec{k},\omega)f(\omega)d\omega}{\omega-U} \tag{21}$$

For the Hubbard model,

$$A^{\sigma}(\vec{k},\omega) = \delta\left[\frac{\omega(\omega-U)}{\omega-U(1-n_c/2)} - \varepsilon(\vec{k})\right] , \tag{22}$$

and therefore

$$E = \sum_{\sigma} \int_{-\infty}^{\infty} f(\omega)\left[\omega - \frac{Un_c/4}{\omega-U(1-n_c/2)}\right]d\omega. \tag{23}$$

If we use the Galitskii-Migdal expression Eq. (B.8)

$$E = \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} \left[\frac{\omega+\varepsilon(\vec{k})}{2}\right] A^{\sigma}(\vec{k},\omega)f(\omega)d\omega \tag{24}$$

and substitute Eq. (22) for $A^{\sigma}(\vec{k},\omega)$ we obtain

$$E = \sum_{\sigma}\int_{-\infty}^{\infty} f(\omega)\left[\omega - \frac{Un_c/4}{\omega-U(1-n_c/2)}\right]d\omega, \tag{25}$$

which is the same as Eq. (23) above.

We can use the preceding derivation as a guide for the case we are considering in this section; i.e., the two-band model. For this model,

$$\Gamma^{dd} = \left[\frac{n_c/2-C_F}{\omega-U-2G} + \frac{C_F}{\omega-U-G}\right]\left[1+\varepsilon(\vec{k})G^{\sigma}(\vec{k},\omega)\right] \tag{26}$$

and, using Eq. (A.8) we obtain

$$\sum_i \langle n^{d}_{i\sigma} n^{d}_{i\bar{\sigma}}\rangle = \int_{-\infty}^{\infty} \left[\frac{n_c/2-C_F}{\omega-U-2G} + \frac{C_F}{\omega-U-G}\right] \sum_{\vec{k}} \varepsilon(\vec{k}) A^{\sigma}(\vec{k},\omega) f(\omega)\, d\omega. \tag{27}$$

The total ground-state energy at T=0 is then

$$E = (\Delta + .5 - 2G)n_c + \int_{-\infty}^{\mu} \sum_{\vec{k}\sigma} A^{\sigma}(\vec{k},\omega)\, d\omega$$

$$- \frac{U}{2} \int_{-\infty}^{\mu} \left[\frac{n_c/2-C_F}{\omega-U-2G} + \frac{C_F}{\omega-U-G}\right] \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) A^{\sigma}(\vec{k},\omega)\, d\omega. \tag{28}$$

The chemical energy, μ , is found by using the condition

$$n_c = \sum_{\vec{k}\sigma} \int_{-\infty}^{\mu} A^{\sigma}(\vec{k},\omega)\, d\omega. \tag{29}$$

Then, the total ground-state energy can be written as

$$E = (\Delta + .5 - 2G)n_c$$

$$+ \int_{-\infty}^{\mu} \left[\omega - \frac{U}{2}\left(\frac{n_c/2-C_F}{\omega-U-2G} + \frac{C_F}{\omega-U-G}\right) S(\omega)\right] \rho_o\, S(\omega)\, d\omega, \tag{30}$$

where $S(\omega)$ is defined in Eq. (14).

C. Results

The density of states is plotted in Figure 14 . The solid line represents the unperturbed density of states.

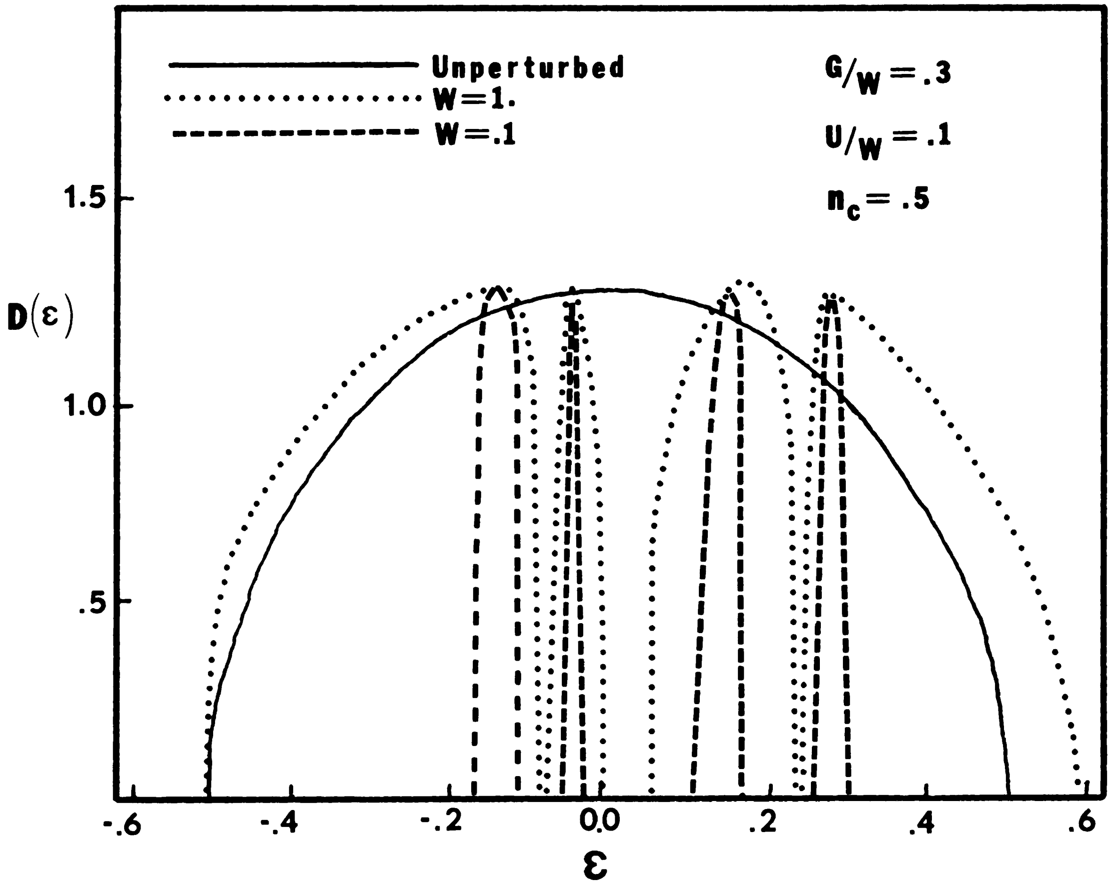


Figure 14. Density of states in Hubbard approx.

The dotted line is the perturbed density of states for W=1., where W is the bandwidth. The dashed line is the perturbed density of states for W=.1 (scaled by 1/10). As the band narrows, the density of states approaches the atomic limit which corresponds to four atomic levels at G, G+U, 2G, 2G+U.

Figure 15 shows the value of n_c, the number of conduction electrons, which minimizes the total energy. This was found using the procedure outlined in Appendix C. The three curves correspond to U=0., .1, and .3. When U=0. we recover the results of Mazzaferro and Ceva at zero temperature. However, as the gap parameter, Δ, varies with pressure, we get a first-order transition to a value of $n_c < 1$; i.e., a state with intermediate valence. The presence of d-electron correlation affects the critical gap and the value of n_c just after the transition in a way similar to the mean-field treatments in Section IV.

