Theory of intermediate-valence semiconductors

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A description is given of the narrow-gap intermediate-valence state within the framework of the Falicov-Kimball model including hybridization by treating the intermediate-valence state as a large-radius exciton condensate. The value of the energy gap is determined by both hybridization and correlation effects. We study the single-particle excitation spectrum, the temperature dependence of the energy gap, the electronic specific heat and the optical properties (including the Franz-Keldysh effect). The results obtained agree qualitatively with experimental data on the optical and thermodynamic properties of such compounds as SmB_6, the "gold" phase of SmS, and YbB_{12}.

INTRODUCTION

At present, we can consider it firmly established that a number of intermediate-valence (I-V) compounds, e.g., SmB_6,[1,2] the "gold" phase of SmS,[3] TmSe,[4] and YbB_{12},[5] are actually not metals but rather narrow-gap semiconductors. This is confirmed both by investigations of their low-temperature kinetic and thermodynamic properties[1] and by direct optical measurements.[2,3] Questions relating to the nature of the semiconducting state and the methods of describing it theoretically are rather complicated. In particular, all is not yet clear regarding the relative importance of hybridization versus many-electron (excitonic) effects in the origin of the energy gap; also, there is no detailed explanation for the behavior of the optical properties of such systems. The present work is devoted to consideration of these problems.

Because the problem of providing a rigorous description of the ground states of I-V compounds is still far from being solved, variational methods are often used in approximate treatments of these systems.[6–9] As a rule, these methods are based on the concept of a condensate of excitons, i.e., bound states of conduction electron with f-holes. Calculations using some corresponding trial function usually are carried out within the framework of the periodic Anderson model, and come up against special difficulties connected with the single-electron wave functions, i.e., the "non-orthogonality problem." This forced the authors of Refs. 6–9 to restrict themselves to single-parameter trial functions, and also to resort to supplementary (and uncontrolled) approximations in their calculations. In modelling the "gold" phase of SmS, Kikoin has proposed a description of the ground state of that system as an exciton condensate.[9] The nonorthogonality problem was solved in Refs. 6–9 with the help of the method of Levin and Carr.[10] However, the Levin–Carr method allows one to include in the ground-state description only exciton states with radii no larger than one coordination sphere, whereas it is expected that excitons which are associated with a narrow-gap state should be large-radius excitons.

In this work, we will set up the ground state within the framework of the Falicov-Kimball model with hybridization[11]; using the variational method, we will investigate theoretically a wide range of properties of narrow-gap I-V semiconductors. It is found that in this model, the nonorthogonality problem admits an exact solution for a very general class of trial functions. The total energy which corresponds to the multi-exciton wave function under investigation is always bounded from below by the energy resulting from the usual u-v Bogolyubov transformation; nevertheless, in a number of cases (for example, in the interpretation of optical properties) the excitonic language is more convenient and physically transparent. Certain results of the present work have previously been published in a short communication.[12] Along with a more detailed account of these results, we here present calculations of the temperature dependence of the energy gap (these calculations are timely in view of recent experimental work on SmB_6[13] and YbB_{12}[5]) and the specific heat; we also investigate the optical properties, including optical properties in a strong electric field.

1. GROUND STATE TRIAL FUNCTION AND THE EQUATION FOR THE ENERGY GAP

We will study the Falicov-Kimball model with hybridization, whose Hamiltonian takes the form

$$H=\sum_{\mathbf{k}}(t_{\mathbf{k}}c_{\mathbf{k}}^{+}c_{\mathbf{k}}+(\Delta+G)f_{\mathbf{k}}^{+}f_{\mathbf{k}}+V(c_{\mathbf{k}}^{+}f_{-\mathbf{k}}^{+}+f_{-\mathbf{k}}c_{\mathbf{k}}))-\frac{G}{N}\sum_{\mathbf{k},\mathbf{k}'\mathbf{q}}c_{\mathbf{q}-\mathbf{k}}^{+}f_{\mathbf{k}}^{+}f_{\mathbf{k}'}c_{\mathbf{q}-\mathbf{k}'}, \tag{1.1}$$

where $c_{\mathbf{k}}^{+}$ $f_{\mathbf{k}}^{+}$ are creation operators for conduction electrons (c-electrons) and holes in the f subsystem, Δ is the energy difference between the f^n and f^{n+1} configurations at a lattice site, $t_{\mathbf{k}}$ is the single-electron spectrum ($\Sigma_{\mathbf{k}}t_{\mathbf{k}}=0$), G is the Coulomb interaction parameter (for attraction between c-electrons and f-holes), and V is the hybridization parameter, which for simplicity we take to be a contact interaction. This model is apparently the simplest nontrivial model of an I-V system, and is widely used for theoretical descriptions of such systems (see, e.g., Ref. 14). It allows us to take into account easily the strong Coulomb

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repulsion of the f-electrons without having recourse to many-electron operators; however, it does not allow us to investigate effects connected with the presence of conduction electron spin and orbital degeneracy in the f-subsystem.

