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Intermediate valence states in the Falicov-Kimball model

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The Falicov-Kimball model for an electronically driven semiconductor to metal transition is treated within an approximation which includes intra-atomic excitonic correlations. Discontinuous transitions from the semiconducting to a metallic phase with intermediate valence are found in contrast with the mean-field treatments where the transition is always to a pure valence metallic state when discontinuous for simple band densities of states. The results are applied in a description of the phase transitions of samaruim monochalcogenides under pressure. It is demonstrated that this simple model provides a reasonable theoretical description for intermediate valence phenomenon provided excitonic correlations are taken into account.

I. INTRODUCTION

The phenomenon of intermediate valence found in certain rare-earth compounds has been the subject of considerable experimental and theoretical interest.[1] Although the experimental aspects of this phenomenon have been well established, particularly in the samarium monochalcogenides,[2-11] the theoretical picture is uncertain at present, there having been suggested various models[12-23] some of which are quite complicated. It is the purpose of this paper to demonstrate that the very simple Falicov-Kimball model[12] for an electronically driven semiconductor to metal transition, when properly treated, provides a reasonable theoretical description within which to consider the pressure and chemically induced transitions from the semiconducting phase to an intermediate valence metallic phase observed in the samarium chalcogenides.

A system having both localized and itinerant quasiparticle states is described in the Falicov-Kimball model by a Hamiltonian consisting of three terms: the Hamiltonian for the localized ionic states, the Hamiltonian for the one-electron band states, and the intra-atomic Coulomb interaction between the two types of states.

Now it is generally believed, based on treatments of this model within the mean-field approximation, that the Falicov-Kimball model cannot describe the discontinuous transition from semiconducting to an intermediate valence metallic state as observed in SmS under pressure. Although the details of the first-order phase transitions depend on the form of the conduction band, the transition found in mean-field treatments is to a pure valence metallic state for reasonable band shapes. To rectify this assumed deficiency the model has been generalized[24-28] to include hybridization of the localized states with the band states. However, this extended Falicov-Kimball model presents a very formidable problem being something like a "Kondo lattice" when the strongly correlated character of the localized state is taken into account, and therefore the current one-electron-type treatments of this extended model cannot be considered reliable. Although it may be essential to take into account this mixing of localized and band states in order to describe the magnetic properties and the very-low-temperature behavior of these materials, the mixing can probably be ignored in developing a theory for the transition from semiconductor to intermediate valence metal. We find that excitonic correlations neglected in the mean-field treatments of the Falicov-Kimball model can stabilize the intermediate valence state on the metallic side of the transition.

In the Falicov-Kimball model the transition is electronically driven by the Coulomb interaction between the localized $4f$ electrons and the conduction-band electrons. Some other theories[14,15] for the transition have ignored this interaction and have assumed that lattice contributions to the energy provide the mechanism which drives the transition. Also the lattice energy has even been invoked to stabilize the intermediate valence state.[16] Lattice effects may be important, however, we present here results which indicate that the Falicov-Kimball model can yield a transition in qualitative agreement with the experiments on the samarium monochalcogenides with reasonable values for the parameters of the model.

The idealized version of the Falicov-Kimball model Hamiltonian that we consider is presented in Sec. II where we describe our approximate method for treating the excitonic correlations. In Sec. III we discuss the results obtained and apply these to the description of SmS, SmSe, and SmTe

under pressure. Finally, in Sec. IV we make some comparisons with related treatments.

