Electron self-trapping in intermediate-valent SmB$_6$

S. Curnoe$^1$ and K. A. Kikoin$^2$

$^1$Weizmann Institute of Science, Rehovot 76100, Israel
$^2$Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

SmB$_6$ exhibits intermediate valence in the ground state and unusual behaviour at low temperatures. The resistivity and the Hall effect cannot be explained either by conventional $s_f$-hybridization or by hopping transport in an impurity band. At least three different energy scales determine three temperature regimes of electron transport in this system. We consider the ground state properties, the soft valence fluctuations and the spectrum of band carriers in n-doped SmB$_6$. The behaviour of excess conduction electrons in the presence of soft valence fluctuations and the origin of the three energy scales in the spectrum of elementary excitations is discussed. The carriers which determine the low-temperature transport in this system are self-trapped electron-polaron complexes rather than simply electrons in an impurity band. The mechanism of electron trapping is the interaction with soft valence fluctuations.

71.28.+d, 71.30.+h, 71.35.Gg, 75.30.Mb

I. INTRODUCTION

Samarium hexaboride is the first compound in which the phenomenon of intermediate valence (IV) has been seen directly by X-ray absorption [1], but the theory which explains all properties of this compound within a unified physical model remains elusive in spite of unceasing efforts of theoreticians and experimentalists during the recent thirty-five years.

The conventional description of the electronic structure of SmB$_6$ in terms of a two-band promotion model results in a semiconductor-like spectrum with a gap $\Delta$. This gap appears as a result of on-site hybridization between the narrow band formed by electrons from the samarium 4$f$-shell and the wide conduction band formed by boron $p$-states and samarium 5$d$-states. The theory explains, at least phenomenologically, the main body of available experimental data [2]. However, the most intriguing properties of this material (as well as other IV semiconductors from the same family, i.e. SmS, TmSe, YbB$_2$) cannot be described adequately within a framework of such a crude phenomenological picture. Among these properties are the very nature of the IV ground state, the origin of slow valence fluctuations, and the low-temperature anomalies of various physical properties. Recent experimental studies of transport [3,4] and optical [5] properties revealed the existence of several energy scales in the low-energy excitation spectra and several temperature regimes in the low-temperature electron kinetics.

It is found that at least three different activation energies influence the behaviour of electrons. The biggest energy gap $\Delta_{opt} \approx 14 - 20$ meV is observed in the frequency dependent conductivity and dielectric permittivity. Apparently, just this value should be ascribed to the hybridization gap $\Delta$ of the two-band model mentioned above. A substantially smaller value of $\Delta_{act} \approx 3 - 5$ meV is seen in the low-temperature resistivity and Hall effect measurements which display an activation type temperature dependence in the interval $15 > T > 6$ K. This gap was also measured in tunnelling experiments [6]. Below 6K the resistivity is nearly temperature independent, and such behavior seems to be consistent with hopping transport in an impurity band separated by the gap $\Delta_{act}$ from the bottom of conduction band. However, there is still no experimental consensus about the energy scales which control hopping. In ref. [8] part of the low-T interval is presumed to be described by Mott’s $T^{1/4}$ law for variable-range hopping with a scaling energy of $T_0 = 53$ K [9]. In another series of samples an activated term in the conductivity was observed with an activation temperature $T_a = 2.68$ K for $T < 2K$ [10], although the derivation of an activation energy of the order of several K from measurements made in the same temperature interval looks not too trustful. Besides, the pressure dependence of the residual resistivity [11] is extremely strong, and it hardly can be fitted in a picture of non-interacting electrons in an impurity band. In any case, there is no room for additional excitation branches in the mean-field two-band theory, and adding extra localized states in the gap does not improve the situation. The standard hybridization model seems to be too simplistic, and we believe that the generic properties of the intermediate valence state can be described only within a framework that goes beyond the mean field approximation.

In the present paper we offer a description of the low-energy spectrum of IV SmB$_6$ by treating the phenomenon of intermediate valence in rare-earth semiconductors in terms of an excitonic dielectric state. This approach was offered nearly two decades ago [12], and its effectiveness was demonstrated later in explanation of anomalies in the vibration spectra of IV semiconductors [13]. Features of excitonic instability were seen also in studies of the dielectric-metal transition under pressure in the compounds TmSe$_{1-x}$S$_x$ [14]. It is interesting that recently the dramatic observations of a ferromagnetic phase in n-doped divalent hexaborides CaB$_6$ and SrB$_6$ [15] were interpreted in terms of conventional excitonic instability of a Keldysh-Kopayev-Volkov-Rusinov type [16].

The theory of intermediate-valence excitonic dielectric emphasizes the role of soft singlet excitonic states in the formation of the ground IV state and valence fluctuations in the excitation spectrum. The IV state is described as a mixture of singlet $^7F_0$ states of divalent Sm($f^6$) and
the bound electron-hole pairs $f^\uparrow \tilde{b}$ where $\tilde{b}$ is the state of an electron promoted from the $f$-shell to $p$-orbitals spread over neighbouring boron sites but having the same symmetry as the $f$-electron in a central site. In some sense these states are electron-hole analogs of Zhang-Rice two-hole states known in the theory of low-energy states of CuO$_2$ planes in high-$T_c$ perovskites \cite{15}.

Here we consider the case of doped $n$-SmB$_6$ material. We study the behaviour of excess conduction electrons in the presence of soft valence fluctuations and discuss the origin of three energy scales seen in different temperature regimes. We show that the carriers which determine the low-temperature transport properties in this system are self-trapped electron-polaron complexes rather than simply electrons in an impurity band. The mechanism of electron trapping is the interaction with soft valence fluctuations.

II. GROUND STATE OF INTERMEDIATE VALENCE SEMICONDUCTOR

SmB$_6$ together with "golden" SmS is considered to be a classical example of a non-magnetic intermediate valence (IV) semiconductor (see \cite{2} and references therein). Both of these compounds possess a singlet ground state with intermediate valence $v \sim 2.6$. The main difference in the properties of these two compounds is that SmS transforms into an IV semiconductor only at finite pressure (or under the chemical pressure of rare earth ions of smaller radius substituting for Sm) whereas SmB$_6$ possesses intermediate valence and concomitant anomalous properties at ambient pressure.

Apparent, differences in the electron band spectra of these two materials are the eventual source of differences in their properties. SmS at ambient pressure is known to be a normal semiconductor with a relatively wide gap in the energy spectrum $\Delta = 0.23$eV. This gap divides the filled $f$-levels of Sm$^{2+}$ ($f^6$) ions from the bottom of the conduction band formed mainly by Sm $d$-states. The $4f$-levels, in turn, form a nearly dispersionless valence band within a wide forbidden gap $E_g \gg \Delta$ between the conduction band and conventional valence band formed mainly by $p$-electrons of the chalcogen sublattice. At finite pressure the gap is suppressed, but instead of collapsing to zero it transforms into a microgap $\Delta_{\mu}$ at some critical pressure $P_c$, and the material acquires the properties of an IV semiconductor. On the other hand, the "parent" divalent hexaborides without a $4f$-shell (CaB$_6$, SrB$_6$), as well as trivalent LaB$_6$ with an empty $4f$-shell, have a band structure without a gap in the actual energy interval. The density of states near the Fermi level in hexaborides is predetermined by a single degenerate band with a minimum in the $X$-point of the Brillouin zone. This band is formed mainly by $p$-electrons of the boron sublattice with a small admixture of $d$-states of the cation sublattice. It is nearly empty in divalent semimetallic hexaborides $\Delta_2 \uparrow \uparrow$ and more than half-filled in trivalent LaB$_6$ \cite{18}. Thus, one can expect that the $f$-level which is responsible for the intermediate valence of SmB$_6$ should cross this simple band. Indeed, conventional band calculations \cite{19} give a band structure compatible with this presumption.

Despite the differences between the parent (unhybridized) spectra of SmS and SmB$_6$, the decisive similarity of these two cases is the closeness or overlapping of the highly correlated 4$f$-levels of Sm$^{2+}$ ($4f^6$) and the nondegenerate conduction band. In SmB$_6$ these states overlap at ambient pressure, whereas in SmS the closeness is achieved under external pressure which induces the excitonic instability \cite{10} at $P_c$. The closeness results in promotion of electrons to delocalized band states. Crucial is the fact that the number $y$ of promoted electrons is the deviation from the divalent state in both Sm$^{2+y}$+S and Sm$^{2+y}$+B$_6$ IV semiconductors. According to the conventional band scheme which treats the $ff$-interaction in a self-consistent mean-field approximation, the $fp$-mixing results in the appearance of a hybridization gap $\Delta$ in case of SmB$_6$ and a pseudogap in the mixed valent phase of SmS. To take into account strong on-site correlations, this scheme should be modified.