In the model under discussion, the exciton state can be written as follows

$$|\Phi_{ex}\rangle = B^+|0\rangle, \quad B^+ = \sum_{\mathbf{k}} \varphi(\mathbf{k}) c_{\mathbf{k}}^+ f_{-\mathbf{k}}^+, \tag{1.2}$$

where $|0\rangle$ is the "vacuum" state (all electrons are found on f levels). The multi-exciton wave function which describes the intrinsic I-V semiconductor (i.e., the total number of electrons equals the number of lattice sites N) can be written as a superposition of M-exciton states

$$|\Phi\rangle = \sum_M (M!)^{-1/2} \exp\left(\frac{\lambda(M)}{2}\right) |\Phi_M\rangle,$$

$$|\Phi_M\rangle = (M!)^{-1/2} (B^+)^M |0\rangle, \tag{1.3}$$

where now $\varphi(\mathbf{k})$ and $\lambda(M)$ are trial functions. The normalization factor for the function (1.3) equals

$$\langle\Phi|\Phi\rangle = \sum_M \exp(\lambda(M)) \frac{\langle\Phi_M|\Phi_M\rangle}{M!}. \tag{1.4}$$

The quantity $\langle\Phi_M|\Phi_M\rangle$ can be evaluated in the thermodynamic limit $M,N\to\infty$ by introducing the appropriate generating function and using methods from the theory of graph enumeration.[15,16]

$$\langle\Phi_M|\Phi_M\rangle = \sum_{\mathbf{k}_1 \ldots \mathbf{k}_M} \prod_i \varphi^2(\mathbf{k}_i) \prod_{i<j} [1-\delta_{\mathbf{k}_i,\mathbf{k}_j}]$$
$$= \beta_M M! [z(M)]^{-M} \prod_{\mathbf{k}} [1+z(M)\varphi^2(\mathbf{k})], \tag{1.5}$$

where β_M is a multiplier which is a weak function of M, and $z(M)$ is a saddle point which arises when we calculate the contour integral which determines the coefficient of the generating function, for which we have the equation

$$\sum_{\mathbf{k}} z(M)\varphi^2(\mathbf{k})[1+z(M)\varphi^2(\mathbf{k})]^{-1} = M. \tag{1.6}$$

Replacing the sum in (1.4) by an integral, and evaluating it by the saddle-point method, we find

$$\langle\Phi|\Phi\rangle = \text{const} \exp(\lambda(M_0))\,(z(M_0))^{-M_0} \prod_{\mathbf{k}} [1+\psi^2(\mathbf{k})], \tag{1.7}$$

where $\psi(\mathbf{k}) = z^{1/2}(M_0)\varphi(\mathbf{k})$ and the saddle point M_0 is determined by the equation

$$(d\lambda(M)/dM)_{M=M_0} = \ln z(M_0). \tag{1.8}$$

A calculation of the average, which we need to find the total energy

$$E = \langle H\rangle = \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle,$$

gives (see Refs. 12,15,16)

$$\langle c_{\mathbf{k}}^+ c_{\mathbf{k}}\rangle = \langle f_{\mathbf{k}}^+ f_{\mathbf{k}}\rangle = \psi^2(\mathbf{k}) \frac{\partial}{\partial\psi^2(\mathbf{k})} \ln\langle\Phi|\Phi\rangle = v_{\mathbf{k}}^2, \tag{1.9}$$

$$\langle c_{\mathbf{k}}^+ f_{-\mathbf{k}}^+ f_{-\mathbf{k}'} c_{\mathbf{k}'}\rangle = \frac{\psi(\mathbf{k})\psi(\mathbf{k}')}{\langle\Phi|\Phi\rangle} \frac{\partial^2\langle\Phi|\Phi\rangle}{\partial\psi^2(\mathbf{k})\partial\psi^2(\mathbf{k}')} = u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}'} v_{\mathbf{k}'}, \tag{1.10}$$

$$\langle c_{\mathbf{q}-\mathbf{k}}^+ f_{\mathbf{k}}^+ f_{\mathbf{k}'} c_{\mathbf{q}-\mathbf{k}'}\rangle = v_{\mathbf{k}}^2 v_{\mathbf{k}-\mathbf{q}}^2 \delta_{\mathbf{k}'\mathbf{k}}, \quad \mathbf{q}\neq 0, \tag{1.11}$$

$$\langle f_{-\mathbf{k}} c_{\mathbf{k}}\rangle = \exp\left[\frac{\lambda(M_0+1)-\lambda(M_0)}{2}\right] \frac{\varphi(\mathbf{k})}{1+\psi^2(\mathbf{k})} = u_{\mathbf{k}} v_{\mathbf{k}}, \tag{1.12}$$

