SmB\(_6\): A material with anomalous energy distribution function of charge carriers?

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We argue that because of valence-fluctuation caused dynamical changes (fluctuations) of impurity energies in an impurity band of valence fluctuating semiconductors both occupied and unoccupied sites can be found in the impurity band above as well as below the Fermi level even in the ground state. As a consequence, the ground state energy distribution function of the subsystem of localized charge carriers for valence fluctuating semiconductors is qualitatively different than one for conventional semiconductors. 

Sm\(_{1-x}\)B\(_6\) is a prototypical mixed valence material revealing properties of a narrow-gap semiconductor down to few Kelvins. Paradoxically, at lowest temperatures its conductivity exhibits presence of a temperature non-activated term, which however, cannot be attributed to any scattering scenario known for metals, because very high value of corresponding residual resistivity would require superunitary scattering. According to Mott-Ioffe-Regel viewpoint, conventional resistivity would require superunitary scattering, namely (i) presence of valence fluctuations (VFs), (ii) existence of an impurity band (IB), and (iii) the Fermi level lying in the IB, are in agreement with theoretical studies of impurity states in mixed-valent materials, studies of electrodynamic properties of Sm\(_6\) in the low-frequency regime, optical conductivity studies of Sm\(_6\), and many other experimental observations reported for Sm\(_6\). As explained in [18], the energy of an impurity in the semiconductor with an IB that contains metallic ions in two different valency states can be a natural consequence of the changed EDF.

The second above mentioned approach is represented by the scenario of valence-fluctuation induced hopping transport that is applicable also to vacant Sm\(_6\)-based samples. The key assumptions of this scenario, namely (i) presence of valence fluctuations, (ii) existence of an impurity band, and (iii) the Fermi level lying in the IB, are in agreement with theoretical studies of impurity states in mixed-valent materials, studies of electrodynamic properties of Sm\(_6\) in the low-frequency regime, optical conductivity studies of Sm\(_6\), observation of presence of variable-range hopping transport in Sm\(_6\) at lowest temperatures, and many other experimental observations reported for Sm\(_6\). Because very high value of corresponding residual resistivity can shift under different conditions cause corresponding changes of the impurity energies and can be modeled by a rearrangement process (RP) with a characteristic time constant, \(t\) [18].

Thus, the energy \(E_i\) of the impurity \(i\) is not constant in time, but varies within some interval \([E_i, min, E_i, max]\) [18]. Therefore, if the Fermi level, \(E_F\), lies in the IB, there has to exist a subnetwork of impurities for which it is true that due to the RP some occupied impurity energy levels can shift from the region below \(E_F\) to the region above \(E_F\), and analogously, some empty levels from the region above \(E_F\) can shift under \(E_F\). This not only creates favorable conditions for temperature non-activated hops that are responsible for temperature non-activated transport, but also causes a change of energy distribution function (EDF) of charge carriers. It is the purpose of this work to point out that the EDF of localized charge carriers in the ground state of valence fluctuating semiconductors qualitatively differs from one expected for conventional semiconductors at \(T = 0\) K, and that the absence of low temperature resistivity divergence in (real) Sm\(_6\)-based samples containing lattice imperfections can be a natural consequence of the changed EDF.

According to the “quantum-limit” hopping formula, the intrinsic transition rate \(\gamma_{ij}\) for an electron hop-
ping from a site $i$ with energy $E_i$ to an empty site $j$ with energy $E_j$, in the simplest case, when $|E_j - E_i|$ is of the order of the Debye energy or smaller, and $kT$ is small compared to $|E_j - E_i|$, can be expressed as

$$\gamma_{ij} = \gamma_0 e^{-2\alpha R_{ij}} \frac{(E_j - E_i)/kT}{1 + \exp[(E_j - E_i)/kT]} \text{ for } E_j > E_i,$$  