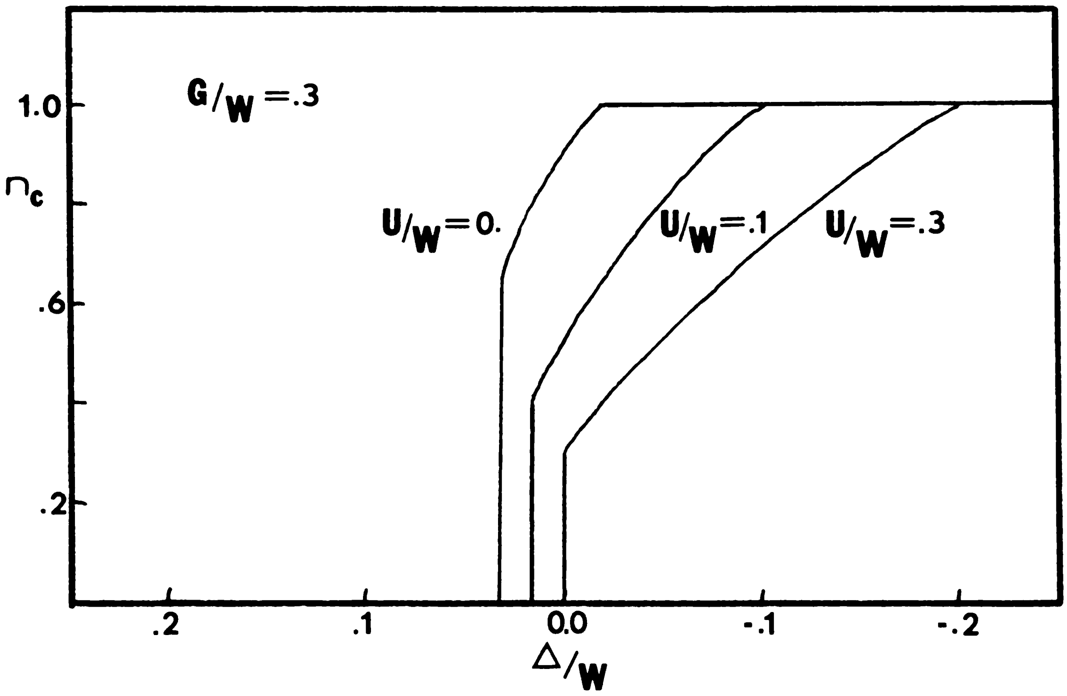


Figure 15. n_c vs. band gap in Hubbard approx.

VII. IMPROVED APPROXIMATION OF THE TWO-BAND MODEL

In this section we present an improvement of the previous approximations in Section IV, which treated the d-electron interaction in the mean-field approximation. In Section A the equation of motion method is used to derive the d-electron Green function. The decoupling scheme is guided by the following conditions:

i) The Green function should reduce to the results of Schweitzer when U=0.

ii) The Green function should reduce to the results of Hubbard when G=0.

iii) In the atomic limit $\varepsilon(\vec{k}) \rightarrow \varepsilon_d = 0$, the Green function should reduce to the exact result.

The f-d correlation function which arises in the derivation of the d-electron Green function is derived in Section B. Section C contains the expressions for the ground-state energy of the system and Section D contains the results of calculations of the ground-state properties.

The Hamiltonian for the model being considered here will be written in two representations: the localized and the itinerant representations. Each one is more convenient when dealing with the Hubbard and the Schweitzer approximations, respectively. In addition, we will use the hole notation for the f-electrons:

$\bar{n}^f_{i\sigma} = 1 - n^f_{i\sigma}$.

The Hamiltonian in the localized representation is

$$H^L = H^f + \sum_{rs\tau} (\varepsilon_{rs} + 2G\delta_{rs}) c^+_{r\tau} c_{s\tau}$$

$$+ \frac{U}{2} \sum_{s\tau} n^d_{s\tau} n^d_{s\bar{\tau}} - G \sum_{s\tau\tau'} \bar{n}^f_{s\tau'} n^d_{s\tau} . \qquad (1)$$

In the itinerant representation, we have

$$H^I = H^f + \sum_{\vec{q}\tau} \varepsilon(\vec{q}) + 2G\, c^+_{\vec{q}\tau} c_{\vec{q}\tau} + \frac{U}{2} \sum_{s\tau} n^d_{s\tau} n^d_{s\bar{\tau}}$$

$$- \frac{G}{N} \sum_{s\tau'} \bar{n}^f_{s\tau'} \sum_{\vec{q}\vec{q}'\tau} e^{i(\vec{q}-\vec{q}')\cdot\vec{R}_s} c^+_{\vec{q}\tau'} c_{\vec{q}'\tau'} . \qquad (2)$$

A. <u>Derivation of the d-Electron Green Function</u>

We are interested in finding the d-electron Green function for this model, since from this we can find the total energy of the system. We define the Green function as

$$G^\sigma(\vec{k},\omega) = \langle\langle C_{\vec{k}\sigma} ; C^+_{\vec{k}\sigma} \rangle\rangle . \qquad (3)$$

This Green function obeys the equation of motion

$$\omega \langle\langle C_{\vec{k}\sigma} ; C^+_{\vec{k}\sigma} \rangle\rangle = 1 + \langle\langle [C_{\vec{k}\sigma}, H^I] ; C^+_{\vec{k}\sigma} \rangle\rangle , \qquad (4)$$

where we have used the itinerant Hamiltonian H^I. The commutator is found to be

$$\left[C_{\vec{k}\sigma}, H^I\right] = \varepsilon(\vec{k}) + 2G\, C_{\vec{k}\sigma} + \frac{U}{\sqrt{N}} \sum_s e^{i\vec{k}\cdot\vec{R}_s} n_{s\bar{\sigma}} C_{s\sigma} .$$

$$- \frac{G}{\sqrt{N}} \sum_{s\tau'} e^{ikR_s} \bar{n}^f_{s\tau'} C_{s\sigma} . \qquad (5)$$

Therefore,

$$\left(\omega - \varepsilon(\vec{k}) - 2G\right)\langle\langle C_{\vec{k}\sigma}; C^{+}_{k\sigma}\rangle\rangle = 1 + \frac{U}{\sqrt{N}}\sum_{i} e^{i\vec{k}\vec{R}_i}\langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}; C^{+}_{\vec{k}\sigma}\rangle\rangle$$

$$- \frac{G}{\sqrt{N}}\sum_{i\sigma'} e^{i\vec{k}\cdot\vec{R}_i}\langle\langle \bar{n}^{f}_{i\sigma'}, C_{i\sigma}; C^{+}_{\vec{k}\sigma}\rangle\rangle$$

$$\equiv 1 + \Gamma^{dd} + \Gamma^{fd} \qquad (6)$$

A.1. Derivation of Γ^{dd}

The equation of motion for the two-particle Green function $\Gamma^{dd} = \langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}; C^{+}_{k\sigma}\rangle\rangle$ can be simplified if we use the localized Hamiltonian H^{L} and write $C^{+}_{k\sigma}$ in terms of $C^{+}_{i\sigma}$, so that

$$\langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}; C^{+}_{\vec{k}\sigma}\rangle\rangle = \frac{1}{\sqrt{N}}\sum_{\ell} e^{-i\vec{k}\cdot\vec{R}_\ell}\langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}; C^{+}_{\ell\sigma}\rangle\rangle \qquad (7)$$

Then we have for the equation of motion for the d-d Green function, Γ^{dd},

$$\omega\langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}; C^{+}_{\ell\sigma}\rangle\rangle = \left\langle\left[n^{d}_{i\bar{\sigma}}C_{i\sigma}, C^{+}_{\ell\sigma}\right]\right\rangle + \langle\langle n^{d}_{i\bar{\sigma}}C_{i\sigma}, C^{+}_{\ell\sigma}\rangle\rangle \,. \qquad (8)$$

Now, $\left[n^{d}_{i\bar{\sigma}}C_{i\sigma}, H^{L}\right] = 2Gn^{d}_{i\bar{\sigma}}C_{i\sigma} + \sum_{s}\varepsilon_{is}n^{d}_{i\bar{\sigma}}C_{s\sigma}$

$$+ \sum_{s}\varepsilon_{is}\left(C^{+}_{i\bar{\sigma}}C_{s\bar{\sigma}}C_{i\sigma} - C^{+}_{s\bar{\sigma}}C_{i\bar{\sigma}}C_{i\sigma}\right)$$

$$+ Un^{d}_{i\bar{\sigma}}\,C_{i\sigma} - G\sum_{\tau}\bar{n}^{f}_{i\tau}n^{d}_{i\bar{\sigma}}C_{i\sigma} \qquad (9)$$

and

$$\left[n^{d}_{i\bar{\sigma}} C_{i\sigma}, C^{+}_{\ell\sigma} \right] = n^{d}_{i\bar{\sigma}} \delta_{i\ell} \, , \tag{10}$$

and therefore

$$\begin{aligned}
(\omega - U - 2G) \langle\langle n^{d}_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle = {} & \langle n^{d}_{\bar{\sigma}} \rangle \, \delta_{i\ell} \\
& + \sum_{s} \varepsilon_{is} \langle\langle n^{d}_{i\bar{\sigma}} C_{s\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \\
& + \sum_{s} \varepsilon_{is} \langle\langle C^{+}_{i\bar{\sigma}} C_{s\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \\
& - \langle\langle C^{+}_{s\bar{\sigma}} C_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \\
& - G \sum_{\tau} \langle\langle \bar{n}^{f}_{i\sigma} n^{d}_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle .
\end{aligned} \tag{11}$$