where we introduce the notation

$$u_{\mathbf{k}}^2 = \frac{1}{1+\psi^2(\mathbf{k})}, \quad v_{\mathbf{k}}^2 = \frac{\psi^2(\mathbf{k})}{1+\psi^2(\mathbf{k})}, \tag{1.13}$$

and Eq. (1.8) is used along with the result (1.12). It is easy to see that the average we obtain coincides with the corresponding averages for BCS-type states[17]

$$|\Phi'\rangle = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}}^+ f_{-\mathbf{k}}^+)|0\rangle. \tag{1.14}$$

Thus, the calculation we have performed, which uses a multi-exciton wave function of the most general kind (if we only include excitons with the same momentum in our investigation) corresponds in its results to the "optimum," i.e., Hartree-Fock, type of approximation. The approaches employed earlier all reduce to simplified forms of this approximation. Thus, in the work of Khomskii and Kocharian reviewed in Ref. 11), a decoupling of the Green's function is used in which an anomalous average $\langle c_i^+ f_i^+\rangle$ is introduced on one site, which is equivalent to replacing the function $\varphi(\mathbf{k})$ by a constant. The investigation in which the excitonic states whose radius was one coordination sphere were included[9] is also not entirely justified, since in the narrow-gap state the binding energy is small; consequently, according to the uncertainty principle, the exciton radius must be large. A Green's function decoupling equivalent to the u-v transformation was applied to the I-V problem in Ref. 18, whose author, however, did not analyze the equations he obtained, but limited himself to numerical calculations for determining the parameter values.

Substituting expressions (1.9)–(1.12) in E and performing the variation, we obtain the system of equations

$$X\left[\frac{G}{N}\sum_{\mathbf{k}} \varepsilon^{-1}(\mathbf{k}) - 1\right] = 2V, \tag{1.15}$$

$$Y+\Delta = \frac{G}{N}\sum_{\mathbf{k}} (Y-t_{\mathbf{k}})\varepsilon^{-1}(\mathbf{k}), \tag{1.16}$$

where we have introduced the quantities

$$X = \frac{2G}{N}\sum_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} - 2V, \quad Y = -\Delta - G + \frac{2G}{N}\sum_{\mathbf{k}} v_{\mathbf{k}}^2, \tag{1.17}$$

$$\varepsilon(\mathbf{k}) = [X^2 + (t_{\mathbf{k}}-Y)^2]^{1/2} \tag{1.18}$$

(it is easy to verify that choosing the other sign of the square root for determining $\varepsilon(\mathbf{k})$ leads to an energetically unfavorable solution). In order to clarify the physical meaning of the quantity X, we calculate the energy of a state with only one electron and hole:

$$|\Phi_{\mathbf{k}}^{(e)}\rangle = c_{\mathbf{k}}^+|\Phi\rangle, \quad |\Phi_{\mathbf{k}}^{(h)}\rangle = f_{\mathbf{k}}^+|\Phi\rangle.$$

Introducing the chemical potential μ, we find

$$\varepsilon_{\mathbf{k}}^{(e,h)}=\langle\Phi_{\mathbf{k}}^{(e,h)}|H-\mu\mathcal{N}|\Phi_{\mathbf{k}}^{(e,h)}\rangle/\langle\Phi_{\mathbf{k}}^{(e,h)}|\Phi_{\mathbf{k}}^{(e,h)}\rangle$$
$$-\langle H-\mu\mathcal{N}\rangle={}^1/_2[\varepsilon(\mathbf{k})\pm(t_{\mathbf{k}}-\Delta-G-2\mu)].$$

Thus

$$|X|=\min_{\mathbf{k}}\{\varepsilon_{\mathbf{k}}^{(e)}+\varepsilon_{\mathbf{k}}^{(h)}\}$$

coincides with the (direct) single-particle energy gap. It is necessary to emphasize that the equation for X always has a nontrivial solution (whereas in the one-exciton problem, a bound state exists only if G exceeds a certain critical value G_c). This difference arises from the fact that in the case we are investigating the origin of the bound state is the finite occupation of the conduction band; as a consequence of this, there is a solution for arbitrarily small interactions which is similar to a Cooper pair in the theory of superconductivity (see also the situation in the Hubbard model[15]). In addition, hybridization plays an essential role in this model, so that even for $G=0$ we obtain a solution $|X|=2|V|$ corresponding to the simple hybridization model.