$$\gamma_{ij} = \gamma_0 e^{-2\alpha R_{ij}} \text{ for } E_j < E_i,$$  

where $k$ is Boltzmann constant, $R_{ij}$ is the distance between sites $i$ and $j$, and $\gamma_0$ is a constant, which depends on the electron-phonon coupling strength, the phonon density of states, and other properties of the material, but which depends only weakly on the energies $E_i$ and $E_j$ or on $R_{ij}$. According to Eq. (2), the intrinsic transition rate of electron hop to a site of less energy decreases exponentially with increasing energy difference $R_{ij}$. However, because $\gamma_0$ is finite, $\gamma_{ij}$ must be also finite, so there is always non-zero time interval $t_h$ until an electron can hop (tunnel) to some empty site of less energy, while this time interval increases with increasing distance between the sites. If the RP (e.g., represented by VF) is the ground state property of a material, finite $\gamma_{ij}$ suggests a non-zero probability of finding some occupied energy levels above $E_F$ also in the ground state. In a conventional semiconductor (i.e., one without the RP) the time averaged occupation number of site $i$ in the thermal equilibrium (at neglecting electron-electron interactions except those causing that not more than one electron can occupy a single site) can be expressed in the form $(n_i) = 1/\{1 + \exp[(E_i - E_F)/kT]\}$, what for $T = 0$ K unconditionally means that all energy levels below $E_F$ are occupied and all energy levels above $E_F$ are empty. Thus, the above mentioned non-zero probability to find occupied energy levels above $E_F$ in the ground state implies that the ground-state EDF of the subsystem of localized charge carriers in materials with the RP is qualitatively different from the EDF in conventional semiconductors at $T = 0$ K. This fundamental conclusion we support by the following discussion.

According to the scenario of valence-fluctuation induced hopping transport, a hopping site $i$ can be characterized by an energy interval of the typical width $E_0 \approx E_{i,\text{max}} - E_{i,\text{min}}$ and by the partial DOS, $g_i(E)$, which is non-zero and constant within the interval $(E_{i,\text{min}}, E_{i,\text{max}})$ and zero outside it (see Fig. 1b). Let us moreover characterize the site $i$ by a time averaged probability of the occupation of this site by an electron, $p_i \in (0,1)$. Because time interval $t_h$ until the electron can hop (tunnel) to an empty site of less energy increases with increasing distance between the sites, at very low concentration of impurities, or in case of the RP with a very short $t_h$ (e.g., fast valence fluctuating process), it can be reasonably considered that $t_r << t_h$. This limit case practically means that electron occupies the state for sufficiently long time to receive any energy $E_i$ from the interval $(E_{i,\min}, E_{i,\max})$. We define the time averaged probability of the occupation of site $i$ by an electron, $p_i$, as the average value of the Fermi-Dirac distribution function (FDDF), $f_0(E_i, T) = 1/\{1 + \exp[(E_i - E_F)/kT]\}$, over the energy interval $(E_{i,\min}, E_{i,\max})$. Assuming that all energy intervals have the typical width $E_0$ (i.e., $E_0 \equiv E_{i,\max} - E_{i,\min}$), $p_i$ can be expressed in the form

$$p_i(E_i, T, E_0) = \frac{1}{E_0} \int_{E_{i,\min} - E_0/2}^{E_{i,\max} + E_0/2} f_0(E_i, T) dE_i,$$  

where $E_{i,c} = (E_{i,\min} + E_{i,\max})/2$. Fig. 1b shows $p_i$ as defined by Eq. (3) calculated for $T = 0$ K and for fixed parameter $E_0$. As can be seen, $p_i = 1$ for

$$E_{i,c} \leq E_F - E_0/2, \quad p_i = 0 \text{ for } E_{i,c} \geq E_F + E_0/2, \quad \text{and } p_i \text{ decreases linearly from } 1 \text{ to } 0 \text{ for } E_{i,c} \text{ in the interval } E_F - E_0/2 < E_{i,c} < E_F + E_0/2.$$  

According to the above mentioned, all impurity sites having $E_{i,c}$ in the energy interval $E - E_0/2 < E < E + E_0/2$ are overlapped at energy $E$, and contribute to the probability of occupation of the state at energy $E$ proportionally to $p_i(E_{i,c}, T, E_0)/E_0$. Thus we can determine the time averaged probability of occupation of the state at energy $E$ in the IB (i.e., the EDF) as

$$f^*(E, T, E_0) = \int_{E - E_0/2}^{E + E_0/2} \frac{p_i(E_{i,c}, T, E_0)}{E_0} dE_{i,c}.$$  

Analytical calculation of Eq. (4) for $T = 0$ K and for fixed $E_0$ gives

$$f^* = 1 \text{ for } E \leq E_F - E_0,$$  

$$f^* = -\frac{E^2 - 2E_0E + E_0^2}{2E_0^2} \text{ for } E_F - E_0 < E < E_F,$$  

$$f^* = \frac{E^2 - 2E_0E + E_0^2}{2E_0^2} \text{ for } E_F < E \leq E_F + E_0.$$  