Using Hubbard's[23] approximation (Eq. (III.13) we have

$$\begin{aligned}
\sum_{s} \varepsilon_{is} \langle\langle n^{d}_{i\bar{\sigma}} C_{s\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle & + \langle\langle C^{+}_{i\bar{\sigma}} C_{s\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \\
& - \langle\langle C^{+}_{s\bar{\sigma}} C_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \\
& \simeq \langle n^{d}_{\bar{\sigma}} \rangle \sum_{s \neq i} \varepsilon_{is} \langle\langle C_{s\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle \quad .
\end{aligned} \tag{12}$$

Then, $\langle\langle n^{d}_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle = \frac{1}{\sqrt{N}} \sum_{\ell} e^{-i\vec{k}\cdot\vec{R}_{\ell}} \langle\langle n^{d}_{i\bar{\sigma}} C_{i\sigma} ; C^{+}_{\ell\sigma} \rangle\rangle$

$$= \frac{\langle n^{d}_{\bar{\sigma}}\rangle}{\omega - U - 2G} \quad \frac{1}{\sqrt{N}} e^{-i\vec{k}\cdot\vec{R}_i} + \frac{1}{\sqrt{N}} \sum_{\ell} e^{-i\vec{k}\cdot\vec{R}_\ell}$$

$$\times \sum_{s} \varepsilon_{is} \langle\langle C_{s\sigma}; C^{+}_{\ell\sigma}\rangle\rangle$$

$$- \frac{G}{\omega - U - 2G} \sum_{\tau} \langle\langle \bar{n}^{f}_{i\tau} n^{d}_{i\bar{\sigma}} C_{i\sigma}; C^{+}_{\vec{k}\sigma}\rangle\rangle \; . \qquad (13)$$

Finally Γ^{dd} is given by

$$\Gamma^{dd} = \frac{U}{\sqrt{N}} \sum_{i} e^{ikR_i} \langle\langle n^{d}_{i\bar{\sigma}} C_{i\sigma}; C^{+}_{k\sigma}\rangle\rangle$$

$$= \frac{U\langle n^{d}_{\bar{\sigma}}\rangle}{\omega - U - 2G} \quad 1 + \varepsilon_{k} \langle\langle C_{k\sigma}; C^{+}_{k\sigma}\rangle\rangle$$

$$- \frac{UG}{\omega - U - 2G} \frac{1}{\sqrt{N}} \sum_{i\tau} e^{ikR_i} \langle\langle \bar{n}^{f}_{i\tau} n^{d}_{i\bar{\sigma}} C_{i\sigma}; C^{+}_{k\sigma}\rangle\rangle . \qquad (14)$$

A.2. Derivation of Γ^{fd}

In order to simplify the derivation of the two-particle f-d Green function Γ^{fd}, in which we will use Schweitzer's[21] approximation, we write the equation of motion using the itinerant representation. Also, we first derive the Green function

$$\langle\langle \bar{n}^{f}_{i\sigma'} C_{k'\sigma'} C^{+}_{k\sigma}\rangle\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}'} e^{+i\vec{k}'\cdot\vec{R}_i} \langle\langle \bar{n}^{f}_{i\sigma'} C_{i\sigma'}; C^{+}_{\vec{k}\sigma}\rangle\rangle . \qquad (15)$$

Using the itinerant Hamiltonian (2), we find

$$\left(\omega - \varepsilon(\vec{k}') - 2G\right) \langle\langle \bar{n}^f_{i\sigma'}, C_{k'\sigma}; C^+_{k\sigma} \rangle\rangle = \langle \bar{n}^f_{\sigma'} \rangle$$

$$+ \frac{U}{\sqrt{N}} \sum_j e^{-\vec{k}'\cdot\vec{R}_i} \langle\langle \bar{n}^f_{i\sigma'}, n^d_{j\bar{\sigma}} C_{j\sigma}; C^+_{k\sigma} \rangle\rangle \tag{16}$$

$$- \frac{G}{\sqrt{N}} \sum_{j\sigma'\sigma''} e^{-i\vec{k}'\cdot\vec{R}_j} \langle\langle \bar{n}^f_{i\sigma'}, \bar{n}^f_{j\sigma''} C_{j\sigma}; C^+_{k\sigma} \rangle\rangle .$$

If we now use Schweitzer's approximation (II.24) on the three-particle f-f-d Green function, we obtain

$$\Gamma^{fd} = - \frac{G}{\sqrt{N}} \sum_{i\sigma'} e^{i\vec{k}\cdot\vec{R}_i} \langle\langle \bar{n}^f_{i\bar{\sigma}'}, C_{i\sigma}; C^+_{k\sigma} \rangle\rangle$$

$$= \frac{-n_c G}{\omega' - \varepsilon(\vec{k})} + n_c^2 G^2 \, F(\omega') \langle\langle C_{\vec{k}\sigma}; C^+_{\vec{k}\sigma} \rangle\rangle$$

$$- \frac{n_c{}^2 G^2}{\omega' - \varepsilon(\vec{k})} \langle\langle C_{\vec{k}\sigma}; C^+_{\vec{k}\sigma} \rangle\rangle - \frac{UG}{N^{3/2}} \sum_{\substack{j\ell\vec{k}' \\ \sigma'}} \frac{e^{-i\vec{k}\cdot\vec{R}_j} e^{i\vec{k}'\cdot(\vec{R}_j - \vec{R}_\ell)}}{\omega' - \varepsilon(\vec{k}')}$$

$$\times \langle\langle \bar{n}^f_{i\sigma}, n^d_{\ell\bar{\sigma}} C_{\ell\sigma}; C^+_{\vec{k}\sigma} \rangle\rangle \Big/ \left[1 + (1-2n_c) GF(\omega') + \frac{n_c G}{\omega' - \varepsilon(\vec{k})}\right],$$

where $n_c = \sum_{\sigma'} \langle \bar{n}^f_{\sigma'} \rangle$, $\omega' = \omega - (2-n_c)G$, and

$$F(\omega) = \frac{1}{N} \sum_{\vec{k}} \frac{1}{\omega - \varepsilon(\vec{k})} \quad . \tag{18}$$

If we combine (6), (14), and (17) and rearrange, we obtain the following equation for the d-electron Green function:

$$\left[\omega-\varepsilon(\vec{k})-2G-\frac{Un_c/2}{\omega-U-2G}\,\varepsilon(\vec{k})+\frac{n_c^2G^2\;1-(\omega'-\varepsilon(\vec{k}))F(\omega')}{\omega'-\varepsilon(\vec{k})\quad 1+(1-2n_c)GF(\omega')\;+n_cG}\right]$$

$$\times <<C_{\vec{k}\sigma};C^{+}_{\vec{k}\sigma}>>$$

$$= 1+\frac{Un_c/2}{\omega-U-2G}-\frac{n_cG}{\omega'-\varepsilon(\vec{k})\quad 1+(1-2n_c)GF(\omega')\;+n_cG}$$

$$- UG\;\frac{1}{\sqrt{N}}\sum_{i\sigma'} e^{i\vec{k}\cdot\vec{R}_i}\,\frac{<<\bar{n}^f_{i\sigma'}n^d_{i\bar{\sigma}}C_{i\sigma};C^{+}_{k\sigma}>>}{\omega-U-2G}$$

$$+\frac{\omega'-\varepsilon(\vec{k})}{\omega'-\varepsilon(\vec{k})\quad 1+(1-2n_c)GF(\omega')\;+n_cG}\,\frac{1}{N^{3/2}}$$

$$\times\sum_{\substack{j\ell k'\\ \sigma'}}\frac{e^{-i\vec{k}\cdot\vec{R}_j}e^{i\vec{k}'(\vec{R}_j-\vec{R}_\ell)}}{\omega'-\varepsilon(\vec{k}')}\times<<\bar{n}^f_{j\sigma'}n^d_{\ell\bar{\sigma}}C_{\ell\sigma};C^{+}_{\vec{k}\sigma}>> \quad (19)$$

In the present form this Green function gives the correct Hubbard Green function when G=0. and the correct Schweitzer Green function when U=0. This is easily seen since the additional "cross terms", which are different from those arising in the Hubbard and Schweitzer solutions, are multiplied by the product UG and are therefore not present in these two limits. Therefore, whatever approximation is made on the f-d-d Green function, we still keep the correct limits of U=0 and G=0.