The quantity Y determines the average concentration of holes in the f-level, and consequently the valence:

$$\langle f_i^+ f_i\rangle=\frac{1}{N}\sum_{\mathbf{k}}\langle c_{\mathbf{k}}^+ c_{\mathbf{k}}\rangle=\frac{M_0}{N}=\frac{1}{2}\left(1+\frac{\Delta+Y}{G}\right). \quad (1.20)$$

We limit ourselves to investigting the case when the hybridization parameter is small compared to the half-width W of the conduction band, which corresponds to real I-V compounds, and we seek a narrow-gap solution with $|X|\ll W$. Then from (1.16), (1.20) we find

$$\langle f_i^+ f_i\rangle\approx\frac{1}{N}\sum_{\mathbf{k}}\theta(Y-t_{\mathbf{k}}).$$

Thus, Y is approximately equal to the Fermi energy E_F, i.e., the chemical potential in the conduction band in the absence of hybridization and interaction. The intermediate valence arises when Y lies close to the conduction band center. In the case $|X|\ll W$, Eq. (1.15) can be used in the form

$$X=2V[2\lambda\ln(\alpha W/|X|)-1]^{-1},\quad \lambda=Gg(E_F), \quad (1.21)$$

where $\alpha\sim 1$ and $g(E)$ is the "bare" c-electron density of states. The solution to Eq. (1.21)

$$X_1\approx 2V[2\lambda\ln(\alpha W/|V|)-1]^{-1} \quad (1.22)$$

describes states with a hybridization gap, renormalized by correlation effects. We emphasize that the latter lead to a significant decrease in the direct gap $|X|$ compared to its one-electron value $2|V|$. From the structure of (1.21), it is clear that the approach we are using corresponds to the summation of direct parquet diagrams. As is well known, in the case of a single impurity (equivalent to the Kondo problem[19]) this approximation gives results which are not entirely satisfactory for the description of the ground state. However, in the situation under discussion here it seems to be more rewarding, since in the semiconducting phase all the "Kondo" divergences are cut off at an energy on the order of the width of the gap (i.e., of order of the "Kondo temperature"), so that the system does not fall within the strong-coupling regime. In Ref. 20 a renormalization of the form of the effective hybridization parameter is also obtained within the formalism of the renormalization group; in this work, however, the corresponding quantity is not interpreted as the width of an energy gap. We note also that not long ago a full calculation of the band structure of SmS in its "gold" phase demonstrated the appearance of an energy gap at E_F (which obviously is in origin a purely single-electron gap). In this case, the magnitude of the calculated gap differed essentially from the one observed experimentally, which attests to the importance of including many-electron effects. The temperature dependence of the energy gap observed in SmB_6[13] and YbB_{12}[5] provides direct confirmation of the essential role played by these latter effects.

For $\lambda\gtrsim 1$, expression (1.22) gives a unique narrow-gap solution to Eq. (1.21). In this case, there are also two wide-gap solutions, which (neglecting V) are approximately determined from the equation

$$\frac{G}{N}\sum_{\mathbf{k}}\varepsilon^{-1}(\mathbf{k})=1, \quad (1.23)$$

which describes the "exciton" state; these solutions are similar to those investigated in Ref. 15 within the framework of the Hubbard model. If the solution X_0 to Eq. (1.23) is much larger than $|V|$, Eq. (1.21) has solutions

$$X_2=X_0+O(V),\quad X_3=-X_0+O(V).$$

In the case $\lambda\ll 1$, Eq. (1.21) has additonal narrow-gap solutions if the inequality

$$|V|<V_c\equiv\alpha W\lambda\exp(-1/2\lambda-1) \quad (1.24)$$

is fulfilled. For $|V|\ll V_c$, the two additional solutions have the form

$$|X_{2,3}|=\alpha W\exp(-1/2\lambda)\pm|V|/\lambda, \quad (1.25)$$

which describe states with an excitonic gap. It can be shown that the total energy corresponding to them is lower than for the state with hybridization gap X_1. Thus, in the model under investigation here, for a given valence there are metastable insulator states (corresponding to only local extrema of the total energy).

The exciton gap can be small enough to explain the value of the indirect gap $X^2/4W$ observed in SmB_6, which amounts to 30–60° K, if we use $\lambda\approx 0.2$. Apparently, $|V|\sim V_c$, so that the magnitude of the gap is determined by a combination of hybridization and excitonic effects.

