A possible scenario of metallization in boron doped diamond CB_x

Yu.G. Pogorelov

CFP and Departamento de Física, Faculdade de Ciencias,
Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

V.M. Loktev

Bogolyubov Institute for Theoretical Physics, Metrologichna str. 14-b, Kiev, 03143 Ukraine

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Possibility for collectivization of acceptor states in a semiconductor, converting it to metal, is discussed within the scope of Anderson s-d hybride model. This model is generalized for multi-component band structure and composite acceptor states, localized on pairs of neighbor dopants (impurity “dumbbells”), in order to describe the boron doped diamond CB_x. The resulting parameters of band structure, in particular, position of the Fermi level, are compared to the recent experimental data on metallized and superconducting CB_x.

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Recent discovery of superconducting transition in boron doped diamond CB_x [1] brought a new attention to the problem of impurity induced metallization in semiconductors. This topic is already at the center of discussion on high-Tc metal-oxide perovskites (HTSC), where shallow acceptors by, e.g., divalent alcali earth substitutes A for trivalent lanthanum in La_{2-x}A_xCuO_4, give rise to metallic and superconducting state in basal CuO_2 planes at doping x above some critical level ∼ 5%. A description of this process on the basis of Lifshitz model of impurity states was proposed by the authors [2]. However the situation in CB_x differs from HTSC in essential aspects: diamond has an exemplary 3D isotropic (cubic) lattice structure [3] and B atoms at relevant doping levels (x ∼ 4%) mostly occupy interstitial positions in it [4],[5],[6],[7] where they nominally should stay neutral. Even at lower doping (x ≲ 0.5%), when they are mostly acceptor substitutes [8], it was already recognized that common effective mass approach does not apply for the deep 0.37 eV level by isolated acceptor [9] whereas the conductivity may result from the interplay between that and some “additional”, much more shallow levels (∼ 0.06 eV) by acceptor clusters [10].

This clustering effect should be even more important at higher doping, as seen from statistical weights of configurations around an interstitial impurity (Fig.1 at x = 4% (8% per diamond unit cell), reaching maximum ∼ 38% for its clusters with another impurity in one of 12 nearest neighbor interstices. The facts that carrier density still grows with doping and that energy would be gained when doped holes are spread around the pair of impurities by B-C covalency effects suggest that such clustered B interstitials (impurity “dumbbells”) also give rise to shallow acceptor levels, supposedly not described by effective mass, like those from clusters of substitutional impurities.

When choosing an adequate model for such perturbation of electronic spectrum, one have to rule out either the Mott metallization (since the effective Bohr radius is too small, ∼ 3 Å [11]) and the Lifshitz impurity model (which does not provide metallization in 3D doped systems [12]). Then the most natural choice is perhaps the Anderson s-d hybride model [13], where the possibility for metallization was studied long ago [14]. Here we try to adapt the latter results for the intriguing physics of doped diamond, leaving aside the issue of pairing mechanism in the metallized CB_x (discussed recently in RVB [11] or bond-stretching [15] scenarios).

FIG. 1: Unit cell of diamond (bigger circles for carbons) where boron dopants (dark circles) occupy an interstitial site at the center and one of 12 nearest neighbor interstices (dashed circles). The resulting impurity “dumbbell” has two acceptor levels, one of them, shallow antibonding, being of principal importance for metallization.

Referring to the well established theoretical band structure of pure diamond [3],[10] and recent ARPES measurement data [17], the analysis should concentrate around the top of the valence band (chosen as the energy reference). Here the three valence subbands have almost isotropic dispersion \( \varepsilon_{j,k} = - \hbar^2 k^2 / 2 m_j \) with effec-
tive masses $m_{1,2,3} \approx 2.12, 1.06, 0.7 m_e$ (neglecting a small spin-orbit splitting down by $\approx 6$ meV for $j = 2$). Considering the most relevant acceptor level $\varepsilon_i$ by impurity cluster, closely atop the valence band, and neglecting all other (much higher or/and much fewer) levels by clustered or isolated impurities, the corresponding generalization of hybride model can be presented by the Hamiltonian

$$H = \sum_{j,k} \varepsilon_{j,k} a_{j,k}^\dagger a_{j,k} + \sum_p \varepsilon_0 b_p^\dagger b_p + \frac{1}{\sqrt{N}} \sum_{j,k,p} \left( \gamma_j e^{i k \cdot p} a_{j,k}^\dagger b_p + h.c. \right), \quad (1)$$

where $N$ is the number of unit cells in crystal, $a_{j,k}$ and $b_p$ are the Fermi operators (spin indices suppressed) for excitations of $j$th subband and of impurity clusters (called simply impurities in what follows) randomly located at $p$ with concentration $c \approx x/2$ (per unit cell), and $\gamma_j$ is the constant of hybridization between them.[13]

The resulting spectrum generally includes either bandlike and localized states and, since each of $cN$ impurities provides one (hole) carrier to the system, the issue of metallization depends on whether the Fermi level $\varepsilon_F$ from the equation

$$c = \int_{\varepsilon_F}^{\infty} \rho(\varepsilon) d\varepsilon \quad (2)$$

lies within the domain of band states. The density of states (DOS, per unit cell) $\rho(\varepsilon) = N^{-1} \text{ImTr}(\varepsilon - H)^{-1}$ in the relevant basis of states for Eq.[1] $\{ |j,k\rangle, |p\rangle \}$ (ignoring the conduction band), is calculated through the respective diagonal Green functions.