The starting Hamiltonian for treating IV semiconductors is the Anderson lattice Hamiltonian supplemented by an interband Coulomb interaction (see, e.g., \cite{20}):

$$H = \sum_{k\sigma} \epsilon_k a_{k\sigma}^{\dagger} a_{k\sigma} + \sum_{\Lambda=0,(\Gamma\mu)} \sum_{m} E_{\Lambda} |m\Lambda\rangle \langle m\Lambda| + \sum_{mk\sigma\Gamma\mu} V_{mk\sigma\Gamma\mu} a_{k\sigma}^\dagger a_{\Gamma\mu}^\dagger |m0\rangle \langle m0| + H.c. + \sum_{j\nu\mu\sigma} U_{j\nu\mu\sigma} n_{\nu\mu\sigma} a_{\nu\mu\sigma}^\dagger a_{\nu\mu\sigma}. \quad (1)$$

Here $\epsilon_k$ is a simple spin-degenerate dispersion law for the band electrons (we assume for the sake of simplicity that these electrons come from the boron 2$p$-shells). The states $|m\Lambda\rangle$ of the Sm ion at site $m$ are represented by two configurations, $|m\Lambda\rangle = |m0\rangle \equiv |m\uparrow F_0\rangle$ for the divalent state $4f^6$ and $|m\Lambda\rangle = |m\Gamma\mu\rangle$ for the trivalent state $4f^5$. $\Gamma$ stands for the multiplet $6H_{\nu/2}$ of the $4f^5$ configuration which splits into a $\Gamma_{\uparrow\downarrow}\mu$ doublet and a $\Gamma_{\uparrow\uparrow}\mu$ quartet by the cubic crystal field $\Delta_{CF}$: $\mu$ enumerates the states of corresponding irreducible representations, and $n_{\nu\mu\sigma} = \sum_{\nu\mu\sigma} |m\nu\mu\sigma\rangle \langle m\nu\mu\sigma|$ is the $f$-electron occupation number. The hybridization interaction describes the promotion of electrons from the $f$-shell to the conduction band accompanied by a change of atomic configuration. The strong interband Coulomb interaction is given by $U_{j\mu\nu\sigma}$. The hybridization matrix element is $V_{mk\sigma\Gamma\mu} = (k\sigma, m\nu\mu\sigma|H|m0\rangle$. At $T \ll \Delta_{CF}$ only the lowest doublet state $\Gamma_{\downarrow\uparrow}\mu$ should be taken into account, so one should deal with hybridization of two doubly degenerate states.

The strong intrashell interaction is inserted in the configuration change operators $X_{m\Lambda}^{\nu\mu\sigma} = |m\Lambda\rangle \langle m\Lambda'|$. To make the hybridization problem solvable the nondiagonal operators are usually represented in a factorized form $X_{m\Lambda}^{\nu\mu\sigma} = f_{m\Lambda} b_{m\nu\mu\sigma}^\dagger$ (see, e.g., \cite{21}), where $f_{m\Lambda}$ and $b_{m\nu\mu\sigma}$ describe auxiliary fermion and boson fields which correspond to charge and spin degrees of freedom. This proce-
dure gives reasonable results in the case of nearly integer valence, but in the IV state the spin charge separation procedure can hardly be useful even as a starting approximation. We prefer to use another approach \cite{22} which seems to be adequate in the nonmetallic case when one can hope that hybridization will result in the separation of strongly correlated and weakly correlated bands in the energy space.

According to the prescription of this approach, we pick out the one-electron band Hamiltonian $H_b$ which describes the hybridization of band electrons with the mean-field level $\varepsilon_f$, which is defined as the energy difference

$$\varepsilon_f = E_0 - E_{\Gamma_\gamma},$$

where $E_{\Gamma_\gamma}$ is the lowest (doubly degenerate) state in the multiplet $F^{6}H_{5/2}$, and then represent the Hamiltonian \cite{1} in the form $H = H_0 + \Delta H$. The term $\Delta H$ describes the excitations above the ground state. Then the mean field spectrum in the actual energy interval can be described approximately by a Hamiltonian

$$H_b = \sum_{s=1,2} \sum_{k\sigma} \varepsilon_s(k)c_{s,k\sigma}^\dagger c_{s,k\sigma}.$$  \(2\)

Here

$$\varepsilon_{1,2}(k) = \frac{1}{2}(\varepsilon_k + \varepsilon_f) \pm \sqrt{\frac{1}{4}((\varepsilon_k - \varepsilon_f)^2 + |V(k)|^2)},$$  \(3\)

where $\epsilon^{m\cdot k}V(k) = V_{mn}$ from Eq. (1). Hybridization between $p$- and $f$-states due to the matrix elements $V(k)$ results in the wavefunctions

$$c_{1,k\sigma} = u_k f_\sigma + v_k c_{k\sigma},$$

$$c_{2,k\sigma} = -u_k c_{\sigma} + v_k f_\sigma,$$

where the coefficients of the canonical transformation are

$$u_k = \frac{1}{2} \left[ 1 + \frac{\varepsilon_k - \varepsilon_f}{\sqrt{(\varepsilon_k - \varepsilon_f)^2 + 4|V(k)|^2}} \right]$$

$$v_k^2 = 1 - u_k^2.$$  \(5\)

Since the band states and the $f$-states have the same symmetry at the points $X_7$, $R_7$, $\Gamma_7$ and $\Delta_7$ \cite{20} a hybridization gap opens, and the lower band $\varepsilon_1$ is filled in the ground state of “divalent” SmB$_6$ because two electrons transferred from the $f_{\Gamma_\gamma}$ level to the (initially empty) band $\varepsilon_1$ fill it completely. Then we assume that the level $\varepsilon_f$ crosses the band $\varepsilon(k)$ in its lower part, so that the band $\varepsilon_1(k)$ has mainly $f$-character. Then the square root in Eq. (3) can be expanded in $V(k)/|\varepsilon_k - \varepsilon_f|$ for most of the Brillouin zone, and the Wannier states given by the operators $c_{1,m\sigma} = N^{-1/2} \sum_k \exp(i k \cdot m) c_{1,k\sigma}$ can be approximated by the following equations,

$$c_{1,m\sigma} \approx f_{m\sigma} + N^{-1/2} \sum_k \sum_{jNN} \frac{V(m-j) \exp[i k \cdot (m-j)]}{\epsilon_k - \varepsilon_f} a_j.$$  \(6\)

Here $(j)_{NN}$ are the nearest neighbours (boron sites) of a Sm ion in a given crystal cell and $V(m - j)$ is the Fourier transform of $V(k)$. The width $T$ of the lower band is determined by a hopping integral which can be estimated as

$$T_{mn} \approx N^{-1/2} \sum_{kj} \frac{V(m-j)V^*(n-j) \exp[i k \cdot (m-n)]}{\epsilon_k - \varepsilon_f}$$  \(7\)

(here $j$ are the nearest neighbors of both $m$ and $n$).

To study the real carriers, one should go beyond the mean-field Hamiltonian, i.e. take into account the term $\Delta H$ which includes, in particular, the interaction between holes in the narrow band $\varepsilon_1(k)$ and the electron-hole interaction between carriers in different bands. The former contribution stems from a strong Coulomb interaction between electrons in the Sm $f$-shell $U = \langle f_m f_n U \rangle \langle f_m f_n \rangle$. This Hubbard interaction is reduced due to slight delocalization of Wannier functions

$$\tilde{U} = \langle c_{1,m} c_{1,m} | U | c_{1,m} c_{1,m} \rangle = r^4 U,$$

where $r = \int S(\varepsilon) u(\varepsilon) d\varepsilon$ is the reduction (nephelauxetic) factor \cite{22}. This factor depends on the density of states $S(\varepsilon)$ in the unhybridized band $\varepsilon_k$ (see Eq. \cite{1}), and the coefficient $u(\varepsilon)$ is that which appears in Eq. \cite{1} but written as a function of energy. In our case the condition $T < \tilde{U}$ is assumed to be valid, and this means that no more than a single hole per site can be created in this narrow “Hubbard” band.

The upper band $\varepsilon_2(k)$ is formed mainly by $p$-electrons with admixture of an $f$-component in the states close to the bottom of this band. If the bottom of the conduction band is close to the center of the Brillouin zone \cite{20}, the Bogolyubov’s coefficients for the electron wavefunction described by the operator $c_{2,m}$ are given by

$$v_k^2 \approx 1 - \frac{|V_0|^2}{|\varepsilon_f - \epsilon_k|^2}, \quad u_k \approx \frac{V_0}{\varepsilon_f - \epsilon_k}.$$  \(8\)

The Wannier operators $c_{2,m}$ have the same form as \cite{1}, except that the sign of the denominator in the second term is negative. The dispersion in this band can be approximated by the effective mass law

$$\varepsilon_2(k) \approx \varepsilon_0 + \frac{\hbar^2(k - k_0)^2}{2m_\varepsilon^*}$$  \(9\)

where $\varepsilon_0$ is the gap in the two-band spectrum \cite{3}. Here $k_0$ is the wavevector corresponding to the bottom of the empty band, and the effective mass can be estimated as

$$m_\varepsilon^*/m_0 \approx \frac{(\varepsilon_f - \epsilon_{k_0})/(V(k_0))^2}{1/\xi_c}.$$  \(10\)