2. TEMPERATURE DEPENDENCE OF THE ENERGY GAP AND THERMODYNAMIC PROPERTIES

We now investigate the equation which determines the energy gap at finite temperatures. As in the theory of superconductivity, the easiest way to obtain it is to transform the Hamiltonian (1.1) by means of the u-v Bogolyubov transformation to new creation and annihilation operators for elementary excitation (however, it is also possible to derive these equations using the "exciton" language, starting from

the trial function (1.3); see Ref. 16). Then in place of (1.15)–(1.17) we have

$$X\left[\frac{G}{N}\sum_{\mathbf{k}}(1-f_{\mathbf{k}}^{(e)}-f_{\mathbf{k}}^{(h)})\varepsilon^{-1}(\mathbf{k})-1\right]=2V, \tag{2.1}$$

$$Y+\Delta=\frac{G}{N}\sum_{\mathbf{k}}(Y-t_{\mathbf{k}})(1-f_{\mathbf{k}}^{(e)}-f_{\mathbf{k}}^{(h)})\varepsilon^{-1}(\mathbf{k}), \tag{2.2}$$

$$\begin{aligned} X&=\frac{2G}{N}\sum_{\mathbf{k}}u_{\mathbf{k}}v_{\mathbf{k}}(1-f_{\mathbf{k}}^{(e)}-f_{\mathbf{k}}^{(h)})-2V,\\ Y&=-\Delta-\frac{G}{N}\sum_{\mathbf{k}}(1-2v_{\mathbf{k}}^2)(1-f_{\mathbf{k}}^{(e)}-f_{\mathbf{k}}^{(h)}), \end{aligned} \tag{2.3}$$

where $f_{\mathbf{k}}^{(e)}, f_{\mathbf{k}}^{(h)}$ are Fermi distribution functions of the energies $\varepsilon_{\mathbf{k}}^{(e)}, \varepsilon_{\mathbf{k}}^{(h)}$ [see (1.19)]. Speaking in general, equations (2.1)–(2.3) require numerical solution. In order to determine the general form of the temperature dependence $X(T)$, we investigate the analytically simplest case, where the conduction band is symmetric and $\Delta=0$, so that $\langle f_i^+ f_i\rangle = 1/2$, while the chemical potential $\mu = Y - G/2 = -G/2$ does not change as the temperature varies. Then (2.1) takes the form

$$X=2V(GL-1)^{-1}, \quad L=\frac{1}{N}\sum_{\mathbf{k}}\varepsilon^{-1}(\mathbf{k})\,\mathrm{th}\frac{\varepsilon(\mathbf{k})+t_{\mathbf{k}}}{2T}. \tag{2.4}$$

For the condition $|X|\ll W$, we find

$$L=\int_{-W}^{W}\frac{d\varepsilon\, g(\varepsilon)}{(\varepsilon^2+X^2)^{1/2}}\,\mathrm{th}\frac{(\varepsilon^2+X^2)^{1/2}+\varepsilon}{4T}\approx g(0)\int_{\delta/2T}^{W/2T}\frac{d\tau}{\tau}\,\mathrm{th}\,\tau, \tag{2.5}$$

where we introduce the value of the indirect energy gap $\delta = X^2/4W$. In the high temperature case $T\gg\delta$ we obtain

$$L\approx g(0)\ln(\pi W/8\gamma T), \tag{2.6}$$

where $\gamma = \exp C \approx 1.13$, and C is Euler's constant. Thus, the energy gap decreases as the temperature rises and very slowly (logarithmically) falls to zero:

$$\begin{aligned} X(T)&=2V\left(\lambda\ln\frac{T^*}{T}\right)^{-1}, \quad T\gg\delta, T^*,\\ T^*&\equiv\frac{\pi W}{8\gamma}\exp\left(-\frac{1}{\lambda}\right), \quad \lambda=Gg(0). \end{aligned} \tag{2.7}$$

This behavior agrees qualitatively with the experimental data on SmB_6.[13] In the low-temperature case $T\ll\delta$ we have

$$X(T)\approx X(0)+\frac{8TW}{X(0)}\exp\left(-\frac{\delta(0)}{T}\right)\times\left[2\lambda\left(\ln\frac{2W}{|X(0)|}-1\right)-1\right]^{-1}, \tag{2.8}$$

where $X(0)$ is determined by the equation [see (1.21)]

$$X(0)=2V[2\lambda\ln(2W/|X(0)|)-1]^{-1}. \tag{2.9}$$

For not-too-large values of λ, the energy gap $|X(T)|$ decreases monotonically with increasing temperature.

Let us turn to a calculation of the electronic specific heat C. As in the theory of superconductivity,[17] we have

$$C=\frac{1}{T}\sum_{\mathbf{k}}\sum_{i=e,h}\left(-\frac{\partial f_{\mathbf{k}}^{(i)}}{\partial\varepsilon_{\mathbf{k}}^{(i)}}\right)\left(1-\frac{T}{2}\frac{\partial}{\partial T}\right)(\varepsilon_{\mathbf{k}}^{(i)})^2. \tag{2.10}$$

In the special case under consideration here, (2.10) takes the form

$$C=\frac{g(0)}{T}\int_{\delta/2T}^{W/2T}\frac{d\tau}{\mathrm{ch}^2\tau}\left[X^2(T)-T\frac{\partial X^2(T)}{\partial T}+4T^2\tau^2\right]. \tag{2.11}$$