A.3. Derivation of Γ^{fdd}

The approximation for the decoupling of the equation of motion for Γ^{fdd} was guided by the fact that the atomic limit is exact. Therefore, our approximation will be such as to reduce to the atomic limit as $\varepsilon(\vec{k}) \rightarrow \varepsilon_d \equiv 0$.

The first approximation we make is

$$<<\bar{n}^f_{j\sigma}, n^d_{\ell\bar{\sigma}}C_{\ell\sigma}; C^+_{\vec{k}\sigma}>> = \begin{cases} <<\bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}; C^+_{\vec{k}\sigma}>> & \ell=j \\ 0 & \ell\neq j \end{cases} \tag{20}$$

This is within the spirit of the other approximations in which intrasite interactions are thought to be the most important. Then we have for the last term in (19)

$$\frac{1}{N^{3/2}} \sum_{\substack{j\ell k' \\ \sigma'}} \frac{e^{-ikR_j} e^{ik'(R_j-R_\ell)}}{\omega'-\varepsilon(k')} <<\bar{n}^f_{j\sigma}, n^d_{\ell\bar{\sigma}}C_{\ell\sigma}; C^+_{k\sigma}>>$$

$$= \frac{1}{N^{1/2}} \sum_{j\sigma'} \left(\frac{1}{N} \sum_{\vec{k}'} \frac{1}{\omega'-\varepsilon(\vec{k}')}\right) e^{-i\vec{k}\cdot\vec{R}_j} <<\bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}; C^+_{k\sigma}>>,$$

$$= F(\omega') \frac{1}{\sqrt{N}} \sum_{j\sigma'} e^{-i\vec{k}\cdot\vec{R}_j} <<\bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}; C^+_{\vec{k}\sigma}>> , \tag{21}$$

where $F(\omega')$ is defined in (18).

We now have one intrasite f-d-d Green function to derive. The equation of motion is

$$\omega<<\bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}; C^+_{\vec{k}\sigma}>> = < \bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}, C^+_{\vec{k}\sigma} >$$

$$+ <<\bar{n}^f_{j\sigma}, n^d_{j\bar{\sigma}}C_{j\sigma}, H^L ; C^+_{\vec{k}\sigma}>> . \tag{22}$$

Using (1) we obtain

$$(\omega-U-2G)\ \frac{1}{\sqrt{N}} \sum_{j\sigma'} e^{ikR_j} << \bar{n}^f_{j\sigma'}, n^d_{j\sigma} C_{j\sigma}; C^+_{k\sigma} >>$$

$$= \sum_{\sigma'} < \bar{n}^f_{\sigma'}, n^d_{\bar{\sigma}} > + \frac{1}{\sqrt{N}} \sum_{j\ell\sigma'} e^{ikR_j}\ \varepsilon_{j\ell}\ << \bar{n}^f_{j\sigma'}, n^d_{j\bar{\sigma}} C_{\ell\sigma}; C^+_{\vec{k}\sigma} >>$$

$$+ << \bar{n}^f_{j\sigma'}, C^+_{j\bar{\sigma}} C_{\ell\bar{\sigma}} C_{j\sigma}; C^+_{k\sigma} >> - << \bar{n}^f_{j\sigma'}, C^+_{\ell\bar{\sigma}} C_{j\bar{\sigma}} C_{j\sigma}; C^+_{k\sigma} >>$$

$$- \frac{G}{\sqrt{N}} \sum_{j\sigma'\sigma''} e^{ikR_j} << \bar{n}^f_{j\sigma'}, \bar{n}^f_{j\sigma''} n^d_{j\bar{\sigma}} C_{j\sigma}; C^+_{k\sigma} >>. \qquad (23)$$

The second term on the right hand side can be found using the Hubbard-type approximation and is equal to

$$\sum_{\sigma'} < \bar{n}^f_{\sigma'}, n^d_{\bar{\sigma}} >\ \varepsilon(k) << C_{k\sigma}; C^+_{k\sigma} >>. \qquad (24)$$

The third term can be found by using the idempotency of the f-electron number operator and the condition which projects out the state with two f-holes; i.e., $< \bar{n}^f_{\sigma} \bar{n}^f_{\sigma} > = 0$. Then

$$\sum_{\sigma''} << \bar{n}^f_{j\sigma'}, \bar{n}^f_{j\sigma''} n^d_{j\bar{\sigma}} C_{j\sigma}; C^+_{\vec{k}\sigma} >> = << \bar{n}^f_{j\sigma'}, n^d_{j\bar{\sigma}} C_{j\sigma}; C^+_{\vec{k}\sigma} >>. \qquad (25)$$

We thus arrive at an expression for Γ^{fdd}:

$$\frac{1}{\sqrt{N}} \sum_{j\sigma'} e^{i\vec{k}\cdot\vec{R}_j} << \bar{n}^f_{j\sigma'}, n^d_{j\bar{\sigma}} C_{j\sigma}; C^+_{\vec{k}\sigma} >>$$

$$= \frac{1}{\omega-U-G} \sum_{\sigma'} < \bar{n}^f_{\sigma'}, n^d_{\bar{\sigma}} > \left(1+\varepsilon(\vec{k}) << C_{\vec{k}\sigma}\ ' C^+_{\vec{k}\sigma} >> \right). \qquad (26)$$

Upon substituting this equation into (19) and rearranging terms we get for the d-electron Green function

$$\langle\langle C_{\vec{k}\sigma} ; C^{+}_{\vec{k}\sigma} \rangle\rangle = \frac{G^{\sigma}_{NUM}}{G^{\sigma}_{DEN}} , \qquad (27)$$

where

$$G^{\sigma}_{NUM} = 1 + \frac{Un_{c}/2}{\omega-U-2G} - \frac{n_{c}G}{[\omega'-\varepsilon(\vec{k})][1+(1-2n_{c})GF(\omega')]+n_{c}G}$$

$$- \frac{UG \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega-U-G} \left[\frac{1}{\omega-U-2G} + \frac{[\omega'-\varepsilon(\vec{k})] \; F(\omega')}{[\omega'-\varepsilon(\vec{k})] \, [1+(1-2n_{c})GF(\omega')]+n_{c}G} \right] \qquad (28)$$

and

$$G^{\sigma}_{DEN} = \omega - \varepsilon(\vec{k}) - 2G - \frac{Un_{c}/2 \; \varepsilon(\vec{k})}{\omega-U-2G}$$

$$+ \frac{n_{c}^{2} \; G^{2}\left[1-[\omega'-\varepsilon(\vec{k})]F(\omega')\right]}{[\omega'-\varepsilon(\vec{k})] \, [1+(1-2n_{c})GF(\omega')]+n_{c}G}$$

$$+ \frac{UG \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle}{\omega-U-G} \; \varepsilon(\vec{k}) \; \frac{1}{\omega-U-2G}$$

$$+ \frac{\omega'-\varepsilon(\vec{k}) \; F(\omega')}{\left[\omega'-\varepsilon(\vec{k})\right]\left[1+(1-2n_{c})GF(\omega')\right]+n_{c}G} \; . \qquad (29)$$

B. Derivation of the f-d Correlation Function

We will now derive the correlation function

$$C^{fd} = \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma'} n^{d}_{\bar{\sigma}} \rangle \qquad (30)$$

which appears in the d-electron Green function. Since we don't know the exact eigenstates of the Hamiltonian, the partition function cannot be calculated and another method must be used.

If we try to derive C^{fd} from the f-d Green function, we find that, since Γ^{fd} depends on $G^{\sigma}(k,\omega)$, the correlation function we seek would have to calculate self-consistently. That calculation would be sufficiently complicated that a simpler approximation is necessary. Therefore, we will adhere to the basic requirement that the Green function be exact in the atomic limit and begin with the atomic-limit f-d correlation function.