II. MODEL AND TREATMENT

For simplicity we assume the following idealized form for the Falicov-Kimball model Hamiltonian:

$$H=\sum_{i\sigma}(\epsilon_f f^\dagger_{i\sigma}f_{i\sigma}+\tfrac{1}{2}Uf^\dagger_{i-\sigma}f_{i-\sigma}f^\dagger_{i\sigma}f_{i\sigma}) + \sum_{k\sigma}\epsilon(k)c^\dagger_{k\sigma}c_{k\sigma}+\frac{G}{N}\sum_{i\sigma}f^\dagger_{i\sigma}f_{i\sigma} \times\sum_{kk'\sigma'}c^\dagger_{k\sigma'}c_{k'\sigma'}e^{-i(k-k')R_i}. \tag{2.1}$$

Here $f^\dagger_{i\sigma}$ and $f_{i\sigma}$ are creation and destruction operators for an electron of spin σ in the localized state at R_i with binding energy ϵ_f and intra-atomic Coulomb correlation energy U, and $c^\dagger_{k\sigma}$ and $c_{k\sigma}$ are operators for an electron in the conduction band with energy $\epsilon(k)$. Thus the localized ionic states are approximated by a nondegenerate Hubbard Hamiltonian with zero configuration width while the conduction electrons are assumed to be uncorrelated. The last term describes the Coulomb repulsion between the localized and conduction electrons which is taken to be completely intra-atomic.

For the case of the samarium monochalcogenides, the localized states correspond to the $4f$ levels of samarium. In our simplified description the state with two "f electrons" corresponds to the $4f^6$ configuration of Sm, the state with one to the $4f^5$ configuration, and the parameters ϵ_f and U are assumed to be such that

$$\langle\langle(1-f^\dagger_{i\sigma}f_{i\sigma})(1-f^\dagger_{i-\sigma}f_{i-\sigma})\rangle\rangle=0, \tag{2.2}$$

i.e., the state with zero occupation has a negligible expectation at all temperatures of interest. The doubly occupied localized state is a singlet like the $^7F_0$ ground state of the $4f^6$ configuration of Sm; and while the singly occupied state is a doublet unlike the actual $^6H_{5/2}$ ground state of the $4f^5$ configuration, this is not important for the physics of the transition. Finally the nondegenerate band states correspond to the lowest submultiplet of the $5d$-$6s$ bands.

We have used the equation of motion method[29] to obtain an approximate one-electron Green's function for the electrons in the band states which takes into account excitonic correlations between the localized and band electrons. Our result for the Green's function is

$$G_c(k,\omega)=\left(\omega-\epsilon(k)-\sum(\omega)\right)^{-1}, \tag{2.3}$$

with the self-energy $\sum(\omega)$ given by

$$\sum(\omega)=(2-n_c)G+\frac{n_c(1-n_c)G^2F(\omega-(2-n_c)G)}{1+(1-2n_c)G\,F(\omega-(2-n_c)G)}, \tag{2.4}$$

where

$$F(\omega)=N^{-1}\sum_k[\omega-\epsilon(k)]^{-1}. \tag{2.5}$$

Here n_c equals the number of conduction-band electrons per site ($0\leq n\leq 1$) which is constrained to be equal to the number of holes per site in the localized state.

This result was obtained by decoupling the equations of motion using the following approximation for the three-particle Green's function $\langle\langle\bar f_{i\sigma'}\bar f_{j\sigma''}\bar f_{j\sigma''}c_{i\sigma};c^\dagger_{k\sigma}\rangle\rangle$ (Zubarev notation[29]), where $\bar f$ denotes the corresponding operator for holes in the localized state:

$$\sum_{\sigma'\sigma''}\langle\langle\bar f^\dagger_{i\sigma'}\bar f_{i\sigma'}\bar f^\dagger_{j\sigma''}\bar f_{j\sigma''}c_{i\sigma};c^\dagger_{k\sigma}\rangle\rangle \simeq n_c\sum_{\sigma'}\langle\langle\bar f^\dagger_{i\sigma'}\bar f_{i\sigma'}c_{i\sigma};c^\dagger_{k\sigma}\rangle\rangle + n_c\sum_{\sigma'}\langle\langle\bar f^\dagger_{j\sigma'}\bar f_{j\sigma'}c_{i\sigma},c^\dagger_{k\sigma}\rangle\rangle-n_c^2\langle\langle c_{i\sigma};\ c^\dagger_{k\sigma}\rangle\rangle. \tag{2.6}$$

Also, condition (2.2) has been used in obtaining the simple form of expression (2.4) for the self-energy. Owing to the intra-atomic character of the interactions, approximation (2.6) is reasonable, and, furthermore, it does not neglect excitonic-type correlations which are completely ignored in the usual mean-field approximation. In the limit of zero bandwidth the treatment is exact.