In the high-temperature limit $T\gg\delta$, taking into account (2.7) we find that

$$C=\frac{g(0)}{T}X^2(T)\left[1-2\ln^{-1}\left(\frac{T}{T^*}\right)\right]+\frac{\pi^2}{3}g(0)T. \tag{2.12}$$

The first term in (2.12) dominates the linear contribution for a rather wide temperature interval $\delta\ll T\lesssim|X|$ (for $T\gtrsim|X|$ the usual lattice contribution dominates). For low temperatures, expression (2.11) gives an exponentially small specific heat, as in BCS theory:

$$C=\frac{2g(0)}{T}X^2(0)\exp\left[-\frac{\delta(0)}{T}\right]. \tag{2.13}$$

We point out that in the high temperature region our approach is apparently quite reliable, since it realistically corresponds to inclusion of the leading "Kondo" corrections. On the other hand, an investigation of the specific heat for low temperatures many require a more rigorous analysis, in particular an account of contribution from collective excitations.

On the whole, the behavior obtained for the specific heat is similar to the behavior of the Schottky contribution, as was remarked in Ref. 2 in a discussion of the experimental data for SmB_6. However, the finiteness of the bandwidth gives rise to essential differences, in particular to a $1/T$ dependence instead of $1/T^2$ at high temperatures.

In connection with the large linear term observed in the specific heat of the "gold" phase of SmS for low temperatures,[22] it is interesting to investigate the case of a heavily-doped semiconductor, in which the chemical potential is near the top of the hole band. We show that for the model we are investigating here there is a large enhancement in the effective mass m^*/m. The density of states corresponding to the spectrum

$$E(\mathbf{k})=\tfrac{1}{2}[(t_{\mathbf{k}}^2+X^2)^{1/2}-t_{\mathbf{k}}],$$

takes the form

$$N(E)=\left(1+\frac{X^2}{4E^2}\right)g\left(\frac{X^2}{4E}-E\right). \tag{2.14}$$

Near the upper edge of the band we have

$$\begin{aligned} g(t)&\approx A(t_{max}-t)^{1/2}=A(1+X^2/4E_{max}^2)^{1/2}(E_{max}-E)^{1/2},\\ E_{max}&\approx X^2/4t_{max}. \end{aligned} \tag{2.15}$$

From (2.14) and (2.15) we obtain

$$N(E)\approx A(1+X^2/4E_{max}^2)^{1/2}(E_{max}-E)^{1/2}\equiv A^*(E_{max}-E)^{1/2}$$
$$A^*\approx A(2t_{max}/X)^2=AW/\delta. \tag{2.16}$$

Taking into account the renormalized chemical potential ζ (measured from the top of the band), for a specific concentration of current carriers we find that

$$\frac{m^*}{m}=\frac{N(\zeta^*)}{g(\zeta)}=\frac{A^*}{A}\left(\frac{\zeta^*}{\zeta}\right)^{1/2}=\left(\frac{A^*}{A}\right)^{3/2}=\left(\frac{W}{\delta}\right)^{3/2}. \tag{2.17}$$

The result (2.17) allows us to obtain an enhancement of the linear term in the electronic specific heat on the order of 40 to 50. The experimentally observed enhancement is on the order of hundreds; the fact that our coefficient is too small can be related to our neglect of the effective electron-phonon interaction, many-valley effects (see the qualitative discussion in Ref. 9) and also to the increase in the correlation-induced renormalization of the electronic specific heat mentioned in Ref. 23 in the case when the Fermi level is close to peaks in the density of states.

3. OPTICAL PROPERTIES OF THE NARROW-GAP STATE

Let us investigate the effect of a time-varying electric field $\mathbf{F}(t)$ on the structure of the narrow-gap state. To do this, we write down the time-dependent Schroedinger equation

$$(i\partial/\partial t-H+e\mathbf{F}(t)\mathbf{x})\,|\Phi(t)\rangle=0, \tag{3.1}$$

where $\mathbf{x}$ is the coordinate operator and e the electron charge. Equation (3.1) is equivalent to a corresponding variational principle, for which $|\Phi(t)\rangle$ again can be taken in the form (1.3) with a function $\varphi(k,t)$ which depends on time. In the absence of the field, we have

$$|\Phi(t)\rangle=|\Phi\rangle\exp(-iEt),\ \psi(\mathbf{k},t)=\psi(\mathbf{k})\exp\left(-\frac{iEt}{M_0}\right). \tag{3.2}$$

For finite $\mathbf{F}$ we seek a solution in the form

$$\psi(\mathbf{k},t)=\exp\left(-\frac{iEt}{M_0}\right)[\psi(\mathbf{k})+\psi_1(\mathbf{k},t)]. \tag{3.3}$$