The f-d correlation function, C^{fd}, can be found by extending the atomic-limit correlation function to a finite band. From Eq. (V.24),

$$C^{fd} = \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma}, n^{d}_{\bar{\sigma}} \rangle = \frac{f(G)}{1-f(U+G)+f(G)} \tag{31}$$

where

$$f(x) = \left[e^{\beta(x-\mu)} + 1 \right]^{-1} \tag{32}$$

is the Fermi function.

Since we are dealing with finite bands and not atomic d-levels, we will replace the Fermi function at a discrete energy by a sum over $\vec{k}$ of the Fermi function at $\varepsilon(\vec{k})$:

$$\begin{aligned} H(x) &= \frac{1}{N} \sum_{\vec{k}} \left[e^{\beta[\varepsilon(\vec{k})+x-\mu]} + 1 \right]^{-1} \\ &= \int \frac{\rho_o(E)\,dE}{e^{\beta(E+x-\mu)}+1}, \end{aligned} \tag{33}$$

where $\rho_o(E)$ is the unperturbed density of states for the d band centered on $\varepsilon_d=0$. Then

$$C^{fd} = \sum_{\sigma'} \langle \bar{n}^{f}_{\sigma}, n^{d}_{\bar{\sigma}} \rangle = \frac{H(G)}{1-H(U+G)+H(G)} \quad . \tag{34}$$

This ansatz requires calculating C^{fd} by using the unperturbed density of states, $\rho_o(E)$. Therefore, the calculation is not self-consistent. However, the Green function is exact in the atomic limit and gives the correct Green functions when U or G is zero.

C. The Total Ground-State Energy

The ground-state energy of the model system described by the Hamiltonian (2) can be calculated using the d-electron Green function only. This is fortunate, since the f-electron Green function would be difficult to derive. The d-electron Green function is easier to calculate since $n^{d}_{i\sigma}$ commutes with the Hamiltonian (2), whereas $n^{d}_{i\sigma}$ doesn't.

The total energy is given by

$$E = (\Delta + .5 - 2G)n_c + E_b \ , \tag{35}$$

where Δ is the gap energy, defined in Section II, n_c is the number of conduction electrons in the d-band, and E_b is the total energy of the band electrons. Since the electrons in the conduction band interact not only with the f-electrons but also with themselves, the energy of the band electrons can be calculated by using the expression derived in

Appendix B. We can use either (B.17) or (B.18), depending on which correlation function we use.

If we use (B.18), the f-d correlation function is required. As stated before, the f-d correlation function is difficult to calculate. We also find that if we use the same approximation for the f-d correlation function in this expression as we did in the approximate calculation of the Green function, we would not obtain the same ground-state energy when U=0 as in the Schweitzer calculation. This is because, whereas the term including the f-d correlation function in the Green function drops out when U=0, it remains and is necessary in the expression for the total energy. Therefore, we cannot accept this approximation to the energy.

Equation (B.17), on the other hand, uses the d-d correlation function. Therefore, we shall use (B.17) and we derive the d-d correlation function in the next subsection.

C.1. Derivation of the d-d Correlation Function

If we attempt to use the atomic-limit d-d Green function and to use this in Eq. (B.17) for the energy of the present model, we find that we do not recover the ground-state energy of the Hubbard model when G=0. Therefore, we must derive an expression for the finite-bandwidth d-d correlation function which gives the correct Hubbard limit. The equation for the total energy is given by (B.17)

$$E = \sum_{\vec{k}\sigma} \int_{-\infty}^{\mu} \omega f(\omega) A^{\sigma}(\vec{k},\omega)\, d\omega - \frac{UN}{2} \sum_{\sigma} \langle n^{d}_{-\sigma} n^{d}_{\sigma} \rangle \quad . \tag{36}$$

We follow the example derived in Section VI.B. and the d-d correlation function for the present model is approximated in such a way as to give the Hubbard value for the total energy when G=0. The d-d Green function is given by

$$\sum_i \langle\langle n^d_{i\bar{\sigma}} C_{i\sigma}; C^+_{i\sigma}\rangle\rangle = \left[\frac{n_c/2 - C^{fd}}{\omega-U-2G} + \frac{C^{fd}}{\omega-U-G}\right]$$

$$\cdot \quad N + \sum_{\vec{k}} \varepsilon(\vec{k})\langle\langle C_{\vec{k}\sigma}; C^+_{\vec{k}\sigma}\rangle\rangle \quad . \qquad (37)$$

Then the d-d correlation function is given by

$$\sum_i \langle n^d_{i\sigma} n^d_{i\bar{\sigma}}\rangle = \int_{-\infty}^{\mu} \left[\frac{n_c/2 - C^{fd}}{\omega-U-2G} + \frac{C^{fd}}{\omega-U-G}\right] \sum_{\vec{k}} \varepsilon(\vec{k}) A^{\sigma}(\vec{k},\omega)\, d\omega \qquad (38)$$

and the total ground-state energy is

$$E_T = (\Delta + .5 - 2G)n_c + \int_{-\infty}^{\mu} \omega \sum_{\vec{k}\sigma} A^{\sigma}(\vec{k},\omega)\, d\omega$$

$$- \frac{U}{2} \int_{-\infty}^{\mu} \left[\frac{n_c/2 - C^{fd}}{\omega-U-2G} + \frac{C^{fd}}{\omega-U-G}\right] \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) A^{\sigma}(\vec{k},\omega)\, d\omega. \qquad (39)$$

Therefore, we have the total energy given by Eq. (39) which agrees with Schweitzer's results when U=0, since then $A^{\sigma}(\vec{k},\omega)$ is just the spectral weight function derived from Schweitzer's Green function. In addition, when G=0 (39) agrees with the Galitskii-Migdal expression for the total energy of a band of interacting Fermions.

Equation (39) has the proper limits when G=0. and U=0. When U and G are not zero, C^{fd} is required and is given by Eq. (34). This expression is not self-consistent but gives the correct atomic limit for the total energy.

D. Results

In this section we present the results of calculations using the improved approximation described above. The ground state occupation of the conduction band was found by the method described in Appendix C.

Figure 18 shows the perturbed density of states (the unperturbed density of states is given by Eq. II.16) for G/W=.3, U/W=.3, and n_c=.4, for which the chemical potential is -.221. The band has an increase in the density of available states at the bottom, which is the contribution of the attractive particle-hole potential of the Falicov-Kimball model. In addition, the band is split, due to the conduction-electron correlation. According to the Hubbard model approximation, this splitting takes place for any non-zero value of U.

Figure 16 is the available phase space calculated within the improved approximation. The region of intermediate valence accessible via a first-order transition is of the same general shape as the same region in the mean-field approximations of section IV.