The first term in our expression (2.4) for the self-energy is the mean-field self-energy to which our result reduces in the small-G limit. One can gain some insight into the physics contained in our expression by considering values of n_c near zero and one. To first order

$$\sum(\omega)\underset{n_c\to0}{\sim}2G-\frac{n_cG}{1+GF(\omega-2G)}, \tag{2.7}$$

$$\sum(\omega)\underset{n_c\to1}{\sim}G+\frac{(1-n_c)G}{1-GF(\omega-G)}. \tag{2.8}$$

The quantity $-N^{-1}G[1+GF(\omega-2G)]^{-1}$ is just the t matrix for the scattering of a conduction-band electron in a f^2 lattice by a single f hole, and $N^{-1}G[1-GF(\omega-G)]^{-1}$ is the t matrix for scattering in a f^1 lattice by a single f^2 site. For G sufficiently large the scattering produces in the first case, where the scattering is attractive, an excitonic state (bound f hole and conduction-electron pair) at an energy ϵ given by

$$\mathrm{Re}[1+GF(\epsilon+i0^+-2G)]=0 \tag{2.9}$$

for ϵ below the band continuum. In the second case the excitonic state is pulled out above the continuum. Thus our expression for the self-energy (2.4) is seen to contain excitonic correlations that are associated with fluctuations in the number of f electrons at the sites.

It would be very difficult to construct a suitable approximate Green's function for the electrons in the localized states. The simplicity in the case of $G_c(k,\omega)$ is derived from $f_{i\sigma}^\dagger f_{i\sigma}$ commuting with the Hamiltonian whereas $c_{i\sigma}^\dagger c_{i\sigma}$ does not commute with the Hamiltonian for a finite bandwidth. Fortunately it is not necessary to evaluate this localized-state Green's function since the total energy is completely determined as a function of n_c by $G_c(k,\omega)$. The total energy is simply

$$\mathcal{E}(n_c)=(2\epsilon_f+U)-(\epsilon_f+U)n_c + 2\int \epsilon\rho(\epsilon)f(\epsilon)\,d\epsilon, \tag{2.10}$$

where

$$\rho(\epsilon)=-\frac{1}{\pi}N^{-1}\sum_k ImG_c(k,\epsilon+i0^+). \tag{2.11}$$

Here $f(\epsilon)$ is the Fermi function and the chemical potential is determined by

$$n_c=2\int \rho(\epsilon)f(\epsilon)\,d\epsilon. \tag{2.12}$$

At zero temperature the number n_c of conduction electrons per site is determined by the absolute minimum of the total energy while at finite temperatures n_c is determined by the absolute minimum of the free energy[27]

$$F(n_c,T)=\mathcal{E}(n_c,0)-T\int_0^T \frac{dT'\mathcal{E}(n_c,T')-\mathcal{E}(n_c,0)}{(T')^2}. \tag{2.13}$$

In general this problem must be solved numerically for a given choice for the one-electron band density of states.

III. RESULTS

A. Intermediate valence states

In order to illustrate the effects of the correlations included in our treatment of the Falicov-Kimball model, results are shown in Fig. 1 for the case of a semielliptic density of states

$$D(\epsilon)\equiv N^{-1}\sum_k \delta(\epsilon-\epsilon(k))=\frac{8}{\pi W^2}[\tfrac{1}{4}W^2-(\epsilon-\epsilon_d)^2]^{1/2}, \tag{3.1}$$

which has a bandwidth W and is centered at the energy ϵ_d. In Fig. 1 the electron concentration n_c in the band states at zero temperature is given for various values of G as a function of the gap parameter