Performing the variation of the functional

$$\left\langle i\frac{\partial}{\partial t}-H+e\mathbf{F}(t)\mathbf{x}-\nu\sum_{\mathbf{k}}\frac{|\psi(\mathbf{k},t)|^2}{1+|\psi(\mathbf{k},t)|^2}\right\rangle$$

(ν is a Lagrange multiplier, introduced because of the condition $\langle f_i^+ f_i\rangle = M_0$; it is easy to convince oneself that $\nu = E/M_0 - Y$). Using a linear approximation in ψ we obtain the equation

$$\left[i\frac{\partial}{\partial t}+ie\mathbf{F}(t)\frac{\partial}{\partial\mathbf{k}}-\varepsilon(\mathbf{k})\right]\psi_1(\mathbf{k},t)+\frac{G}{N}(1+\psi^2(\mathbf{k}))\times\sum_{\mathbf{q}}\frac{\psi_1(\mathbf{q},t)}{1+\psi^2(\mathbf{q})}=-ie\frac{\partial\psi(\mathbf{k})}{\partial\mathbf{k}}\mathbf{F}(k). \tag{3.4}$$

The high-frequency dielectric susceptibility $\alpha_{ij}(\omega)\,(i,j=x,y,z)$ in a weak electric field

$$\mathbf{F}(t)=\mathbf{F}\cos(\omega t)\exp(\eta t),\quad \eta\to+0,$$

is determined from the expression

$$e\langle x_i\rangle={}^1/_2N\Omega_0\sum_j[\alpha_{ij}(\omega)\exp(-i\omega t+\eta t)+\alpha_{ij}(-\omega)\exp(i\omega t+\eta t)]F_j,$$

where Ω_0 is the volume of a unit cell. Taking (3.4) into account by linearizing, i.e., to first order in $\mathbf{F}$, we obtain (note the analogous calculation in the framework of the Hubbard model[15])

$$\alpha_{ij}(\omega)=\frac{e^2X^2}{2N\Omega_0}\sum_{\mathbf{k}}\frac{\partial t_{\mathbf{k}}}{\partial k_i}\frac{\partial t_{\mathbf{k}}}{\partial k_j}\frac{\varepsilon^{-3}(\mathbf{k})}{\varepsilon^2(\mathbf{k})-(\omega+i\eta)^2}. \tag{3.5}$$

For the imaginary part of the dielectric susceptibility, which determines the optical absorption spectrum, we find

$$\operatorname{Im}\alpha_{ij}(\omega)=\frac{\pi e^2X^2}{4N\Omega_0\omega^4}\sum_{\mathbf{k}}\frac{\partial t_{\mathbf{k}}}{\partial k_i}\frac{\partial t_{\mathbf{k}}}{\partial k_i}\times[\delta(\omega-\varepsilon(\mathbf{k}))-\delta(\omega+\varepsilon(\mathbf{k}))]. \tag{3.6}$$

The absorption edge corresponding to direct optical transitions equals $\omega_{\min}=|X|$; near it $\operatorname{Im}\alpha_{ij}(\omega)$ has a rather sharp maximum due to the factor of ω^{-4}. (As the experimental data on SmB_6[2] and SmS[3] show, the important contribution to the optical absorption is given by the indirect transition, whose gap equals δ). For the static dielectric permeability in the case of small $|X|$ we obtain

$$\varepsilon_{ij}(0)=\delta_{ij}+4\pi\alpha_{ij}(0)\approx\frac{8\pi e^2g(E_F)}{3\Omega_0X^2}\left\langle\frac{\partial t_{\mathbf{k}}}{\partial k_i}\frac{\partial t_{\mathbf{k}}}{\partial k_j}\right\rangle_F, \tag{3.7}$$

where $\langle\ldots\rangle$ denotes an average over the surface $t_{\mathbf{k}}=Y\approx E_F$. In the case of cubic symmetry, for large ω we obtain

$$\varepsilon_{ij}(\omega)=\delta_{ij}(1-\omega_p^2/\omega^2), \tag{3.8}$$

where the square of the plasma frequency equals

$$\omega_p^2=\frac{4\pi e^2}{\Omega_0}g(E_F)\left\langle\left(\frac{\partial t_{\mathbf{k}}}{\partial k_x}\right)^2\right\rangle_F. \tag{3.9}$$