FIG. 1: Schematic depiction of the partial DOS, $g_i(E)$, of the impurity center in the IB as introduced in [18] (a), time averaged probability $p_i$ of the occupation the site $i$ having its energy interval centered at $E_{i,c}$ (b), and a time averaged probability of occupation of the state at energy $E$ in the IB (c).
lence fluctuations (VFs). Approaching temperatures $T > T_c$ (than thermal broadening) the EDF of localized charge carriers will reflect energy broadening of an energy $E$ similar to temperature $T$ analogue as temperature enhanced to the value of $E_0/4kT$. Thus, $E_0$ can represent a “driving force” to minimize the total energy of the system. For instance, "tuning" of the processes associated with VFs (e.g. reasonable change of fluctuations in magnetic subsystem and the associated magnetic interactions/correlations) can yield such value of $E_0$ that the total energy will be minimized. Although at high temperatures ($T > T_c$) $E_0$ will practically not affect the $f^*(E,T,E_0)$, the influence of $E_0$ can become essential approaching temperatures close to $T_c$. As can be deduced from the above provided picture we would like to emphasize a “phase transition” to explain experimental results and emphasized the importance of re-considering “5 K anomaly” in context of modern topological physics of SmB$_6$.

Finally, we would like to emphasize that presented results enable to explain absence of resistivity divergence at lowest temperatures in both stoichiometric, as well as in vacant SmB$_6$ samples. The scenario of valence-fluctuation induced hopping transport [18] and its consequences discussed here shed new light onto observations associated with “5 K anomaly” by inferring possible existence of new phenomena “driven” by the subsystem of localized charge carriers, while all these phenomena can be considered simultaneously with possible presence of

FIG. 2: Plots of $f^*$ (solid lines) compared with FDDFs (dashed lines) for temperatures $T = 0$ K (black), $T = E_0/8k$ (blue), $T = E_0/4k$ (green) and $T = E_0/2k$ (red).

as depicted in Fig. 2. As follows from Eqs. (5-8), the $f^*(E,0 K,E_0)$ for $T = 0$ K is a continuous function with the finite slope $f^*(E,0 K,E_0)/\partial E = -1/E_0$ at the Fermi level. This represents a qualitative difference in comparison with FDDF, since $f^*(E,T)/\partial E = -1/4kT$ at $E_F$ (giving infinite slope for $T = 0$ K). Considering that the slope of the EDF at $E_F$ reflects energy broadening (either due to a non-zero temperature or due to the RP), both slopes can be compared yielding

$$E_0 \approx 4kT. \quad (9)$$

Fig. 2 shows numerically calculated plots of $f^*(E,T,E_0)$ for $T = 0$ K, $T = E_0/8k$, $T = E_0/4k$ and $T = E_0/2k$ compared with FDDFs calculated for the same temperatures. As can be seen, $f^*$ for $T = 0$ K strongly differs from the FDDF at $T = 0$ K, and can be much better approximated by the FDDF at the finite temperature $T = E_0/4k$. As can be deduced from the plots for $T = E_0/8k$, the EDF of the system with the RP can be at sufficiently low temperatures much better approximated by the FDDF at $T = E_0/4k$ than by the FDDF at real temperature of the system. Thus it seems that the RP at lowest temperatures affects the EDF analogously as temperature enhanced to the value of $E_0/4k$. In general, all $f^*$ curves have less (negative) slope at $E_F$ in comparison with the slope of the FDDF (at $E_F$) at the same temperature, resembling the effect of a temperature enhancement due to the RP.

We suppose that the energy broadening as discussed above (for $t_v << t_b$) can be adopted also to the case of SmB$_6$ because of the fast valence fluctuation rates in this material [31]. Deducing from Eqs. (5-8) and Fig. 2 at sufficiently high temperatures (where $E_0$ is much less than thermal broadening) the EDF of localized charge carriers in SmB$_6$ will be practically unaffected by valence fluctuations (VFs). Approaching temperatures $T \approx E_0/4k$ the EDF will exhibit essential deviation from the FDDF due to VFs, while at temperatures $T << E_0/4k$ the EDF will resemble the FDDF corresponding to significantly greater temperature, $T \approx E_0/4k$. Consequently, physical characteristics of SmB$_6$ that are governed by the EDF (e.g. electrical resistivity) will for $T \rightarrow 0$ K converge to those expected at a non-zero temperature, providing another reason for the absence of the resistivity divergence.
topologically protected or/and polarity-driven metallic surface states in SmB$_6$. We believe that our findings not only represent a base for understanding the underlying physics in valence fluctuating semiconducting compounds at lowest temperatures, but that they also indicate a necessity to consider similar phenomena in many other materials with "dynamical ground state", especially those obeying physical properties which cannot be adequately understood presumably supposing the ground state being associated with the FDDF for absolute zero.

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