The effective mass is noticeably heavier than the bare mass $m_0$ of the conduction electron (experimentally, $m_\varepsilon^* \approx 100 m_0$ \cite{3}). We suppose that the hybridization gap is seen as the biggest gap $\Delta_{opt}$ in the experiments mentioned in the Introduction.
Now, taking the energy of the state with filled lower band as a reference point in our calculations of the excitation energy spectrum, we have the effective Hamiltonian

$$\tilde{H} = \sum_{mn,\sigma} t_{mn} \hat{c}_{1,m\sigma}^\dagger \hat{c}_{1,n\sigma} + \frac{\tilde{U}}{2} \sum_{m\sigma} n_{1,m\sigma} n_{1,m\sigma} - \sum_{k\sigma} \varepsilon_2(k) \hat{c}_{2,k\sigma}^\dagger \hat{c}_{2,k\sigma} + H_{12} \tag{11}$$

where $t_{mn} = \sum_k e^{ik(m-n)} \varepsilon_1(k)$ and $\varepsilon_{1,2}(k)$ are given by Eq. (4). The electron states in the hopping term for hole excitations are dressed in projection operators, $\hat{c}_{1,m\sigma} = c_{1,m\sigma} n_{1,m\sigma}$. This projection inserts the kinematic restriction for the hole motion: the hole can be created at a given site only provided the electron with the opposite spin is still at the same site. Therefore, the holes are practically immobile. The last term $H_{12}$ is responsible for the electron-hole interaction,

$$H_{12} = \sum_{k,\sigma} \sum_{\sigma'} W(k, \mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) \hat{c}_{1,k_1,\sigma_1}^\dagger \hat{c}_{1,k_2,\sigma_2}^\dagger \hat{c}_{2,k_3,\sigma_3} \hat{c}_{2,k_4,\sigma_4} \tag{12}$$

where $W$ is derived from the Coulomb interaction [last term in the Hamiltonian (4)].

The two-band Hamiltonian $\tilde{H}$ contains hybridisation built into the electron and hole states, and the average occupation numbers $\bar{n}_{1f} \equiv \bar{n}_f$ are formally less than one in the lower “Hubbard” band $\varepsilon_1$. However, it should be emphasized that this deviation from integer value ($\bar{n}_f = 1$ corresponds to the Sm$^{2+}$ state) is not the true IV state. The one-electron picture given by the mean-field Hamiltonian $H_b$ (4) implies that interband transitions given by the operator

$$S_q = \sum_k c_{2,k+q\sigma}^\dagger \hat{c}_{1,k\sigma} = N^{-1} \sum_{mj} e^{-i\mathbf{q}\cdot\mathbf{r}_j} m_{2,mj\sigma} n_{1,m\sigma} \tag{13}$$

form the fundamental branch of elementary excitations in this semiconductor. However, free electron-hole excitations alone cannot explain the unusual properties of IV SmB$_6$. We believe that in the IV state an extra branch of charge transfer excitations exists. These are valence fluctuations, and are responsible for the unusual low-energy electron spectra and the numerous anomalies of the physical properties of SmB$_6$. According to the scenario suggested in (14,24,25) and verified in (26,27), the true IV ground state arises as a result of admixture of singlet excitonic states to the ground state of the same symmetry, and this admixture is non-negligible when the binding energy of the exciton is comparable with the band gap, i.e. when the system is close to the excitonic instability. To realize this scenario, one should construct the singlet exciton for the specific case of SmB$_6$.

According to the theory of IV rare-earth semiconductors (10,24,25), the singlet exciton is a bound state of a hole in the samarium $f$-shell and an electron spread over the $p$-states of the surrounding NN boron atoms with the same crystal point symmetry as an $f$-electron in the central cell. This state is constructed from electron-hole pairs (13) by means of an envelope function $F_0(m - j)$. When $q = 0$, the exciton operator can be written as

$$|\Psi_{ex}\rangle = N^{-1/2} \sum_{m\sigma} \sum_{(j)NN} F_0(m - j) p_{m\sigma}^j f_{m\sigma} |0\rangle \tag{14}$$

Here a basis of $f$ and $p$-orbitals is chosen. As mentioned above, the $f$-electron has $\Gamma_7$ symmetry, and its angular dependence is determined by the $xyz$ cubic harmonics. The envelope amplitude $F_0$ is a function of exciton energy $E_{ex}$ (see, e.g., Ref. (10) where this function is calculated in the NN-approximation). It also contains the phase factor which orders the phases of the $p_x$, $p_y$ and $p_z$ boron orbitals in accordance with the required symmetry (cf. (13)),

$$F_0(m - j) = F(E_{ex}) (-1)^{M_{m,j}} \tag{15}$$

where the phase $(-1)^{M_{m,j}}$ follows the arrangement shown in Fig. 3.

In fact, it will be shown below that the IV ground state resembles in some sense the Zhang-Rice (ZR) singlets (15), which are believed to be formed in Cu-O planes of high-$T_c$ materials. The Emery Hamiltonian (24), which is the starting point for the description of hybridization between weakly interacting oxygen $p$-electrons and strongly correlated copper $d$-horses is similar to the Anderson Hamiltonian describing the hybridization of nearly free $b$-electrons in the conduction band with strongly localized electrons in samarium $f$-shells. The difference is that the ZR bound states of a local Cu spin and a hole distributed over $p$-orbitals of the surrounding O ions are formed as excitations in doped oxicuprates, while the IV singlets are formed in the ground state as bound state consisting of a hole in the $f$-shell of the Sm ion and an electron distributed over the $p$-orbitals of the surrounding B ions of the cation sublattice. The binding mechanisms are the antiferromagnetic $dp$-exchange in ZR case and the Coulomb $fp$-attraction in our case.

Now, inserting (17) into (14), we have

$$|\Psi_{ex}\rangle = F(E_{ex}) N^{-1/2} \sum_{m\sigma} P_{m\sigma}^j f_{m\sigma} |0\rangle \tag{16}$$

where $P_{m\sigma}^j$ is a localised state which is defined as follows. SmB$_6$ has a simple cubic lattice structure, with an Sm atom in the centre of each cell, and a B$_6$ group on each corner. To simplify the treatment, we approximate the electronic wavefunctions for the boron clusters by the $p$-orbital directed along the diagonal of the cube (see Fig. 8). These orbitals are responsible for the covalent bonding between the boron clusters and Sm sublattice (6). We introduce the linear combinations

$$p_{q}^{xyz} \equiv \frac{1}{\sqrt{3}} (p_x(j) + p_y(j) + p_z(j))$$

$$p_{q}^{yz} \equiv \frac{1}{\sqrt{3}} (p_x(j) - p_y(j) + p_z(j)),$$
etc. which represent \( p \)-type electronic wavefunctions centred at \( j \) and oriented in the direction \( \hat{z} + \hat{y} + \hat{z} \). In analogy with the Zhang-Rice construction, we write down a localised state for the Sm site \( m \) consisting of eight nearest neighbour \( p \)-orbitals oriented to have the same symmetry as a central \( f \)-orbital, as shown in Fig. 1.

\[
P_{m\sigma} = \frac{1}{\sqrt{8}} \left[ p_{x^2-y^2 m+}^{yz} + p_{x^2-y^2 m-}^{yz} + p_{\bar{x}y z}^{z} + p_{\bar{x}y z m+}^{z} \right] \\
+ \left[ p_{m+}^{x^2-y^2} + p_{m+}^{x^2-y^2} + p_{m-}^{\bar{x}y z} + p_{m-}^{\bar{x}y z} \right].
\]

(17)

\( P_{m\sigma} \)

FIG. 1. A \( 4f \)-orbital located at the centre surrounded by eight \( p \)-orbitals on the \( \{\frac{1}{2},\frac{1}{2},0\} \) corners. The signs of the \( p \)-orbitals are chosen to have the same symmetry as the \( f \)-orbital.

States on neighbouring sites are non-orthogonal because of shared \( p \)-electrons. Therefore, it is useful to make a canonical transformation to the orthonormalized Wannier or Bloch operators \( d^\dag \),

\[
P_n^\dag = \sum_m \lambda(n-m)d_m^\dag = N^{-1/2} \sum_k \beta_k^{1/2} d_k^\dag e^{-ik\cdot n},
\]

(18)

where

\[
\lambda(n-m) = N^{-1} \sum_k \beta_k^{1/2} e^{ik\cdot (m-n)},
\]

(19)

\[
\beta_k = \frac{8}{3} \left[ \cos^2 \frac{k_x}{2} \sin^2 \frac{k_y}{2} + \sin^2 \frac{k_x}{2} \cos^2 \frac{k_y}{2} + \sin^2 \frac{k_z}{2} \cos^2 \frac{k_z}{2} + \sin^2 \frac{k_x}{2} \sin^2 \frac{k_y}{2} \cos^2 \frac{k_z}{2} \right].
\]

(20)

Then the exciton operator acquires the form

\[
|\Psi_{ex}\rangle = F(E_{ex}) \frac{1}{N} \sum_{m\sigma} \left[ \lambda_0 d_m^\dag f_{m\sigma} + \lambda_1 \sum_i \lambda_i \sum_{(n),i} d_{n,i}^\dag f_{m\sigma} \right] f_{m\sigma} |0\rangle
\]

\[
\equiv \frac{1}{N} \sum_m |\psi_m\rangle.
\]

(21)

Here the index \( i = 1,2 \ldots \) enumerates the coordination spheres, and the coefficients \( \lambda_i \) fall rapidly with increasing distance.

\[
\begin{array}{c|cc}
\hline
(i, j, k) & \lambda \\
\hline
(0, 0, 0) & 0.935 \\
(1, 0, 0) & -0.104 \\
(1, 1, 1) & 0.056 \\
(1, 1, 0) & -0.052 \\
\hline
\end{array}
\]

TABLE 1. The coefficients \( \lambda(m-n) \) where \( m-n = ix + jy + kz \).