Thus, ω_p is determined by the same expression as in the case of free electrons, and the presence of a narrow energy gap does not change its value. This is true for all the high-frequency properties, including the metallic lustre of SmS (a discussion of this question is given in Ref. 9). Taking (3.9) into account, expression (3.7) takes the form

$$\varepsilon(0)\approx{}^2/_3(\omega_p/X)^2. \tag{3.10}$$

According to the experimental data on SmB_6[2], $\omega_p\approx 1.75$ eV, and if we take for $|X|$ a value on the order of 0.1 eV, which corresponds to the peak in the direct optical absorption,[2] then for the static dielectric permeability we obtain $\varepsilon(0)\approx 200$. In reality, $\varepsilon(\omega)$ for low frequencies is a strong function of frequency and temperature (probably because of the contribution from the indirect transitions); however, the estimate presented here is of the same order of magnitude as the observed data. In Ref. 2 it was concluded that the latter data argue in favor of the hybridization model. As was shown above, the exciton effects do not change the structure of the single-particle excitation spectrum, once we have

made the substitution $2|V|\to|X|$. In view of this, the large-radius exciton-condensate model (i.e., with $|X|\ll W$) can give agreement with experiment for SmB_6 which is as good as that of the hybridization model. The question of the relative contribution of hybridization versus Coulomb interaction in the formation of the gap is determined as a function of the relative magnitudes of the model parameters. Experimentally, it could be clarified by precise measurement of the temperature dependence of $X(T)$.

There is also considerable interest in investigating the optical properties of the narrow-gap state in a strong external electric field. Let us assume

$$\mathbf{F}(t)=F_0+\mathbf{F}\cos(\omega t)e^{\eta t}.$$

In the presence of the field $\mathbf{F}_0$, all values of the electronic energy become allowed, and a finite probability emerges for an electron to cross the forbidden gap, even if the photon frequency ω is smaller than the value of the gap $|X|$ (the Franz-Keldysh effect; see, e.g., Ref. 24). For purposes of calculation, it is necessary to retain the quantity $\mathbf{F}_0$ on the left-hand side of equation (3.4). The solution to (3.4) has the form

$$\psi_1(\mathbf{k},t)=\exp\left[-i\int_0^t d\tau\,\varepsilon(\mathbf{k}(\tau))\right]\chi(\mathbf{k},t),$$

$$\chi(\mathbf{k},t)=-e\mathbf{F}\int_0^t dt'\,\frac{\partial\psi(\mathbf{k}(t'))}{\partial\mathbf{k}(t')}\exp\left\{i\int_0^{t'}d\tau\,\varepsilon(\mathbf{k}(\tau))\right\}, \quad (3.11)$$

$$\mathbf{k}(t)=\mathbf{k}-e\mathbf{F}_0t.$$

For the imaginary part of the dielectric permeability, we obtain to logarithmic accuracy in the exponent[24]:

$$\operatorname{Im}\varepsilon(\omega,F_0)\propto J(\omega,F_0)$$

$$=\frac{1}{N}\sum_{\mathbf{k}}\lim_{t^*\to\infty}\frac{1}{t^*}\left|\int_0^{t^*}d\tau\exp\left\{i\int_0^{\tau}dt[\varepsilon(\mathbf{k}(t))-\omega]\right\}\right|^2. \quad (3.12)$$

From here on we will limit ourselves for simplicity to the one-dimensional case, which affects only the numerical value of the multiplier in the final result. Computing the integral by the saddle-point method (see Ref. 25), we find

$$J(\omega,F_0)\propto\exp\left\{-\frac{2}{|e|F_0}\int_0^{k_2}dk[\varepsilon(k_1+ik)-\omega]\right\}, \quad (3.13)$$

where the saddle-point $k_0=k_1+ik_2$ is determined from the equation

$$t_{k_0}-Y=\pm i(X^2-\omega^2)^{1/2}.$$

For the narrow-gap state, we can use an expansion in

$$|t_k-Y|=v_F|k-k_F|,$$

which gives

$$k_1=k_F, \qquad k_2=(X^2-\omega^2)^{1/2}/v_F.$$

Performing the integration in (3.13), we obtain

$$\operatorname{Im}\varepsilon(\omega,F_0)\propto\exp\left[-\frac{X^2}{|e|F_0v_F}A\left(\frac{\omega}{|X|}\right)\right], \quad (3.14)$$

$$A(y)=\arcsin(1-y^2)^{1/2}-y(1-y^2)^{1/2}.$$

The breakdown probability in a static field (Zener breakdown) is proportional to

$$\operatorname{Im}\varepsilon(0,F_0)\propto\exp(-\pi X^2/2|e|F_0\hbar v_F). \quad (3.15)$$

In the case $|X|-\omega\ll|X|$, (3.14) takes the form

$$\operatorname{Im}\varepsilon(\omega,F_0)\propto\exp\left[-\frac{4(2|X|)^{1/2}(|X|-\omega)^{3/2}}{3|e|F_0\hbar v_F}\right]. \quad (3.16)$$

Thus, under the action of a static field, for a narrow gap semiconductor the direct optical absorption develops a fairly deep exponential "tail" into the forbidden gap. Because $|X|$ is small, the relative shift in the absorption edge in the external electric field must be considerably larger than in ordinary semiconductors.

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