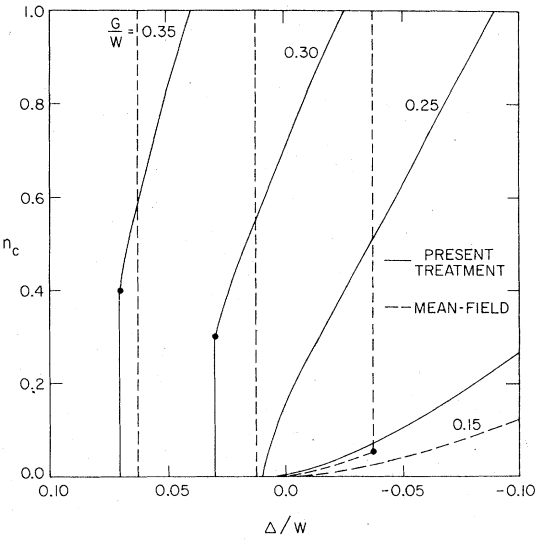

FIG. 1. Plot of the electron concentration in the conduction band as a function of Δ/W for several values of G/W. Solid-line curves are results of the calculations which included intra-atomic excitonic correlations and dashed-line curves are results of mean-field calculations.

$$\Delta=(\epsilon_f+2G+\epsilon_d-\tfrac{1}{2}W)-(2\epsilon_f+U), \tag{3.2}$$

which is the energy required to excite an electron out of the insulating state into a state at the bottom of the band ignoring excitonic correlations. The solid-line curves correspond to the solutions obtained using our expression (2.4) for the self-energy, while the dashed-line curves show the mean-field solutions for comparison.

One finds in our treatment that for $G>\frac{1}{2}W$ there is a discontinuous transition from $n_c=0$ (semiconducting) to $n_c=1$ (metallic, pure valence) as Δ decreases at $\Delta=G-\frac{1}{2}(1-4/3\pi)W$ just as in the mean-field treatment. However, for $G<\frac{1}{2}W$ there exists a range of values of G for which the transition from $n_c=0$ is also discontinuous but where it is to a value of n_c less than one (i.e., from a semiconducting pure-valence state to a metallic intermediate valence state). This transition takes place at smaller values of Δ with decreasing G values. For sufficiently small values of G the transition becomes continuous.

In the mean-field approximation the transitions are continuous for $G<\frac{1}{16}\pi W$, for $\frac{1}{16}\pi W<G<\frac{1}{2}(1-4/3\pi)W$ there are discontinuous transitions from $n_c\neq 0$ to $n_c=1$, and for large G the transition goes from $n_c=0$ to $n_c=1$. (Note that this differs with

the familiar mean-field result for a rectangular density of states where the transition is continuous for $G<\frac{1}{4}W$, while for $G>\frac{1}{4}W$ it is discontinuous from $n_c=0$ to $n_c=1$ at $\Delta=G-\frac{1}{4}W$.) It is characteristic of the mean-field treatment of the Falicov-Kimball model that the discontinuous transitions go to a pure valence metallic state for simple band densities of states. However, this is clearly not the case in our treatment which includes excitonic correlations. Our approximation is seen to stabilize the intermediate valence states for n_c on the metallic side of the transition. For the semi-elliptic density of states (3.1) the condition for an excitonic state satisfying (2.9) is $G>\frac{1}{4}W$. Clearly excitonic correlations cannot be neglected when G is comparable to $\frac{1}{4}W$, but this is just where one finds the discontinuous transitions in the mean-field approximation. Therefore it is not surprising that we obtain qualitatively different results for the discontinuous transitions.

Compared with the zero-temperature results of Fig. 1, the results that we obtain at finite temperatures show a thermal occupation where at $T=0$ there is a pure valence state and a decrease with increasing temperature of the change in n_c for the discontinuous transitions. This discontinuity also moves to smaller Δ before it terminates in a critical point.