By construction, the states \( |0\rangle \) and \( |\Psi_{ex}\rangle \) belong to the set of eigenstates of the Hamiltonian \( H \) [11] with nonlocal terms \( H_{nl} = \sum m \delta m \sum_{\sigma} \sum_{\sigma'} \sum_{\sigma''} p_{m\sigma} \sum_{\sigma'} \sum_{\sigma''} \sum_{\sigma'''} \delta H_{12} \) (defined below) excluded.

However, these nonlocal interactions are responsible for forming the IV state. In a simplest approximation we restrict ourselves by considering only the first term \( \sim \lambda_0 \) in the expansion [21] and take the nonlocal interaction in the form

\[
\delta H_{12} = \sum_{m\sigma} W(m-n) f_m^\dag f_n f_n^\dag d_{m\sigma} + H.c.
\]

(22)

This component of electrostatic interaction violates the point crystalline symmetry and induces \( f p \) hybridization at the site \( m \) in presence of a hole in the neighbouring cell \( n \). The operator \( \delta H_{12} \) has a property

\[
\delta H_{12} |\psi_m\rangle = W(m-n)|\psi_m\rangle |0_m\rangle
\]

where \( 0_n \) stands for the cell \( n \) in the ground state configuration. Thus this interaction intermixes the states \( |0\rangle = \prod_n |0_n\rangle \) and \( |\Psi_{ex}\rangle \). The mixing constant is \( w = \langle 0 | \delta H_{12} | \Psi_{ex}\rangle = zF(E_{ex}) \lambda_0 W \) where \( z \) is the coordination number for Sm sublattice and \( W \) is the NN interaction matrix element. After diagonalization the local neutral states in each cell \( m \) are represented by the linear combinations

\[
|\tilde{0}_m\rangle = \cos \theta |0_m\rangle + \sin \theta |\psi_m\rangle,
\]

\[
|\tilde{\psi}_m\rangle = -\cos \theta |\psi_m\rangle + \sin \theta |0_m\rangle
\]

(23)

where \( \tan 2\theta \approx 2w/E_{ex} \), and the valence is determined by the value of \( \sin^2 \theta \). As was mentioned, the local states [23] are in some sense the electron-hole analogs of two-hole Zhang-Rice singlets and triplets [13, 23]. Finally, the ground state of IV semiconductor is

\[
|\Psi_0^{(iv)}\rangle = \prod_m |\tilde{0}_m\rangle
\]

(24)

and the low-lying local excitations are described by the vector
The valence and the energy scale of these local excitations (valence fluctuations) are characterised by the degree of admixture of the excitonic state, in which an electron is promoted to a loosely bound “molecular orbit” \( P_m \). If the exciton energy \( E_{ex} \) is small enough (the exciton binding energy is comparable with the gap width), the value of \( \sin^2 \theta \) is close to 1/2. Having in mind also the mean-field part of hybridization given by Eq. (4), we conclude that in this case the valence
\[
n_v = 3 - \bar{n}_f + \sin^2 \theta
\] (26)
can exceed 2.5 both in SmS and SmB\(_6\). Thus, the large deviation of valence from the integer value and the softness of local valence fluctuations are, apparently, the correlated phenomena. Further discussion of internal consistency of the model can be found in the last section.

### III. TRAPPING OF CONDUCTION ELECTRONS AND HOPPING CONDUCTIVITY

The samples of good quality which were studied in the experiments of the past decade mentioned in the Introduction are \( n \)-type semiconductors at low temperature, unlike the \( p \)-type samples of the first generation \[34]. The electron concentration in these samples is estimated at \( n_e \approx 10^{17} \text{ cm}^{-3} \) at ambient pressure and liquid helium temperature \[35\]. In order to interpret the transport properties of these samples one should determine the spectrum of electrons at the bottom of the conduction band in the presence of soft valence fluctuations. In our model the local valence fluctuations arise as transitions between the states \( |\bar{0}_m \rangle \) and \( |\bar{\psi}_m \rangle \) given by Eq. (18). It is known that these valence fluctuations are the source of strong anomalies in the vibration spectra because the characteristic time \( \tau_{ex} \) of valence fluctuations is close to phonon times \( \tau_{ph} \approx \omega_{ph}^{-1} \sim 10^{-15} \text{ s} \). Therefore, one can expect that these “slow” excitations could dress the carriers and form an electron-polaron cloud similar to the phonon cloud which results in polaron self-trapping in dielectric crystals (see, e.g., \[27\]).

To describe electron self-trapping we start with a Hamiltonian including the interaction between the conduction electron and the local valence fluctuations in a single lattice site \( n = 0 \),
\[
H_e = \sum_k \varepsilon(k) c_k^\dagger c_k + \Omega_0 A^\dagger A + \sum_{k_1, k_2} W_{ef}(k_1, k_2) c_{k_1}^\dagger c_{k_2} A^\dagger + H.c.
\] (27)
This Hamiltonian stems from our basic Hamiltonian \[11\]. It includes the electrons in the upper conduction band (the spin summation and band index \( s = 2 \) are omitted). Only the term which corresponds to momentary, local redistributions of charge and valency at the site of the exciton due to the interaction with the charge carrier is retained in \( H_{12} \). The valence fluctuations with the energy \( \Omega_0 \) are described by the local operator \( A^\dagger = |\bar{\psi}\rangle \langle 0| \).

This Hamiltonian stems from our basic Hamiltonian \[11\]. It includes the electrons in the upper conduction band (the spin summation and band index \( s = 2 \) are omitted). Only the term which corresponds to momentary, local redistributions of charge and valency at the site of the exciton due to the interaction with the charge carrier is retained in \( H_{12} \). The valence fluctuations with the energy \( \Omega_0 \) are described by the local operator \( A^\dagger = |\bar{\psi}\rangle \langle 0| \).

The matrix element \( W_{ef}(k_1, k_2) \) is given by the integral
\[
W_{ef}(k_1, k_2) = \int dr_1 dr_2 \bar{\psi}_{ex}^* (r_1) \bar{\psi}_0 (r_1) W(r_1, r_2) \psi_{k_1}^* (r_2) \psi_{k_2} (r_2)
\] (28)
where \( \psi_k (r) \) are the Bloch functions for the conduction electrons, \( \bar{\psi}_0 (r) \) and \( \bar{\psi}_{ex} (r) \) are the wavefunctions of the states created by the operators \[23\]. Their product is
\[
\psi_{ex}(r) \bar{\psi}_0 (r) = D(r)
\]
\[
= \frac{1}{2} (|\sin 2\theta \rho_p (r) - \rho_f (r)| - \cos 2\theta f_{xyz} (r) d_{xyz} (r))
\] (28)
where \( \rho_f (r) = |f_{xyz} (r)|^2 \) is the f-electron density in the centre of the cell (see Fig. 1) and \( \rho_p (r) = F^2 (E_{ex}) \lambda_0^2 |d_{xyz} (r)|^2 \) is the p-electron density in a central cell given by the first term in the r.h.s. of Eq. (24). The conduction electron density operator \( \rho_{k_1, k_2} (r_1) = \bar{\psi}_{k_1}^* (r_2) \psi_{k_2} (r_2) \) is determined by the Bloch functions \[3\]. Near the bottom of conduction band this operator can be approximately presented as
\[
\rho_{k_1, k_2} (r_1) \approx \rho_f (r_1) + \zeta_c \rho_p^0 (k_1, k_2) (r_1)
\] (29)
by means of Eq. (3). Here \( \zeta_c = V_0^2 / \varepsilon_{fB}^2 \).

\[
\rho_p^0 (k_1, k_2) = \sum_{j \in NN} \frac{e^{-i(k_1-k_2) \cdot j}}{2} |\psi_j (r_1)|^2
\] (31)
and \( \varepsilon_{fB} = \varepsilon_f - \varepsilon_{k_1} \). Then the coupling constant in the Hamiltonian \[27\] acquires the form
\[
W_{ef}(k_1, k_2) \approx w_0 + w_1 \beta_{k_1-k_2}
\] (32)
where
\[
w_0 = \int dr_1 dr_2 D(r_1) W(r_1, r_2) \rho_f (r_2),
\]
\[
w_1 \beta_{k_1-k_2} = \int dr_1 dr_2 D(r_1) W(r_1, r_2) \rho_p^0 (k_1, k_2) (r_2 + j).
\]
The structure factor \( \beta_k \) is given by
\[
\beta_k = 8 \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2}
\] (33)
It is seen that the first term \( w_0 \) dominates in the electron-exciton interaction, therefore we begin with a calculation of the electron self-energy induced by this term within the lowest order of perturbation theory. The theory which allows inclusion of nonlocal corrections due to small term \( \sim w_1 \) in Eq. [24] is described in Appendix. We calculate the electron Green’s function in Matsubara representation

\[
G_{kk'}(\omega_n) = \int_0^\beta \langle T_{\tau} c_k(\tau) c_{k'}^\dagger(0) \rangle e^{i\omega_n \tau} d\tau
\]