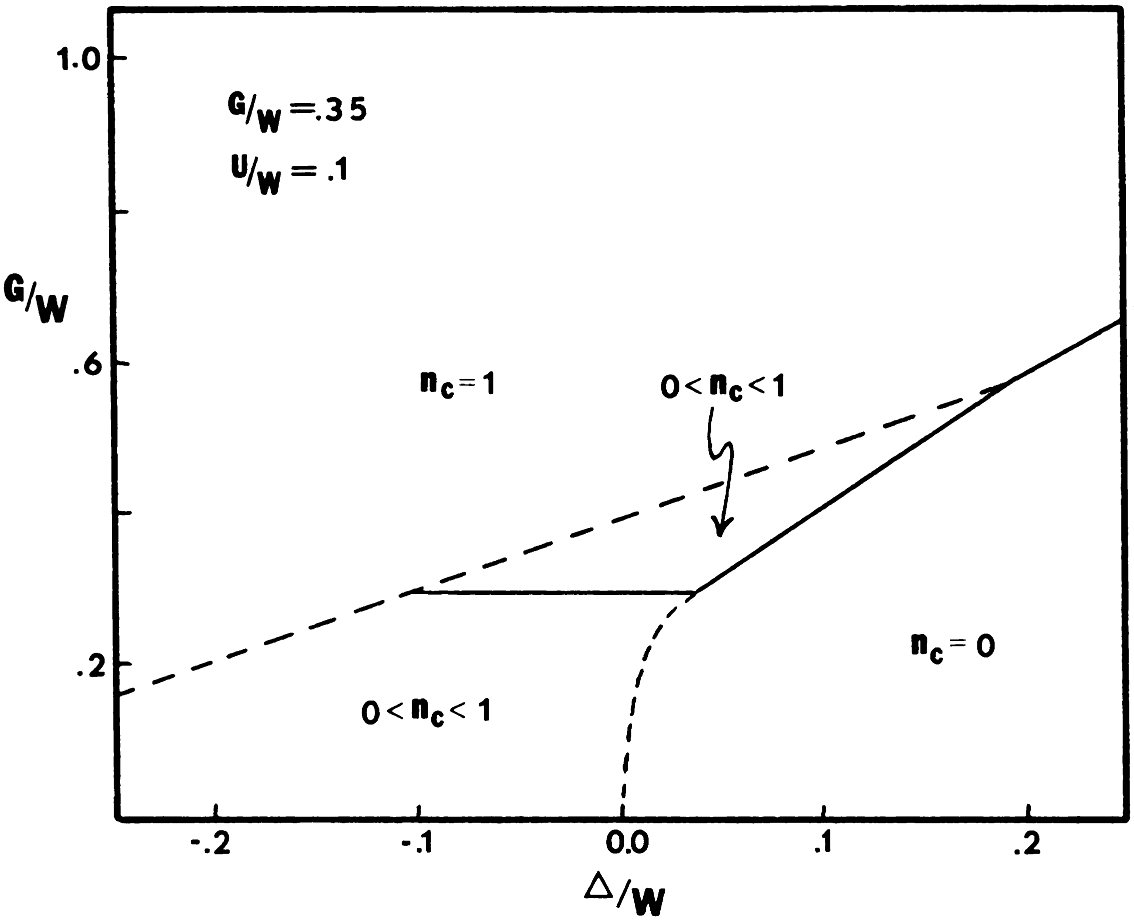


Figure 16. Phase diagram for improved approx.

In Figure 17 we have plotted the value of the conduction band occupation against the gap parameter. This is compared with the case where U=0, which is Schweitzer's result. Once again, the critical values of the gap parameter and the number of conduction-band electrons are shifted by the addition of the correlation effects in such a way as to oppose the first-order transition and the occupation of the conduction band.

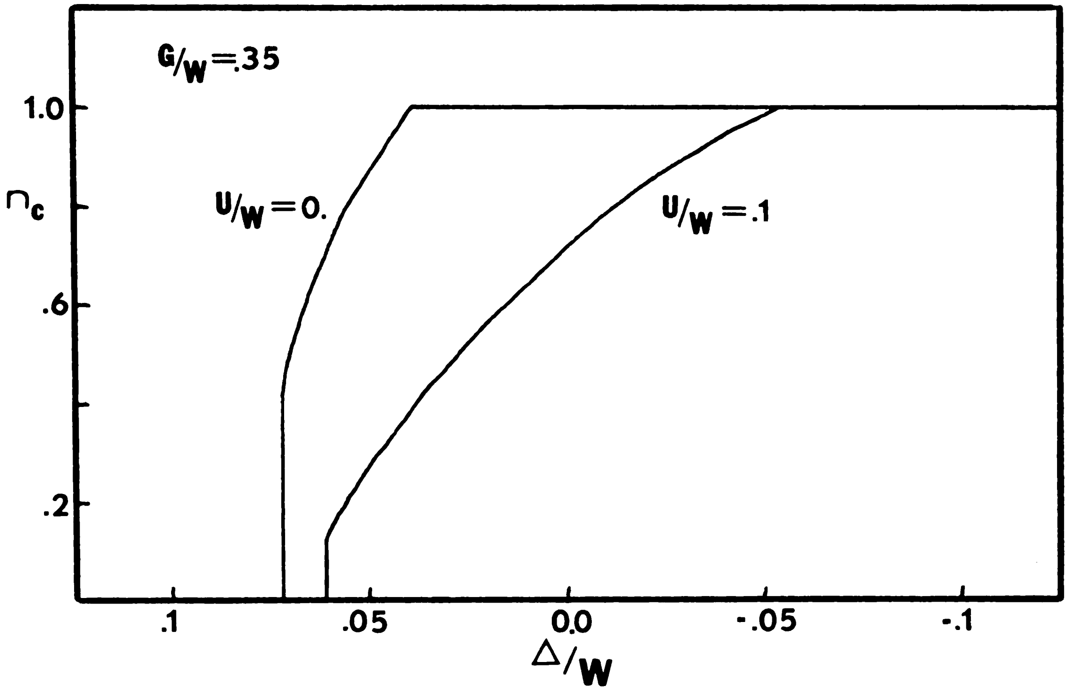


Figure 17. n_c vs. band gap for improved approx.

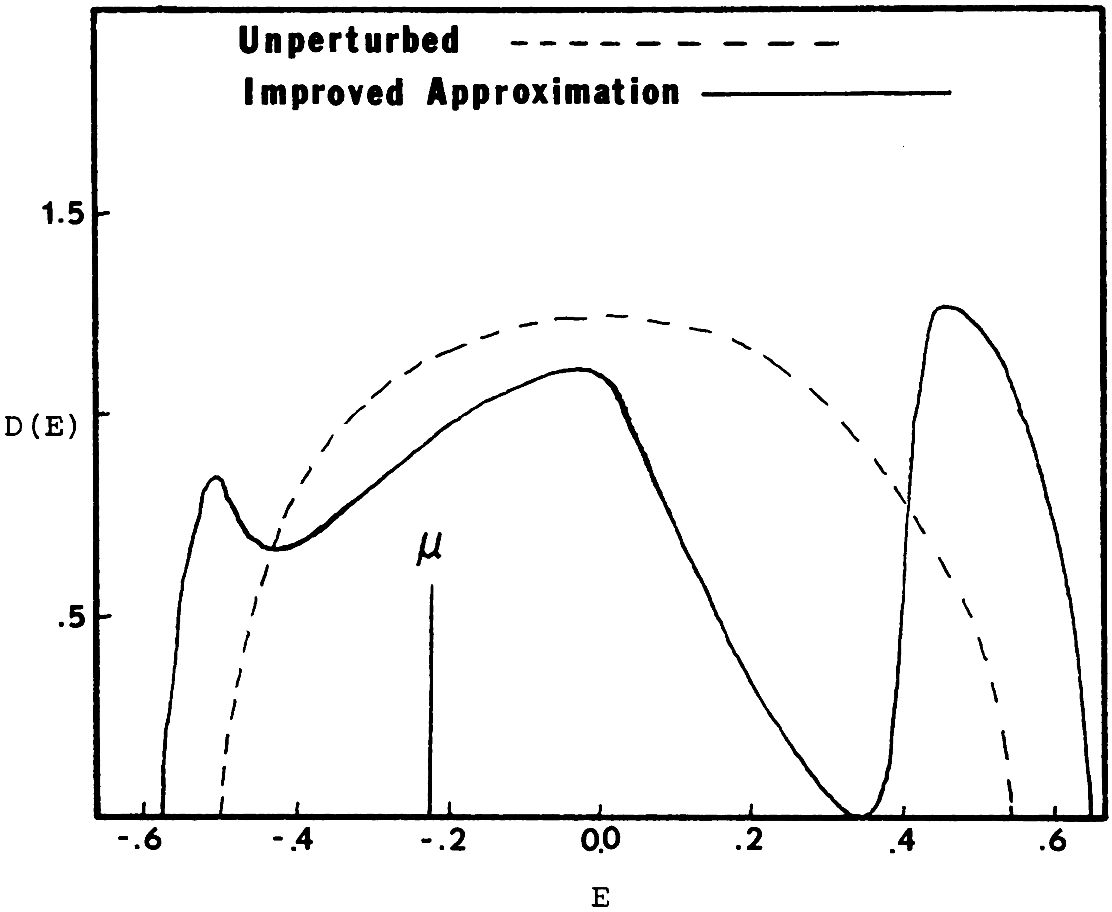


Figure 18. Density of states in improved approx.