B. Phase transitions under pressure

Although we are primarily concerned in this paper with showing the possibility of discontinuous transitions to metallic states with intermediate valence in the Falicov-Kimball model, it is of interest to make a crude estimate of the values of the various parameters required by experiments. In order to make a comparison with the observed transitions in the samarium monochalcogenides under pressure one must consider the Gibb's free energy. At zero temperature

$$G(n_c,p)=E(n_c,v)+pv, \tag{3.3}$$

where the energy E is the sum of the electronic and lattice contributions, and the volume per Sm atom v is given in terms of the pressure and electron concentration n_c by the relation

$$p=\frac{-\partial E(n_c,v)}{\partial v}. \tag{3.4}$$

We will assume for simplicity that the energy is

$$E(n_c,v)=\mathcal{E}(n_c,v)+\tfrac{1}{2}B(v-\overline{v})^2/\overline{v}, \tag{3.5}$$

where $\mathcal{E}(n_c,v)$ is our expression (2.10) from the Falicov-Kimball model with suitable volume dependences for the parameters, B is the bulk modulus of the semiconducting phase, and $\overline{v}$ is the "average volume,"

$$\overline{v}=(1-n_c)v_2+n_cv_3, \tag{3.6}$$

v_2 and v_3 being the volumes for compounds composed of divalent and trivalent Sm ions. This form for the lattice contribution which takes into account the large differences in ionic sizes is similar to that assumed by Varma and Heine[15] except we do not include their nonlinearity parameter attributed to an elastic interaction between ions of the same size. Also we neglect any volume dependence of the bulk modulus.

Aided by the electronic structure of the samarium monochalcogenides given by Batlogg *et al.*[8] based on optical studies, we make the following very simple model for the parameters of $\mathcal{E}(n_c,v)$. In the semiconducting phase the main effect of applying pressure is clearly to decrease the gap parameter Δ owing to the lowering of the $5d(t_{2g})$ band due to increased crystal-field splitting. Hence for $n_c=0$ we assume for the gap parameter

$$\Delta=\Delta_2+\beta(v-v_2)\quad(n_c=0), \tag{3.7a}$$

where β and the zero pressure gap Δ_2 are given by experiments. However, in the metallic state ($n_c\neq 0$) the crystal-field splitting is not resolved in the optical spectra.[8] Furthermore, since the lattice is no longer purely ionic when $n_c\neq 0$, it is difficult to estimate the change in the total energy with volume. For simplicity we will assume Δ does not change with volume when $n_c\neq 0$:

$$\Delta=\Delta_2+\beta(v_c-v_2)\quad(n_c\neq 0), \tag{3.7b}$$

where v_c is the volume at which the semiconducting state becomes unstable. Furthermore we neglect any volume dependence of the bandwidth W and the parameter G since we are only interested in qualitative results. Although (3.7b) appears quite arbitrary it has the advantage of yielding $\overline{v}$ for the $p=0$ equilibrium volume and a very simple correspondence with the original Falicov-Kimball model as seen in the following.

Using our assumed volume dependences Eq. (3.4) yields for the volume as a function of n_c and the pressure the result

$$v=\{1-[(v_2-v_3)/v_2]n_c\}(1-p/B)v_2. \tag{3.8}$$

The Gibb's free energy can then be expressed as a function of n_c and p and the conduction electron concentration n_c determined by the absolute minimum of $G(n_c,p)$ for fixed pressure. The solutions are found to correspond to our previously obtained solutions for the Falicov-Kimball model with an effective gap parameter given by

$$\Delta_{\text{eff}}=\begin{cases}\Delta_2-\dfrac{\beta}{B}pv_2-\left(1-\dfrac{1}{2}\dfrac{p}{B}\right)p(v_2-v_3), & n_c=0,\\ \Delta_2-\dfrac{\beta}{B}p_cv_2-\left(1-\dfrac{1}{2}\dfrac{p}{B}\right)p(v_2-v_3), & n_c\neq 0,\end{cases} \tag{3.9}$$