([\omega_n = (2n + 1)\pi T] interacting with a localized valence fluctuation mode \( \Omega_0 \) described by the propagator

\[
D(\omega_m) = -\frac{2\Omega_0}{\omega_m^2 + \Omega_0^2}
\]

[\omega_m = 2\pi mT]. The Dyson equation for the electron Green’s function is

\[
G_{kk'}(\omega_n) = G^0_{kk'}(\omega) \left[ \delta_{kk'} + \sum_{k_2} \Sigma_{kk_2}(\omega_n) G_{k_2 k'}(\omega_n) \right].
\]

(36)

In the lowest order of perturbation theory the self-energy \( \Sigma_{kk'}(\omega_n) \) after carrying out an analytic continuation into the region of real frequencies acquires the form (see Fig. 2)

\[
\Sigma^R_{kk_2}(\omega) = \sum_{k_1} W_{vf}(k, k_1) W_{vf}(k_1, k_2) \mathcal{P}_{k_1}(\omega, \Omega_0)
\]

(37)

where

\[
\mathcal{P}_{k_1}(\omega, \Omega_0) = \int_{-\infty}^{\infty} \frac{de}{2\pi} \frac{\text{Im} D^R(\epsilon)}{\epsilon + \epsilon(k_1) - \omega - i\delta} \times \left( \tanh \frac{\epsilon(k_1)}{2T} + \coth \frac{\epsilon}{2T} \right).
\]

(38)

FIG. 2. The self-energy diagram corresponding to Eq. (37). The straight line represents a conduction electron and the wavy line represents a soft valence fluctuation.

Approximating the nonlocal potential \( W_{vf}(k, k_1) \) by its local part \( w_0 \), we come immediately to the following secular equation

\[
1 - w_0^2 m(\omega)m(\omega - \Omega_0) = 0
\]

(39)

where \( m(\omega) = \sum_k G^0_{kk}(\omega) \).

In close analogy with the polaron self-trapping effect [27], one can expect that the attractive polariation potential with effective coupling constant

\[
g^0(\omega) = w^0_0 \sum_{k_2} G^0_{k_2}(\omega - \Omega_0)
\]

results in appearance of bound electron-polaron states. As usual in 3D problems, the threshold value of the attractive potential determines the onset of the bound state. To find the constraints on the solutions with negative energy (corresponding to bound states) we examine the function \( m(\omega) \) defined in (39),

\[
m(\omega) = \int_{-\pi}^{\pi} \frac{dk_2 dk_y dk_z}{(2\pi)^3} \frac{1}{\omega - \epsilon(k)}
\]

(40)

At \( \omega = 0 \) the integral may be evaluated numerically (see Appendix). Fig. 3 demonstrates the graphical solution of Eq. (39) for a reasonable set of model parameters. The value of \( \Omega_0 = 5.5\text{meV} \) correlates the experimentally observed peak in optical reflectivity spectra [38], and the binding energy of localized \( \omega \approx 3.5\text{meV} \) is in good agreement with the activation energy registered in multiple optical and transport measurements in the temperature interval 6 – 14 K (see [3] and references therein).

We have demonstrated the existence of a self-trapped state in the simplest approximation, whereby the local polarisation mode is taken into account in second order perturbation theory. However, the values of the parameters necessary to achieve reasonable agreement with experiment give for the dimensionless coupling constant \( \alpha = w_0/\Omega_0 \) the value of \( \alpha \approx 4.5 \). This means that in fact we are in a strong coupling limit, and a more refined treatment is necessary. The generalisation of the theory to the strong coupling limit can be done in close analogy with the theory of small polaron. One can make the canonical transformation \( \bar{c}_k = e^{-S}c_k e^S \), where

\[
S = \sum_{kq} \frac{W_{vf}(k, q)}{\Omega_0} (c_{k+q}^\dagger A_q^\dagger - c_{k+q} A_q)
\]

(41)

(see, e.g., [28]). We have seen above that the local term \( w_0 \) is dominant in electron-exciton coupling constant [32]. Then neglecting the contribution of the “tail” \( w_1 \) we come to purely local interaction at a given site \( m = 0 \), namely, \( \delta H_{12} = w_0^0 c_0^\dagger A_0^\dagger \). Eliminating this interaction by means of a canonical transformation [11], one comes to the effective Hamiltonian

\[
\tilde{H}_e = e^{-S} H e^S
\]

\[
= \sum_m \tilde{\varepsilon}_m c_m^\dagger c_m + \sum_{m,n \neq 0} T_{mn} c_n^\dagger c_m + \Omega_0 A_0^\dagger A_0
\]

\[
- \tilde{\varepsilon}_{pol} c_0^\dagger c_0 - \sum_{m \neq 0} \left( T_{m0} c_0^\dagger c_m e^{-\alpha(A_0^\dagger A_0) + \text{h.c.}} \right).
\]

(42)

Now the main part of electron-exciton interaction is taken into account exactly, and it is contained in the polaron shift. This shift induces the local scattering at the site \( 0 \) which is given by the operator \( \varepsilon_{pol} \sum_{k_1, k_2} c_{k_1}^\dagger c_{k_2} \).
where $\varepsilon_{\text{pol}} = \alpha \omega_0$. The local scattering can be inserted in the self-energy of the conduction electron in the same manner as it was done in second order of perturbation theory in Eq. (36). However, now the calculation is exact, and instead of Eq. (39) one has

$$0 = 1 + \varepsilon_{\text{pol}} \sum_k (\omega - \varepsilon(k))^{-1} = 1 + \varepsilon_{\text{pol}} m(\omega)$$

(43)

which can be solved by using the same approximation as in Eq. (39). In any case the electron can be trapped by local valence fluctuations provided the polaron shift $\varepsilon_{\text{pol}} = \alpha \omega_0$ given by the bound solution of Eq. (39) exceeds the characteristic kinetic energy of the electrons near the bottom of the conduction band. Therefore the effective mass enhancement due to $p$-$f$ hybridisation favours the formation of a self-trapped state.

![Graphical solutions to Eqs. (39) (solid line) and (43) (dotted line) using $\omega_0 = 5$ meV, $m^* = 100 m_0$, $\Omega_0 = 5.5$ meV, $\varepsilon_0 = 25$ meV and $\varepsilon_{\text{pol}} = 21$ meV.](image)

FIG. 3. Graphical solutions to Eqs. (39) (solid line) and (43) (dotted line) using $\omega_0 = 5$ meV, $m^* = 100 m_0$, $\Omega_0 = 5.5$ meV, $\varepsilon_0 = 25$ meV and $\varepsilon_{\text{pol}} = 21$ meV.

In Fig. 3 we show a bound state solution with energy 3.5 meV in agreement with the activation energy observed in transport measurements and absorption edges in optical experiments. In both cases the coupling constant $\omega_0$ is treated as a free parameter. In the second order perturbation calculation $\omega_0$ is determined to be 25 meV, which as we have discussed above, indicates that our solution lies in the limit of strong coupling. In the non-perturbative calculation we find that $\varepsilon_{\text{pol}} = \frac{\omega_0^2}{\beta \Omega_0} = 21$ meV, which implies that $\omega_0 = 11$ meV. Because we are in the strong coupling limit we do expect a deviation between the exact calculation and the second order perturbation result. However, our results are close enough to suggest that the physical content of the perturbative calculation is correct, that is, that an electron may bind to a single local valence fluctuation and the result is a localised electron-valence fluctuation complex. Moreover, we also observe that our results are not particularly sensitive to the input parameters, and are therefore not the result of any special “fine tuning”. All of this is a consequence of the fact that the relevant energies are all roughly the same: $\Omega_0 = 5.5$ meV, $\hbar^2/\alpha^2 m^* = 5$ meV and $\Delta_{\text{act}} = 3.5$ meV.

The last term in the effective Hamiltonian (12) is responsible for the exciton-assisted hopping in an electron-polaron band. The electron self-trapping can occur around any arbitrary lattice site, so the trapped particle can move from a given cell to the neighboring cells by the mechanism which resembles the polaron propagation (27, 28). Therefore, the electron-polaron drift in electric field is responsible for the conductivity at $T \to 0$ in n-type SmB$_6$. We leave systematic treatment of electron transport in IV semiconductors for future publications, and conclude this article by qualitative discussion of anomalous low-$T$ behavior of SmB$_6$ mentioned in the Introduction.