VIII. SUMMARY AND DISCUSSION

We have presented the results of an investigation into the ground state of a two band Hubbard model. This model differs from other two-band models in that both bands have electron correlation. Although this model is interesting in general, our motivation was the application of this model to the problem of the mixed-valence systems.

We started with the Falicov-Kimball Hamiltonian and added a d-electron interaction term modeled after Hubbard's correlation term. This correlation term was approximated using two mean-field approximations. In the first approximation, the contribution of the correlation term to the total ground-state energy was calculated using the mean-field energy. This total energy was then minimized to find the ground state. The result was that Schweitzer's original prediction of a first order transition to an intermediate valence phase was unchanged. However, the critical parameters had values different from those found by Schweitzer.

The second mean-field approximation consisted of making the approximation in the Hamiltonian and then deriving a new Green function. From the Green function, the ground-state energy was calculated and the ground state found by minimization. As with the first mean-field approximation, Schweitzer's results were not changed qualitatively but required different critical values of the parameters.

As an intermediate calculation, we applied Hubbard's decoupling scheme to the two-band model Hamiltonian. This was done by Mazzaferro and Ceva for the Falicov-Kimball Hamiltonian only (without d-electron correlation). Their work shows no first order transition as a function of temperature. We found that a first-order transition as a function of the gap parameter is possible and that an intermediate valence phase can be stabilized for certain values of the parameters. This implies that Schweitzer's decoupling scheme is not necessary to explain the first order transition to an intermediate valence regime but that Hubbard's approximation is sufficient.

An improved approximation was also presented in which the Green function which was derived has the following limits:

i) agreement with Schweitzer when U=0

ii) agreement with Hubbard when G=0

iii) agreement with exact atomic limit when bandwidth goes to zero.

This Green function was used to calculate the ground state of the system. The results were essentially the same as the mean-field Green function results. The density of states derived using the improved appeoximation is significantly different from the mean-field results and therefore the excitation spectra will be different for the two approximations. However, the ground-state occupation of the conduction band has a similar dependence on the parameters in both approximations. Therefore, within this approximation, which agrees with the limiting cased mintioned above, Schweitzer's results are not changed significantly by the addition of conduction-electron correlation.

Schweitzer used his model to calculate the critical pressure required to give an intermediate valence of 2.6. He found a critical pressure of 5 kbar, which is lower than the experimental value of 6.5 kbar. We have shown that including d-electron predicts a lower occupation of the conduction band at the forst order transition. This implies that the two-band model should give a higher critical pressure and a better agreement with the experimental results.

Possible extensions of these calculations include: i) improvement of the treatment of the d-electron correlation beyond Hubbard I. Since part of Hubbard's later approximation (Hubbard III) is equivalent to CPA and since Schweitzer's approximation seems to be at least numerically equivalent to CPA, it would be interesting to begin with the two-band Hamiltonian and to do a CPA calculation on it.

ii) finite temperature. All of the calculations presented in this thesis are ground state calculations. It would be useful to extend these calculations to investigate the properties of the two-band model at finite temperatures.

The ground state of the two-band Hubbard model within the approximations described in this thesis can be either an insulator, a mixed-valent conductor, or a monovalent conductor, depending upon the values of the parameters. This suggests that SmS, a mixed-valent material under pressure, is a good candidate for a system which can be described by a two-band Hubbard model.

APPENDICES

APPENDIX A

ZUBAREV GREEN FUNCTIONS

The Green functions used in the derivations presented here were introduced by Zubarev. We present a brief summary of the notation and the basic equations which are used throughout the present work.

We consider the grand canonical ensemble such that the average of a quantum mechanical operator A is given by

$$\langle A\rangle = 1/Z \ \mathrm{Tr}\ Ae^{-\mu\tilde{H}} \quad , \tag{A.1}$$

where $\tilde{H} = H - \mu N$ and $Z = \mathrm{Tr}\ e^{-\beta\tilde{H}}$. H is the Hamiltonian, N is the total number operator, and μ is the chemical potential. We write the time dependence of an operator in the Heisenberg representation so that

$$A(t) = e^{iHt}Ae^{-iHt} \tag{A.2}$$

For any operators A and B, the retarded and advanced Green functions are defined by

$$G_{r,a}(t,t') \equiv \langle\langle A(t);B(t')\rangle\rangle_{r,a}$$

$$= \left\{\begin{matrix} -i\theta(t-t') \\ i\theta(t-t') \end{matrix}\right\} < A(t),B(t') >, \tag{A.3}$$

where the upper (lower) term denotes the retarded (advanced) Green function and where

$$\theta(x) = \begin{cases} 1 & x>0 \\ 0 & \text{otherwise} \end{cases} \qquad \text{(A.4)}$$

is the step function.

The equation of motion for the Green function can be derived using the equation of motion of a Heisenberg operator. The result is:

$$i\frac{d}{dt}\langle\langle A(t);B(t')\rangle\rangle = \delta(t-t')\langle[A,B]\rangle + \langle\langle [A(t),H];B(t')\rangle\rangle. \qquad \text{(A.5)}$$

This equation applies to retarded or advanced Green functions. The second term on the right hand side of (A.5) usually involves a more complicated, higher-order double-time Green function. The equation of motion for this new Green function is then derived, which, in general, involves a still more complicated Green function, and so on. This chain of equations is terminated either automatically, as in an exactly soluble case, or by some approximation involving writing a Green function in terms of a less complicated one.

It can be shown that $G_{r,a}(t,t') = G_{r,a}(t-t')$, so that we can define the Fourier transforms

$$G^{r,a}(E) = \langle\langle A;B\rangle\rangle^{r,a}_{E} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle\langle A(t);B\rangle\rangle^{r,a} e^{iEt}\,dt. \qquad \text{(A.6)}$$

The corresponding equation of motion is

$$E\langle\langle A;B\rangle\rangle_E = \frac{1}{2\pi}\langle [A,B]\rangle + \langle\langle [A,H];B\rangle\rangle_E . \qquad (A.7)$$

Correlation functions can easily be derived from the corresponding Green function by using the following equation:

$$\langle B(t')A(t)\rangle = i\int_{-\infty}^{\infty}\left[\langle\langle A;B\rangle\rangle_{E+io^+} - \langle\langle A;B\rangle\rangle_{E-io^+}\right]f(E)\, e^{-E(t-t')}dE \qquad (A.8)$$

where $f(E) = \frac{1}{e^{\beta(E-\mu)}+1}$ is the Fermi function.

APPENDIX B

TOTAL ENERGY

We now derive several expressions for the total energy of a system of interacting Fermions, all of which use the double-time Green function.

We begin with the equation of motion (A.5):

$$i\frac{d}{dt}G(t) = i\frac{d}{dt}<<A(t);B(0)>> = \delta(t)<[A,B]> + <<[A(t),H];B(0)>>. \tag{B.1}$$

Let $A(t) = C_{\vec{k}}(t)$ and $B(0) = C_{\vec{k}}^{+}$ and consider the general Hamiltonian

$$H = \sum_{\vec{k}} \varepsilon(\vec{k}) C_{\vec{k}}^{+} C_{k} + \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}',\vec{q}\vec{q}'} C_{\vec{p}}^{+} C_{\vec{q}}^{+} C_{\vec{p}'} C_{\vec{q}'} \tag{B.2}$$

Then

$$i\frac{d}{dt}<<C_{\vec{k}}(t);C_{\vec{k}}^{+}>> = \delta(t) + \varepsilon(\vec{k})<<C_{\vec{k}}(t);C_{\vec{k}}^{+}>> + \sum_{\vec{p}',\vec{q}\vec{q}'} V_{\vec{k}\vec{p}',\vec{q}\vec{q}'}<<C_{\vec{q}}^{+}(t)C_{\vec{p}'}(t)C_{\vec{q}'}(t);C_{\vec{k}}^{+}>>. \tag{B.3}$$

If we now let $t \to o^{+}$ and use (A.8) we obtain

$$\frac{i}{2\pi}\int_{-\infty}^{\infty} \omega f(\omega)\left[G(\omega+io^{+}) - G(\omega-io^{+})\right]d\omega = \varepsilon(\vec{k})<n_{\vec{k}}> + \sum_{\vec{p}',\vec{q}\vec{q}'} V_{\vec{k}\vec{p}',\vec{q}\vec{q}'}<C_{\vec{q}}^{+}C_{\vec{p}'}C_{\vec{q}'}C_{\vec{k}}^{+}>. \tag{B.4}$$