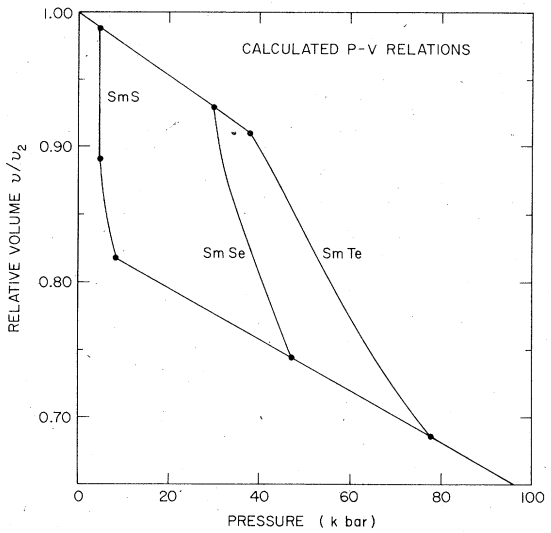

FIG. 2. Calculated pressure-volume relations for the samarium monochalcogenides using the parameters of Table I.

where p_c is the pressure at which nonzero n_c solutions appear. Thus Δ_{eff} is a single-valued function of the pressure in our treatment as is generally assumed in applications[27] of the Falicov-Kimball model and as has been demonstrated for an ionic lattice.[30]

In Fig. 2 we present our results for p-v curves using parameters appropriate to the samarium monochalcogenides which are listed in Table I. Only the parameter G is freely chosen. The zero pressure gap parameter Δ_2 is based on Ref. 8 for SmS and those for SmSe and SmTe are taken from Ref. 2. Since the results are not very sensitive to the other parameters we have simply chosen values that represent an average for the samarium monochalcogenides. Although the model is very crude the essential behavior observed in experiments[3] is seen to be reproduced. Using $G = 0.4$ eV we obtain for SmS a discontinuous transition from the divalent semiconducting state to an intermediate valence state at 5 kbar with a valence of 2.6. For SmSe and SmTe we have chosen G values of 0.25 and 0.2 eV and find continuous transitions which begin at 30 and 40 kbar, respectively. Although the transitions go to the pure trivalent metallic state at a lower pressure than observed experimentally, this could be improved by allowing for an increase in bandwidth with decreasing volume. However in such a crude model as ours it would not be instructive to include such effects without making the model more realistic overall.

These estimates of G of the order of a fraction of an eV are certainly consistent with its identification as an intra-atomic Coulomb matrix element. Also one can speculate that the factor of 2 difference in the value of G required for SmS compared with SmSe and SmTe is due to an increase in the 6s character of the states near the bottom of the band in SmSe and SmTe.

IV. DISCUSSION

Although the form of the Falicov-Kimball model we have considered here is highly idealized, our results clearly show that the model can be used to interpret intermediate valence phenomenon if one takes into account the intra-atomic excitonic correlations. The approximation we have used is quite simple and yet should be reliable for quantitative predictions. Our main result has been to show the possibility of intermediate valence states on the metallic side of a discontinuous transition from the semiconducting state as observed in SmS under pressure. However to make detailed comparisons with experimental observations one should generalize the model to realistic ionic states and realistic band densities of states. Fortunately this generalization does not present any formidable difficulties within our approximation scheme.

Besides yielding pressure-volume relations in good agreement with experiment, our treatment also has the attractive feature of giving a finite lifetime for the band electrons in an intermediate valence state, the imaginary part of the self-energy (2.4) being of order $n_c(1-n_c)(G/W)^2W$ for small G. If we use our previous estimate of G for SmS we obtain a lifetime of 10^{-14} sec for the band electrons on the metallic side of the transition. This would provide an explanation for the rather high resistivity observed[2] in the metallic phase of SmS. Also this lifetime is expected to have a very im-

TABLE I. Parameters used for calculated pressure-volume diagram appropriate to the samarium monochalcogenides.

	G (eV)	Δ_2 (eV)	W (eV)	B (kbar)	β (kbar)	$(v_2-v_3)/v_2$
SmS	0.40	0.20	1.0	450	120	0.17
SmSe	0.25	0.46	1.0	450	120	0.17
SmTe	0.20	0.62	1.0	450	120	0.17

portant effect on the physics of the extended Falicov-Kimball model that includes mixing of the localized and band states.