**IV. CONCLUDING REMARKS**

As a result of above analysis, one can understand the mechanism of reduction from the eV energy scale characteristic of initial Hamiltonian (1) down to meV scale of low-lying charge excitations in the n-type material. First, at the mean-field level of approximation (eqs. 2 to 4) the gap $\Delta_0 \sim 10 - 20$ meV opens, and the states near the bottom of conduction band become heavy. This initial reduction of the energy scale is characterized by the mean-field hybridization coupling constant $W_{\text{hyb}}$, which is consistent with our assumption that the mean-field hybridization gives only part of the actual value of the valence $\nu_e$. According to our previous calculations (23), the value of $r = 1/3$ corresponds to $n_f \approx 0.75$, and the experimentally observed value of $n_e \approx 2.55$ can be reached only by means of excitonic mechanism with the exciton mixing parameter $\theta \sim 0.55$ (see eq. 25). This value, in turn, agrees with our assumption of a soft excitonic mode. Then, we find from (14) $\zeta_c = 0.01$, and taking for the bandwidth $\varepsilon_{fb} = \varepsilon_f$, the value of 4 eV in accordance with the band calculations for the related system (19), we estimate the hybridization coupling constant as $V_0 \approx 0.1$ eV which is a reasonable value for the rare-earth materials. To make these estimates self-consistent, the hybridization gap should be found. The gap is defined via the above parameters as $\Delta_0 \approx \zeta_c \varepsilon_{fb} + \zeta_f \varepsilon_f$. Inserting the values of corresponding parameters, we find $\Delta_0 \approx 13$ meV which is in a reasonable agreement with the experimental data.

Now, turning to the n-doped materials, we deal with heavy electrons, which interact with the valence fluctuations. The kinetic energy of these electrons is estimated as $\sim V_0^2/\varepsilon_{fb} \sim 10^{-2}$ eV, and the energy scale of valence fluctuations is, by their origin, limited from above by the energy gap of the same $10^{-2}$ eV width. The polarization coupling constant $W_{\text{eff}}$ (12) as well as the “superhybridization” matrix elements $W$ in the Hamiltonian
should be at least an order of magnitude less than the mean-field hybridization $V$, so the value of $w_0 = 25$ meV, which is used in our numerical solution of Fig. 3 looks realistic. Eventually, solving the equation (13) for the polaron shift, we descend one more step along the energy scale and find ourselves in a meV region. The propagation of self-trapped electron-polaron can in principle be characterized by even lesser energies of the order of $10^{-1}$ meV.

Thus, we have found that the heavy electrons near the bottom of conduction band can propagate in a lattice only in a polarization cloud of valence fluctuations. It is worth mentioning that this conclusion correlates partly with a recent proposition of Kasuya [29] in spite of the fact that his model of the ground state of a mixed valence semiconductor disagrees with our picture in several respects. He chooses the trial wave function for a local lence semiconductor disagrees with our picture in several respects. He chooses the trial wave function for a local

\[ |\tilde{0}_m\rangle = \alpha_{f m}|0_m\rangle + \alpha_{d m}A_{d m}^\dagger |\psi_{m}\rangle \]  

(45)

where $A_{d m}^\dagger = d_{m}^\dagger c_{d m}$ is a charge transfer operator, which creates an electron in a 5d shell of Sm ion and a hole of d-symmetry spread over surrounding boron sites similarly to our f-like orbital $P_{m}$ entering the state $|\psi_{m}\rangle$ (21). The physical reason of such a choice is conviction that the 5d electrons also constitute a strongly correlated subsystem and have to trend to form a bonding Kondo-like state à la $f$ states in conventional Kondo lattices. However, looking at the real band structure of the rare-earth hexaborides, we see that the admixture of $d$ states to the band $\epsilon_k$ is really small: the center of gravity of $d$ states in divalent hexaborides is at the energy of $\sim 7 - 8$ eV above the bottom $\epsilon_{b0}$ of conduction band (see, e.g., Fig. 5 in Ref. [17]). Therefore, 5d levels are practically unoccupied, and one cannot expect any kind of effective screening in a $d$ channel. Nevertheless, our model includes effective screening of excess electron in conduction band which resembles Kasuya’s mechanism: the canonically transformed operators $\tilde{c}_0$ in a weak coupling limit can be presented as $\tilde{c}_0 \sim c_0 (1 + \alpha A_{0}^d)$, and the operator $A_{0}^d$ returns part of the charge density back to the Sm site from the periphery of the unit cell, i.e. plays the same role as the operator $A_{b0}^d$ in the trial function (13). The screening (or polaron dressing) in our model is due to the same valence fluctuations as all other physical effects, so the totality of experimental data is explained in a self-consistent scheme without appealing to any additional hypotheses.

As a result, our model is free from undesirable features of “Kondo insulator” approach which are not confirmed by the experiment.

(i) We do not appeal to the Kondo mechanism of forming the ground state singlet, and the independence of the activation gap on external magnetic field [30], which rules out the Kondo insulator mechanism, agrees well with the expectations of our model.

(ii) The ground state of our Hamiltonian is absolutely homogeneous, and this statement agrees fairly with available experimental observations, whereas the trial function (13) implies charge modulation in a form of Wigner crystal or Wigner liquid [29].

(iii) The model of ref. [29] gives a single gap which predetermines electronic, optical and magnetic properties of the material, and it is unclear whether it is compatible with a real experimental situation which definitely evidences several energy scales for electronic and optical characteristics of SmB$_6$ [38].

(iv) Unlike the bare ground state $|0\rangle$, the wavefunction (13) is not fully symmetrical, so one can expect a sort of ferroelectric ordering as $T \rightarrow 0$ [31,32].

Turning to the problem of low-temperature transport, we conclude that as $T \rightarrow 0$ the electron propagation is valence fluctuation assisted motion of in extremely narrow “polaron band” separated by the gap $\Delta_{ac}$ from conduction band continuum. The residual resistivity $\rho_0$ is inversely proportional to the hopping rate between two neighboring crystal cells,

\[ \rho_0^{-1} \sim S_{mn} \sim T_{mn} \Phi_{mn}, \]  

(46)

where $\Phi_{mn} = \langle \tilde{\psi}_{m}|\tilde{\psi}_{n}\rangle$ is a function describing the overlap of the valence fluctuation “clouds” centered around the sites $m$ and $n$. As $T \rightarrow 0$ the process is elastic, so the conductivity is temperature independent. In SmB$_6$ this type of conductivity is observed for $T < 3K$ [32,33]. At higher $T$ the hopping is, apparently, assisted by phonon and exciton emission/absorption. Of course, the temperature dependence of this hopping can differ from that for usual variable range hopping in impurity bands. This transient regime can be seen in the range $3K < T < 6K$, although the experimental data on the temperature dependence are still ambiguous [33,34]. In the temperature interval $6K < T < 14K$ thermally activated resistivity in SmB$_6$ with an activation energy of $\Delta_{ac} \approx 3.5meV$ is observed [3,5]. At higher temperatures the electrons dissociate from their local valence fluctuation clouds and as a result of this detrapping find themselves at the bottom of the conduction band. At these temperatures the activation of valence electrons also gives a significant contribution to the electron conductivity.

The same three regimes (III, II and I, respectively, in terms of Ref. [3]) with additional pronounced maximum around $5K$ are observed in the temperature behavior of the Hall constant $R_H(T)$ [34]. This maximum can be explained, at least qualitatively, within a simple phenomenological picture of two groups of carriers with high and low electron mobilities, $\mu_b = cR_{b0}\sigma_b$ and $\mu_h = cR_{h0}\sigma_h$, where $R_{b0}$ and $\sigma_b$, $R_{h0}$ and $\sigma_h$ are the Hall constants and conductivities of light (b) and heavy (h) carriers, respectively. In the case of hopping in impurity bands of doped semiconductors [35], two contributions, $\sigma_b$ (hopping) and $\sigma_h$ (band) in the electron conductivity result in the following equation for the Hall constant,

\[ R_H = \frac{R_{b0}\sigma_b^2 + R_{h0}\sigma_h^2}{(\sigma_b + \sigma_h)^2}. \]  

(47)

Then the maximum in $R_H(T)$ corresponds to a crossover from hopping motion at low $T$ to band motion at high $T$, provided $\mu_b \gg \mu_h$. 

9
In our case the phenomenological background of this equation still exists, but the microscopic origin of all temperature dependences should be revised because of the essentially many-particle nature of heavy carriers.

First of all, it is clear that the standard estimates of the number of “scattering centers” obtained from the value of the residual resistivity \( \rho_0 \) are simply inapplicable in our case, since we deal with hopping of many-particle electron-exciton complexes rather than with the motion of extended band electrons. So, there is no room for the unitarity limit arguments in these estimates, and the “superunitarity scattering” reflects the many-particle nature of current carriers in semiconductors with fluctuating valence \[34\]. Thus, the paradox of the number of scatterers per unit cell.