Since $E_{\text{Tot}} = \langle H \rangle$, then using the general Hamiltonian (B.2) we have

$$E_T = \langle H \rangle = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle + \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}', \vec{q}\vec{q}'} \cdot$$

$$\cdot \langle C^{+}_{\vec{p}} C^{+}_{\vec{q}} C_{\vec{p}'} C_{\vec{q}'} \rangle . \tag{B.5}$$

Therefore, if we sum (B.4) over $\vec{k}$ we get

$$\sum_{\vec{k}} \int_{-\infty}^{\infty} \omega f(\omega) A(\vec{k},\omega) d\omega = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle \quad , \tag{B.6}$$

where $A(\vec{k},\omega) = \frac{i}{2\pi} \left[G(\vec{k},\omega+io^{+}) - G(\vec{k},\omega-io^{+}) \right].$ (B.7)

In order to recover the factor of 1/2 difference between equations (B.5) and (B.6), we add

$$\sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle \tag{B.8}$$

to both sides and divide by 2. We then obtain

$$E = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle + \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}', \vec{q}\vec{q}'} \langle C^{+}_{\vec{p}} C^{+}_{\vec{1}} C_{\vec{p}'} C_{\vec{q}'} \rangle$$

$$= \sum_{\vec{k}} \int_{-\infty}^{\infty} \frac{\omega + \varepsilon(\vec{k})}{2} f(\omega) A(k,\omega) d\omega, \tag{B.9}$$

which is the Galitskii-Migdal expression for the total energy of a system of interacting Fermions.

If we now consider a non-interacting band of electrons interacting with an external potential, we can write a

Hamiltonian of the form

$$H = \sum_{\vec{k}} \varepsilon(\vec{k}) n_{\vec{k}} + \sum_{\vec{p}\vec{p}'} V_{\vec{p}\vec{p}'} C^{+}_{\vec{p}} C_{\vec{p}'} \quad . \tag{B.10}$$

In this case

$$i\frac{d}{dt}\langle\langle C_{\vec{k}}(t); C^{+}_{\vec{k}}\rangle\rangle = \delta(t) + \varepsilon(\vec{k})\langle\langle C_{\vec{k}}(t); C^{+}_{\vec{k}}\rangle\rangle$$

$$+ \sum_{\vec{p}} V_{\vec{k}\vec{p}}\langle\langle C_{\vec{k}}(t); C^{+}_{\vec{p}}\rangle\rangle. \tag{B.11}$$

Converting the Green functions to correlation functions by using (A.8) gives

$$\sum_{\vec{k}} \int_{-\infty}^{\infty} \omega f(\omega) A(\vec{k},\omega) d\omega = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}}\rangle + \sum_{\vec{k}\vec{p}} V_{\vec{k}\vec{p}} \langle C^{+}_{\vec{p}} C_{\vec{k}}\rangle . \tag{B.12}$$

The total energy is given by

$$E_T = \langle H\rangle = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}}\rangle + \sum_{\vec{k}\vec{p}} V_{\vec{k}\vec{p}} \langle C^{+}_{\vec{k}} C_{\vec{p}}\rangle . \tag{B.13}$$

Therefore

$$E_T = \sum_{\vec{k}} \int_{-\infty}^{\infty} \omega A(\vec{k},\omega) f(\omega) d\omega . \tag{B.14}$$

Finally, we will have a need for an expression for the total energy of a system in which both an external potential and a mutual interaction are present. In this case the Hamiltonian can be represented by

$$H = \sum_{\vec{k}} \varepsilon(\vec{k}) n_{\vec{k}} + \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}',\vec{q}\vec{q}'} C^{+}_{\vec{p}} C^{+}_{\vec{q}} C_{\vec{p}'} C_{\vec{q}'}$$

$$+ \sum_{\vec{p}\vec{p}'} V_{\vec{p}\vec{p}'} C^{+}_{\vec{p}} C_{\vec{p}'} . \tag{B.15}$$

As was done in the previous derivations, we find

$$E_T = \langle H \rangle = \sum_{\vec{k}} \varepsilon(\vec{k}) \langle n_{\vec{k}} \rangle + \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}',\vec{q}\vec{q}'} \cdot$$

$$\cdot \langle C^{+}_{\vec{p}} C^{+}_{\vec{q}} C_{\vec{p}'} C_{\vec{q}'} \rangle + \sum_{\vec{p}\vec{p}'} V_{\vec{p}\vec{p}'} \langle C^{+}_{\vec{p}} C_{\vec{p}'} \rangle \tag{B.16}$$

Therefore, (B.15) and (B.16) differ by a factor of 1/2 on the potential energy term. We now have two options, depending on whether we can calculate independently the correlation function $\langle C^{+}_{\vec{p}} C^{+}_{\vec{q}} C_{\vec{p}'} C_{\vec{q}'} \rangle$ or $\langle C^{+}_{\vec{p}} C_{\vec{p}'} \rangle$. The two possible results are found in the same way as in the two previous derivations. The results are

$$E_T = \sum_{\vec{k}} \int_{-\infty}^{\infty} \omega f(\omega) A(\vec{k},\omega) d\omega$$

$$- \frac{1}{2} \sum_{\substack{\vec{p}\vec{p}' \\ \vec{q}\vec{q}'}} V_{\vec{p}\vec{p}',\vec{q}\vec{q}'} \langle C^{+}_{\vec{p}} C^{+}_{\vec{q}} C_{\vec{p}'} C_{\vec{q}'} \rangle \tag{B.17}$$

and

$$E_T = \sum_{\vec{k}} \int_{-\infty}^{\infty} \frac{\omega + \varepsilon(\vec{k})}{2} f(\omega) A(\vec{k},\omega) d\omega + \frac{1}{2} \sum_{\vec{p}\vec{p}'} V_{\vec{p}\vec{p}'} \langle C^{+}_{\vec{p}} C_{\vec{p}'} \rangle . \tag{B.18}$$

When the external potential is due to another band of electrons with number operator n, the total energy is

$$E_T = \sum_{\vec{k}} \int_{-\infty}^{\infty} \frac{\omega+\varepsilon(\vec{k})}{2} f(\omega)A(\vec{k},\omega)d\omega$$

$$+ \frac{1}{2} \sum_{i\vec{p}\vec{p}'} V_{\vec{p}\vec{p}'} \langle n_i C^+_{\vec{p}} C_{\vec{p}'} \rangle . \qquad (B.19)$$

APPENDIX C

GENERAL METHOD FOR OBTAINING THE GROUND STATE

The method used to find the occupancy, n_c, of the conduction band is described in this Appendix. This method was used in Chapters IV, VI, and VII.

Since the ground state of any system corresponds to the state of minimum energy, the usual procedure for finding the ground state is to calculate the total energy as a function of the variable of interest and then to minimize the energy with respect to this variable. The most general expression derived in this thesis for the ground-state energy as a function of n_c can be written as

$$E(n_c) = \int_{-\infty}^{\infty} f(\omega, n_c, \mu)\, d\omega. \tag{C.1}$$

The chemical potential, μ, is found using the condition that

$$n_c = \int_{-\infty}^{\infty} F(\omega, n_c, \mu)\, d\omega. \tag{C.2}$$

In all of the calculations done in this thesis, the chemical potential, μ, was found by calculating the root of the equation

$$I(\mu) = n_c - \int_{-\infty}^{\infty} F(\omega, n_c, \mu)\, d\omega \tag{C.3}$$

for a given value of n_c. A "root-finding" subroutine was used which calculated the root within specified bounds very quickly. The functions f and F contain the sum over $\vec{k}$ of the single-particle spectral weight function,

$$\sum_{\vec{k}} A^{\sigma}(\vec{k},\omega), \qquad (C.4)$$

and this sum usually had to be performed numerically. Therefore, each evaluation of $I(\mu)$ required that a double integration be done numerically.

Once μ is calculated for a given value of n_c, the total energy is given by Eq. (C.1). Thus, the total energy as a function of n_c, $E(n_c)$, is calculated and plotted vs. n_c. Then the occupancy of the conduction band is given by the value of n_c which has the lowest energy.

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