Since the correlations we take into account are excitonic, it is appropriate to contrast our treatment with those[31-33] where the mixed valence state is described as an excitonic insulator.[34] Those treatments make a new Hartree-Fock approximation that allows for the averages $\langle f_{i\sigma}^{\dagger} c_{k\sigma} \rangle$ to be nonzero.[35] This leads to an effective hybridization that produces a gap in the electron energy spectrum which seems unrealistic. In our approximation these anomalous averages are also nonzero in the intermediate valence state, however we include lifetime effects which prevent the appearance of a hybridizationlike gap. The interesting results presented by Khomskii and Kocharjan,[31] which are based on a treatment of the localized states as isolated "impurities," must be considered unreliable since that problem (without explicit hybridization terms) can be solved exactly within our scheme and one obtains qualitatively different results.[36]

In the usual picture of the excitonic insulator[34] there is a coherent pairing in the wave-vector representation $\langle f_{k+q}^{\dagger} C_k \rangle \neq 0$, where q is the common excitonic wave vector. Such pairing is obviously inhibited by the strong local correlations associated with the intra-atomic Coulomb interaction between f electrons. In contrast to the excitonic insulator description, the model of Kaplan and Mahanti,[19] which neglects the itinerant character of the d electrons, yields a very different picture for the intermediate valence state. The mean-field ground state for this model is a homogeneous localized state for which $\langle f_i^{\dagger} C_i \rangle \neq 0$. This localized "exciton" results from an explicit mixing interaction associated with the interatomic Coulomb interaction treated in a mean-field approximation where intra-atomic correlations are treated exactly. However, the neglect of the finite bandwidth of the d electrons appears unrealistic, and one can show that this localized state is not stable for a sufficiently large bandwidth.[20] The present treatment attempts to take into account the very important intra-atomic correlations in the case where the bandwidth is large compared with the mixing interaction, such that the mixing interaction can be explicitly ignored. The resulting picture is intermediate between the excitonic insulator and the Kaplan-Mahanti description. Here we refer only to the original model presented by Kaplan and Mahanti in Ref. 19. However this model has been generalized[37] to allow for a small number of electrons occupying itinerant states in the collapsed phase and holes in the localized excitonic states. The resulting picture is not that different from one where the d-band electrons are strongly correlated with the $4f$ electrons as presented in the present treatment.

A final point concerns the relationship between our treatment of the pressure-volume relations for the samarium monochalcogenides with those of Hirst[16] and Varma and Heine.[15] In the Hirst treatment[16] the parameter β of our Eq. (3.7) is assumed to be unchanged in going to the metallic state and the lattice energy does not take into account the large difference in the ionic radii of the divalent and trivalent Sm ions. Although the p-v curves are reproduced very well in the Hirst treatment without taking into account the parameter G of the Falicov-Kimball model, our treatment of the parameter β and certainly the lattice energy would seem to be more realistic. Varma and Heine[15] also explicitly ignore G but assume a nonlinear generalization for the average volume $\bar{v}$ of the form

$$\bar{v} = (1 - n_c) v_2 + n_c' v_3 + (1 - n_c) n_c v_4, \tag{4.1}$$

as compared with our expression (3.6). The physics of v_4 is associated with an attractive elastic interaction between ions of the same size but it may also include some of the effects of short-range electronic correlations such as are explicitly described by G in the Falicov-Kimball model. Again the p-v curves are well reproduced with the freely chosen parameter v_4 required to be large and negative. However the change in valence for SmS at the discontinuous transition is predicted[15] to be much smaller than observed. Also it is difficult to see how lattice constant measurements give estimates of the valence in agreement with other measurements if v_4/v_2 is of order 1 as required for the p-v curves.

In summary, we have shown that the simple Falicov-Kimball model provides a reasonable theoretical description for certain intermediate valence phenomena, provided intra-atomic excitonic correlations are taken into account. These correlations should also be important in the extended model with explicit mixing interactions.

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