The next question is the enormously strong pressure dependence of the residual resistivity and the Hall coefficient \[4\]. Again, according to our model, one cannot directly apply the notions of charge transport in a band of extended states for an estimation of the carrier concentration. We think that the key to the extraordinary sensitivity of the residual resistivity \( \rho_0 \) and \( R_H(T \to 0) \) to external pressure is the increase of Sm valence with growing pressure \( P \). The eventual source of this increase is growing \( f_p \)-hybridization. Because of increasing valence \( n_e \) as a function of pressure the matrix element \( W_{ef} \) \[32\] decreases. As a result the polaron shift \( \varepsilon_{pol} \) as well as the binding energy of the self-trapped electron decreases too. The excitonic overlap function \( \Phi_{mn} \) also grows due to lattice contraction. Since both the hopping integral \( T_{mn} \) and the function \( \Phi_{mn} \) depend exponentially on the intersite distance, one can expect a very sharp dependence of the hopping rate on external pressure. The radius of the localized state with binding energy 3.5 meV and effective mass \( \sim 100 m_0 \) is estimated to be \( 2-4 \mu m \), and an increase of this radius by an order of magnitude would be enough to get a \( 10^4 \) growth of the hopping rate. Such an increase is achievable under a pressure of 50 kbar. At higher pressures the trap becomes too shallow (the valence too close to 3) to catch the electron, the system transforms into conventional n-doped degenerate semiconductor, and eventually it becomes a metal with trivalent Sm ions in the cation sublattice.

Finally, the question of the variation of electron concentration \( n_e \) with increasing \( P \) and \( T \) also demands special consideration. Usually information about \( n_e \) is extracted from the value of \( R_H \) under the assumption of single band conductivity when \( R_H \approx R_0 = (n_e e c)^{-1} \). According to the experimental data cited above, \( R_H \) is nearly constant in the temperature interval I (below 3 K), but falls drastically with applied pressure: \( R_H(45 \text{ kbar})/R_H(1 \text{ bar}) \sim 10^{-4} \). However, in our case of two-component systems with \( \sigma_H \gg \sigma_r \) the Hall constant takes the form

\[
R_H \approx \frac{\mu_H \sigma_r + \mu_r \sigma_H}{\epsilon \sigma_H^2}.
\]

It is seen immediately that the pressure dependence of this function is determined mainly by the denominator, and the decrease of \( R_H \) with pressure is due to the exponentially growing factor \( S_{mn} \) in Eq. \[46\] for \( \sigma_h \) rather than to increasing \( n_e \).

Generally speaking, \( R_H \) derived from Eq. \[47\] also cannot be used to determine electron concentration neither in region I nor in region II. The low \( T \) limit of \( n_e \sim 10^{17} \text{cm}^{-3} \) which is obtained under the assumption that \( R_H \approx R_0 \) can only be considered as a lower bound. In general the case of two mechanisms of charge transport the Hall constant is \( R_H = (n_e e c)^{-1} \mu_H/\mu_D \), where \( \mu_H, \mu_D \) are the Hall and drift mobilities respectively. If \( \mu_H/\mu_D \gg 1 \) at low \( T \) the real electron concentration \( n_e \) may substantially exceed the value of \( n_{e0} \). Referring to the exponential dependence of \( n_e(T) \) and \( R_H(T) \) in region II we should note that there are at least two causes of such a dependence. First there is the thermal activation of electrons from the polaronic traps to the band continuum states, and second is the temperature dependence of the hopping rate \( S_{mn} \) due to the contribution of thermally activated exciton assisted terms which appear instead of the overlap integral \( \Phi_{mn} \). As both \( \sigma_H(T) \) and \( \sigma_B(T) \) give an exponential contribution with the activation energy of \( 
Delta_{act} \sim 3.5 \text{ meV} \) to the electron conductivity and the Hall constant \[46\]. Again, it is impossible to calculate the variation of the electron concentration \( n_e \) directly from this equation. We have the detailed evaluation of various transport coefficients for a forthcoming paper, but to conclude this qualitative discussion we would like to emphasize that according to the theory proposed in this paper the total carrier concentration in conduction band is \( n_e \sim 10^{17} \text{cm}^{-3} \) at least while the interband electron activation is negligible (\( T \ll \Delta_0 \)), and there is no room for dramatic pressure or temperature variation of \( n_e \) in the mixed-valence phase of \( n\text{-SmB}_6 \). The real semiconductor to metal transition occurs only at \( P > P_c \) when the Sm valence changes to the integer value of +3.

The authors are grateful to M. Aronson, D.I. Khomskii and N.E. Sluchanko for useful discussions. This work was supported by Israeli Academy of Sciences and Humanities Centre for “Strongly Correlated Interacting Electrons in Restricted Geometries”. S.C. acknowledges the support of the Feinberg School of the Weizmann Institute.

**APPENDIX**

We describe below the self-trapped state of the electron captured by the nonlocal potential \[32\]. For the sake of simplicity we consider the case of conduction band with a minimum at the \( \Gamma \) point of the Brillouin zone. To solve the Dyson equation \[50\] we offer the procedure of factorization of the vertex matrix element \( W_{ef} (k_1, k_2) \). The latter can be represented in a form

\[
W_{ef} (k_1, k_2) \equiv \sum_{\alpha} \gamma_{a}^{\alpha} \tilde{\gamma}_{a}^{\alpha}, \text{ where}
\]

\[
\gamma_{a}^{\alpha} \text{ and } \tilde{\gamma}_{a}^{\alpha}
\]

Here the index \( a \) runs over all states of the system and the index \( \alpha \) runs over all channels of the external field. The vertex matrix element \( W_{ef} \) is defined in terms of the elementary vertex amplitudes \( \gamma_{a}^{\alpha} \). The elementary vertex amplitudes characterizing the interaction of the system with the external field are the amplitudes of the process of creation of such a bound state. The external potential \( V^{ext} \) is composed of the separate potentials \( V_{a}^{ext} \) acting on the individual channels of the external field. The vertex amplitudes \( \gamma_{a}^{\alpha} \) are defined by the Dyson equation

\[
\gamma_{a}^{\alpha} = V_{a}^{ext} \sum_{\alpha'} \gamma_{a'}^{\alpha'} \tilde{\gamma}_{a'}^{\alpha'} + \sum_{\alpha'} \gamma_{a'}^{\alpha'} \tilde{\gamma}_{a'}^{\alpha'} \gamma_{a}^{\alpha}.
\]
For the components therefore stands for the nonlocal contribution of the “tail” \(a\) where \(A\) has the form (for \(\zeta\)): 

\[
\gamma_k = \begin{pmatrix}
\sqrt{\zeta w_0} \cos \frac{\sqrt{2}}{a} \cos \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \cos \frac{\sqrt{2}}{a} \cos \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \cos \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \cos \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \sin \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \sin \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \sin \frac{\sqrt{2}}{b} \\
\sqrt{\zeta w_0} \sin \frac{\sqrt{2}}{a} \sin \frac{\sqrt{2}}{b} 
\end{pmatrix}
\]  

(48)

By writing \(G^0_{k} \equiv \sum_{k'} \gamma_{k}^{*} G_{k, k'}\), we obtain a solution for \(G\) of the form

\[
G_{k}^{0}(\omega) = (M^{-1})^{ab} \gamma_{k}^{*} G_{k, k'}^{0}(\omega)
\]  

(49)

where

\[
M^{ab} = \delta^{ab} - \sum_{k_1, k_2}^{8} G_{k_1}^{0}(\omega) \mathcal{P}_{k_2}(\omega, \Omega_{0}) \gamma_{k_1}^{*} \gamma_{k_2}
\]  

(50)

Here the index \(a = 0\) corresponds to the fully symmetric solution described approximately by Eq. (43), and \(a = 1\) stands for the nonlocal contribution of the “tail” \(w_0\) with the same \(A_1\) symmetry. For the indices \(a, b = 2, \ldots, 8\) the matrix \(M\) is actually diagonal since terms in the integrand must be even in \(k_{1x}, k_{1y}, k_{1z}\) and \(k_{2x}, k_{2y}, k_{2z}\) and therefore \(a = c = b\). For these components \(M\) is given by

\[
M^{ab} = \delta^{ab} \left[ 1 - m^{a}(\omega)m^{a}(\omega - \Omega_{0}) \right] \quad a, b = 2, \ldots, 8
\]  

(51)

For the components \(a, b = 0, 1\) \(M\) reduces to a two by two matrix

\[
M = \begin{pmatrix}
1 - m^{1}(\omega)m^{0}(\omega - \Omega_{0}) & -m^{0}(\omega)\tilde{m}(\omega - \Omega_{0}) \\
-m^{0}(\omega)\tilde{m}(\omega - \Omega_{0}) & 1 - m^{1}(\omega)m^{1}(\omega - \Omega_{0}) \\
-\tilde{m}(\omega)m^{0}(\omega - \Omega_{0}) & m^{0}(\omega)\tilde{m}(\omega - \Omega_{0}) \\
-m^{1}(\omega)\tilde{m}(\omega - \Omega_{0}) & m^{1}(\omega)m^{1}(\omega - \Omega_{0})
\end{pmatrix}
\]  

(52)

In Eqs. (51) and (52) \(m(\omega)\) is given by

\[
m^{a}(\omega) = \sum_{k} G_{k}^{0}(\omega) (\gamma_{k}^{*})^{2} \quad a = 0, \ldots, 8
\]  

(53)

\[
\tilde{m}(\omega) = \sum_{k} G_{k}^{0}(\omega) (\gamma_{k}^{*})^{-1}
\]  

(54)

Thus we find that \(M\) is reducible to the different representations of the group of symmetry operations on an octahedron \(O_8\): \(a = 0, 1\) and \(a = 8\) stand for the one-dimensional representations \(A_1\) and \(A_2\) respectively, while \(a = 2, 3, 4\), and \(a = 5, 6, 7\), are the indices of triplet states \(T_1\) and \(T_2\).