Let’s begin supposing that only single (say, $1$st) subband is hybridized with impurity states: $\gamma_{2,3} = 0$, $\gamma_1 = \gamma \neq 0$ (comparison with an alternative choice $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$ will be done at the end), and obtain DOS as a sum of contributions from host (h) and impurity (i) subsystems:

$$\rho(\varepsilon) = \rho_h(\varepsilon) + \rho_i(\varepsilon),$$

$$\rho_h(\varepsilon) = \sqrt{\varepsilon - W_j = 3/2} + W_3 = 3/2 + \frac{1}{\pi N} \text{Im} \sum_k \frac{1}{\varepsilon - \varepsilon_{1,k} - \Sigma_k},$$

$$\rho_i(\varepsilon) = \frac{c}{\pi} \frac{1}{\varepsilon - \varepsilon_0 - \Sigma_i}.$$

Here $W_j = \pi^{1/3} h^2/(m_j v^2 / 3)$ ($v$ being the unit cell volume) is of the order of width of respective subband, whereas the self-energies $\Sigma_k$ and $\Sigma_i$ can be presented as expansions in groups of interacting impurities:[14]

$$\Sigma_k = \frac{c_\gamma^2}{\varepsilon - \varepsilon_0 - \Sigma_i} (1 + c B_k + \ldots)$$

and

$$\Sigma_i = \frac{\gamma^2}{N} \sum_k \frac{1}{\varepsilon - \varepsilon_{1,k} - \Sigma_k} (1 + c B_i + \ldots).$$

The relevant impurity level is defined by the equation $\varepsilon_i = \varepsilon_0 + \text{Re} \Sigma_i(\varepsilon_i)$ in the limit $c \to 0$, whereas the next terms after unity in the group expansions:

$$B_k = -A_{00} - A_{00}^2 + \sum_{n \neq 0} \frac{A_{0n}^2 e^{-i k \cdot n} + A_{0n}^2}{1 - A_{0n}^2},$$

$$B_i = -A_{00}^2 + \sum_{n \neq 0} \frac{A_{0n}^2 e^{i k \cdot n}}{1 - A_{0n}^2},$$

$$A_{0n} = \frac{\gamma^2}{N (\varepsilon - \varepsilon_0 - \Sigma_i)} \sum_k \frac{e^{i k \cdot n}}{\varepsilon - \varepsilon_{1,k} - \Sigma_k}$$

describe all indirect interactions between two impurities (in fact, two “dumbbells”) located at cells 0 and 0, via virtual excitations from 1st subband. The respective contribution to DOS from the states localized at such pairs of “dumbbells” follows from the formula:

$$\text{Im} \sum_n f_n/(1 - A_{0n}^2) \approx (\pi/v) \int \text{d} \delta (1 - \text{Re} A_{0n})$$

(for any real function $f_n$, and the concentration broadening $\Gamma_i$ of the impurity level $\varepsilon_i$ from the condition: $|\text{Re} A_{0n}(\varepsilon_i \pm \Gamma_i)| = 1$, where $\Gamma \sim (v/c)^{1/3}$ is the average distance between impurities.

We construct the solution by analogy with the case of donor impurity level $\varepsilon_i < 0$ hybridized to a single parabolic band $\varepsilon_k = h^2 k^2 / 2 m$.[13] There a qualitative restructuring of spectrum happens when the concentration $c$ surpasses the characteristic (supposedly small) value $c_0 \sim (\varepsilon_i/W)^{3/2}/4 \pi$, where $W = \pi^{4/3} h^2/(m v^2 / 3)$. In other words, the $\Gamma$ turns smaller of the localization radius $r_l \sim v^{1/3} / \sqrt{W/\varepsilon_i}$ and localized impurity states effectively overlap. If $c$ is also greater than other characteristic value $c_{cr} \sim (\gamma/W)^{6}$, this overlapping leads to formation of two separate bands of coherent extended states, whose structure depends on a specific relation between $c_0$ and $c_{cr}$. In particular, if the level $\varepsilon_i$ is so shallow that $\varepsilon_0 < c_{cr}$, the dispersion of two split bands is

$$\varepsilon_k \approx \frac{\varepsilon_k \pm \sqrt{\varepsilon_k^2 + 4 c r^2}}{2}, \quad (3)$$