Hence, the secular equation which generalizes Eq. (39) has the form (for \(\zeta \ll 1\))

\[
0 = \text{Det} M = [1 - m^{0}(\omega)m^{0}(\omega - \Omega_{0}) - 2m^{1}(\omega)m^{1}(\omega - \Omega_{0})] \\
\times \sum_{a=2}^{8} [1 - m^{a}(\omega)m^{a}(\omega - \Omega_{0})] \\
\times m^{A_1, T_1, T_2, A_2}(\omega) = w_1 \int_{-\pi}^{\pi} \frac{dk_x dk_y dk_z}{(2\pi)^3} \left(1 \pm \cos k_x\right) \left(1 \pm \cos k_y\right) \left(1 \pm \cos k_z\right)
\]  

(55)

Here the choice of three + signs corresponds to the \(A_1\) state, two + signs corresponds to the \(T_1\) triplet, two − signs corresponds to the \(T_2\) triplet and three − signs corresponds to the singlet \(A_2\). To study the analytical properties for small \(\omega < 0\), we use the fact that the dominant contribution to the integral comes from small values of \(k\). Near the bottom of conduction band \(E_2(k)\) the hybridization is strong, and the band is nearly flat [see Eq. (4)], so expanding the dispersion around the minimum at the bottom, \(E(k) \approx h^2k^2/2m^*\) in accordance with Eq. (4), we refer to the heavy effective mass of \(m^* \approx 100m_0\), observed experimentally \(48\). Then we find for small \(\omega < 0\),

\[
m^{0}(\omega) \approx \frac{w_0}{\epsilon_0} \left(-0.39 + \frac{1}{2\pi} \sqrt{\frac{2|\omega|}{\epsilon_0}} \right)
\]  

(57)

\[
m^{1}(\omega) \approx \frac{\zeta w_1}{\epsilon_0} \left(-1.31 + \frac{1}{2\pi} \sqrt{\frac{2|\omega|}{\epsilon_0}} \right)
\]  

(58)

\[
m^{T_1}(\omega) \approx \frac{\zeta w_1}{\epsilon_0} \left(-0.35 + 0.28 \frac{|\omega|}{\epsilon_0} \right)
\]  

(59)

\[
m^{T_2}(\omega) \approx \frac{\zeta w_1}{\epsilon_0} \left(-0.20 + 0.06 \frac{|\omega|}{\epsilon_0} \right)
\]  

(60)

\[
m^{A_2}(\omega) \approx \frac{\zeta w_1}{\epsilon_0} \left(-0.14 + 0.02 \frac{|\omega|}{\epsilon_0} \right)
\]  

(61)

where \(\epsilon_0 = h^2/a^2m^* \approx 5\text{meV}\). Solutions of Eq. (55) for the values of the parameters given in Fig. 3 yield no bound states for \(T_1, T_2\) and \(A_2\), so we conclude that the approximation \(W_{ef} \approx w_0\) for the potential \(42\) is sufficient for the description of the bound electron-exciton states.

\[1\] E.E. Vainstein, S.M. Blokhin, and Yu.B. Paderno, Sov. Phys. – Solid State 6, 281 (1965).

\[2\] P. Wachter, in: Handbook on the Physics and Chemistry of Rare Earths, ed. by K.A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam 1994), Vol. 19, p.177.

\[3\] I. Ba’tko, P. Farkašovský, K. Flachbart, E.S. Konovalova and Yu.B. Paderno, Solid State Commun. 88, 405
(1993); S. Gabáni, K. Flachbart, P. Farkašovský, V. Pavlík, I. Baťko, T. Herrmannsdörfer, E. Konovalova and Y. Paderno, Physica B 259-261, 345 (1999).

[4] J.C. Cooley, M.C. Aronson, Z. Fisk and P.C. Canfield, Phys. Rev. Lett. 74, 1629 (1995).

[5] N.E. Sluchanko, A.A. Volkov, V.V. Glushkov, B.P. Gorshunov, S.Y. Demishev, M.V. Kondrin, A.A. Pronin, N.A. Samarín, Y. Bruynseraede, V.V. Moshchalkov and S. Kunii, JETP 88, 533 (1999).

[6] G. Travaglini and P. Wachter, Phys. Rev. B 29, 893 (1984).

[7] H. Ohta, R. Tanaka, M. Motokawa, S. Kunii and T. Kasuya, J. Phys. Soc. Jpn, 60, 1361 (1991); T. Nanba, H. Ohta, M. Motokawa, S. Kimura, S. Kunii and T. Kasuya, Physica B 186-188, 440 (1993).

[8] M. Dressel B. Gorshunov, N. Sluchanko, A. Volkov, G. Knebel, A. Loidl and S. Kunii, Physica B 259-261, 377 (1999); B. Gorshunov, N. Sluchanko, A. Volkov, M. Dressel, G. Knebel, A. Loidl and S. Kunii, Phys. Rev. B 59, 1808 (1999).

[9] G. Güntherodt, W.A. Thompson, F. Holtzberg and Z. Fisk, Phys. Rev. Lett., 49, 1033 (1982).

[10] K.A. Kikoin, JETP 58, 582, (1983); J. Phys. C 17, 6771 (1984).

[11] P.A. Alekseev, A.S. Ivanov, B. Dorner, H. Schober, K.A. Kikoin, A.S. Mishchenko, V.N. Lazoruk, E.S. Konovalova, Yu.B. Paderno, A.Yu. Rumyantsev and I.P. Sadikov, Europhys. Lett. 10, 457 (1989); K.A. Kikoin and A.S. Mishchenko, J. Phys.: Cond. Mat. 3, 5937 (1991); K.A. Kikoin and A.S. Mishchenko, JETP 104, 3810 (1993).

[12] J. Neuenschwander and P. Wachter, Phys. Rev. B 41, 12693 (1990).

[13] D.P. Young, D. Hall, M.E. Torelli, Z. Fisk, J.L. Sarrao, J.D. Thompson, H.-R. Ott, S.B. Oseroff, R.G. Goodrich and R. Zysler, Nature 397, 412 (1999).

[14] M.E. Zhitomirsky, T.M. Rice and V.I. Anisimov, cond-mat/9904330; L. Balents and C.M. Varma, cond-mat/9906259; V. Barzykin and L.P. Gor’kov, cond-mat/9906401.

[15] F.C. Zhang and T.M. Rice, Phys. Rev. B 37, 3759 (1988).

[16] A. Hasegawa and A. Yanase, J. Phys.: Solid State Phys. 12, 5431 (1979).

[17] S. Massida, A. Continenza, T.M. de Pascale, and R. Monnier, Z. Phys. B 102, 83 (1997).

[18] H. Harima, O. Sakai, T. Kasuya and A. Yanase, Solid State Comm. 66, 603 (1988).

[19] A. Yanase and H. Harima, Progr. Theor. Phys., Suppl. No. 108, 19 (1992).

[20] R.M. Martin and J.W. Allen, J. Appl. Phys. 50, 7561 (1979).

[21] S.E. Barnes, J. Phys. F 6, 1375 (1976).

[22] K.A. Kikoin, Solid State Comm. 33, 323 (1980).

[23] K.W.H. Stevens, J. Phys. C: Solid State Phys. 11, 985 (1978).

[24] V.J. Emery, Phys. Rev. Lett. 58, 2794 (1987).

[25] V.I. Belinicher and A.L. Chernyshev, Phys. Rev. B 49, 9746 (1994).

[26] J.C. Nickerson, R.M. White, K.N. Lee, R. Bachman, T.H. Geballe and G.W. Hull, Phys. Rev. B 3, 2030 (1971).

[27] Y. Toyozawa, in Relaxation of Elementary Excitations, ed. by R. Kubo and E. Hanamura (Springer, Berlin 1980), p. 3.

[28] I.G. Lang and Yu.A. Firsov, Sov. Phys. – JETP 16, 1301 (1963).

[29] T. Kasuya, Europhys. Lett. 26, 277, 283 (1994).

[30] J.C. Cooley, M.C. Aronson, A. Lacerda, Z. Fisk, P.C. Canfield, and R.P. Guertin, Phys. Rev. B 52, 7322 (1995).

[31] T. Portengen, Th. Ostreich, and L.J. Sham, Phys. Rev. B 54, 17452 (1996).

[32] see K.A. Kikoin and A.S. Mishchenko, J. Phys.: Condens. Matter 7, 307 (1995) for more comments on the approach based on d-electron screening.

[33] B.I. Shklovskii and A.L. Efros, Electronic Properties of Doped Semiconductors (Springer, Berlin, 1984).

[34] C. Varma in Windsurfing the Fermi Sea, eds. T.T.S. Kuo and J. Speth (North-Holland, Amsterdam, 1987), p. 69.