for wave numbers $k$ restricted to $k \gtrsim k_{min} \sim (c_{cr}/v)^{1/3}$ for the upper band, $\varepsilon_+(k)$, and to $k_{min} \lessapprox k \lessapprox k_{max} \sim 1/\sqrt{7}$ for the lower band, $\varepsilon_-(k)$. These restrictions give estimates for the Mott mobility edges separating band and localized states: $\varepsilon_c \sim \varepsilon_+(k_{min}), \varepsilon_c \sim \varepsilon_-(k_{max}), \varepsilon_c' \sim \varepsilon_+(k_{min})$ (Fig. 2). Then it can be shown that the lower band only adopts $\sim N c^{3/4} r^{1/4}$ states, that is less than the total of $N c$ carriers. Hence the rest of carriers should occupy the “tail” states formed by interacting impurity pairs whose density is defined as

$$\rho_i(\varepsilon) \sim \frac{c^{3/2}}{\varepsilon^{1/2}} \text{Im} B_i \sim \frac{c^{2/8}}{W \varepsilon^{5/8}} \quad (4)$$

for $\varepsilon - \varepsilon_i \gg \Gamma_i \sim \varepsilon^{1/3} \gamma^2 / W$ and extends to the edge of the upper band. At $\varepsilon > \varepsilon_i(0)$, the DOS in this band $\rho_h(\varepsilon)$ is much higher than the “tail” function $\rho_i(\varepsilon)$, Eq.[1] so that the number of empty tail states above the Fermi
level approximately equals the number of hole carriers within the upper band:

$$\int_{\varepsilon_F}^{\infty} \rho_h(\varepsilon) d\varepsilon \approx \int_{\varepsilon_F}^{\varepsilon_F} \rho_h(\varepsilon) d\varepsilon.$$  \hspace{1cm} (5)$$

This gives the distance from the upper band edge to the Fermi energy: \(\varepsilon_F - \varepsilon_F(0) \approx \sqrt{c_G}\), which is \(\sqrt{c/c_{cr}}\) times bigger than the distance from this band edge to the mobility edge \(\sim c_{cr} W\). Therefore the system turns to be metal with the band structure as shown in Fig.2.

In the multicomponent valence band case defined by Eq.4 with \(\gamma_1 = \gamma\) and \(\gamma_2,3 \approx 0\), we obtain the same splitting as by Eq.3 for the 1 valence subband (within obvious inversion \(\varepsilon_+ \rightleftharpoons \varepsilon_-\)), but the essential difference from the situation in Fig.2 is that here the excess carriers can fill the two subbands, non-hybridized to impurities, resulting in the metallic state with the Fermi level below zero energy: \(-\varepsilon_F \sim (c - c^{3/4} c_{cr}^{1/4})^{2/3} W\), and two close regions of high occupation, as shown in Fig.3. These two regions can play the same role for the non-monotonic temperature dependence of conductivity as two activation energies, considered in the low doping regime. With tentative values \(\gamma \approx 1\) eV, \(\varepsilon_+ \approx 0.05\) eV, and \(W_1 \approx 3.5\) eV, we obtain from the above formulas: \(c_0 \approx 0.02\%\), \(c_{cr} \approx 0.15\%\), and for \(c \approx 2\%\) arrive at \(\varepsilon_F \approx 150\) meV. This value turns comparable to the splitting \(\sqrt{c_G}\) of the 1st subband and quite sufficient to accommodate possible superconducting gap \(2\Delta \approx 3.52 T_c \approx 0.6\) meV (for the reported \(T_c = 2.3\) K in CBx).

An alternative hybridization scheme, with \(\gamma_2,3 = \gamma\), will produce similar splitting of all three valence subbands, so that the total capacity of upper split bands (about triple of that for the single \(\varepsilon_-(k)\) band in Eq.3) will be most probably sufficient to accommodate the Fermi level at positive energies, as shown in Fig.5. The value of \(\varepsilon_+(0) - \varepsilon_F\) in the resulting conduction band should be comparable to the above estimate for \(|\varepsilon_F|\), but this single region of high occupation looks unlike for the above referred non-monotonic conductivity vs temperature, seen also in the metallized CBx. This favors to the former version of impurity preferential hybridization to a single valence subband.

In conclusion, we analyzed the specifics of impurity induced metallization in a version of Anderson s-d hybride model for multiband semiconductor and showed its difference compared to the simple single band case. The resulting split band structure with a relatively small Fermi surface of radius \(k_F \sim (c/v)^{1/3}\) near the Brillouin zone center also essentially differs from the non-split structures obtained in the simplest approximations of effective mass or virtual crystal. This difference can be verified experimentally, e.g., in the optical response at about 8 \(\mu m\). At least, the proposed metallic state in CBx can be further used to describe the superconducting transition in such doped system, which, regardless of the pairing mechanism (perhaps phonon-mediated), can be effectively enhanced due to multiband spectrum structure.

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