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THE INSULATING SIDE OF THE METAL-INSULATOR TRANSITION IN DOPED SEMICONDUCTORS

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Abstract. — The metal-insulator transition in doped semiconductors is discussed within the framework of a (Hartree-like) self-consistent variational method. This allows us to calculate the critical donor concentration by approaching, at \( T = 0 \), the first-order transition from its insulating side. We predict a large enhancement of the static dielectric constant at the transition and account for the vanishing of the \( \varepsilon_2 \) activation energy. Finally a thermodynamical analysis of the transition is outlined.

1. Introduction. — In doped semiconductors, the vanishing of the conductivity activation energy beyond a charged impurity concentration \( N_c \) has been early recognized as a case of metal-insulator (M-I) transition. Besides the important effect of disorder which arises from the random distribution of charged centers, the transition originates in the effect of correlations between carriers which reduce the potential of charged impurities and also in Coulombic interaction between species. The importance of correlations between free carriers — screening — has been emphasized [1]. When the M-I transition is approached from its metallic side (i.e. from the high impurity concentration), the ionized state of the system being taken as the ground state, one can show that decreasing the impurity concentration results in an instability of this metallic state because the impurity potential is no longer screened enough.

The aim of this paper is to stress the importance of correlations between bound carriers — polarization — which induce an instability of the insulating state of the system (i.e. all carriers being bound to charged impurities) when the impurity concentration increases: the M-I transition is then approached from its insulating side. We thus show, at \( T = 0 \), that the M-I transition appears as a first-order one and that, close to the transition on its insulating side, the static dielectric constant is strongly enhanced, a prediction which agrees with recent experimental results [2]. In addition, we will study the formation of the conducting excited state, made up of two carriers bound to the same impurity center (D\(^-\) state), and will discuss the relevance of this state to the understanding of the conduction process which is specified by the activation energy \( \varepsilon_2 \), in an intermediate range of impurity concentration and of temperature [3].

Finally, the understanding of the transition requires a thermodynamical study which in turn demands a comprehensive analysis, involving on an equal footing screening, polarization and interaction terms. The whole task will be carried out with the help of a (Hartree-like) self-consistent variational method.

2. Self-consistent variational method. — Our model [4] makes use of a set of uncompensated randomly distributed neutral hydrogenic donors embedded in a lattice of static dielectric constant \( \kappa \), at \( T = 0 \). We treat these donors within the effective mass approximation assuming a single isotropic conduction band.

The effective-mass equation to be solved is:

\[
\mathcal{K}\psi(r) = \left[ -\frac{\hbar^2}{2m^*} \mathcal{A}^2 + V^{\text{eff}}(r) + I(r) \right] \psi(r) = E\psi(r)
\]

\( \mathcal{K} \) includes the kinetic energy and two potential energy terms which describe interaction between the electron and its binding center \( V^{\text{eff}} \) and with other donors \( I \). The electron correlations are incorporated in \( V^{\text{eff}} = V^0 + \delta V \), where \( V^0(r) = -\frac{e^2}{kr} \) is the bare Coulomb potential and \( \delta V \) is induced by the response of both bound and free electrons to the potential \( V^0 \). Taking the insulating state as the ground state, we limit ourselves to the polarization...
contribution $\delta V^{(p)}$ to $\delta V$. We first estimate the wavevector-dependent polarizability $\alpha^{(q)}(q)$ of the $N$ non-interacting neutral donors

$$4 \pi N \alpha^0(q) = - \frac{4 \pi N e^2}{k q^2} \sum_{i=0}^{N} \left( | l \rangle \langle m | \right) \left| \begin{array}{c} f_i \cr \epsilon \cr f_m \end{array} \right\rangle \frac{E_i - E_m}{E_m - E_m}$$

(2)

where $| l \rangle$ and $| m \rangle$ are the eigenstates of (1), $E_i$ and $E_m$ the eigenvalues and $f_i$ and $f_m$ the Fermi occupation factors. The relation between the Fourier components of $V^0$ and $\delta V^{(p)}$ which defines the wave-vector-dependent dielectric constant $\epsilon^{(p)}(q)$ is then

$$\delta V^{(p)}(q) = \frac{1}{\epsilon^{(p)}(q)} - 1 = - \frac{4 \pi N \alpha^0(q)}{1 + \frac{8}{3} \pi N \alpha^0(q)}.$$

(3)

Expression (3) accounts [5] for dipolar interactions between neutral donors (Lorentz local-field corrections). We estimate the neutral donors interaction $I^{(p)}$ as

$$I^{(p)}(r) = N \int_{| r - R | > d} d^3 R \cdot i(r - R)$$

with

$$i(r - R) = - \frac{e^2}{\kappa} \left( \frac{1}{a} + \frac{1}{| r - R |} \right) \exp \left( - \frac{2 | r - R |}{a} \right)$$

where $a$ is the effective Bohr radius, $r$ and $R$ the electron and donor position vectors. We approximate the actual distribution of donors by a uniform background except a sphere of radius $d$ centered at the origin, $d = (6/\pi N)^{1/3}$.

To make the calculation consistent, we need not only the ground state solution of (1) but also the excited states solutions which enter the expression of $V^{eff}$ through (2) and (3). We take as trial wave functions a hydrogenic $1s$ function $\psi_{1s} = (\pi a_0^2)^{-1/2} \exp(-r/a)$ for the ground state and corresponding hydrogenic functions with the same parameter $a$ for the excited states $2s$, $2p$, etc... To a fair approximation, the summation in (2) can be limited to the first excited states $2s$ and $2p$. We find it convenient to introduce dimensionless quantities $x = a/a_0$, $\delta_{1s}(x) = E_{1s}(a)/\beta a_0$, $n = N/N_0$ and $\gamma = a_0 q$ where $a_0 = \hbar^2/m^* e^2$, $R = m^* e^2/\hbar^2$ and $N_0 = \pi^3/(4 a_0)^3$ depend only on the parameters $\kappa$ and $m^*$. Then from (1) we get [6] the variational energy to minimize:

$$\delta_{1s}(x) = \frac{1}{x^2} + \frac{1}{2 \pi^2} \int_{0}^{\infty} n_{1s}(-y) \times$$

$$\left[ \frac{V_0(y)}{\epsilon^{(p)}(y)} + I(y) \right] y^2 dy$$

(4)

where $n_{1s}(y)$ is the Fourier transform of $| \psi_{1s}(r) |^2$ and $V_0(y)$ and $I(y)$ those of $V^{(r)}/\beta a_0^3$ and $I(r)/\beta a_0^3$. To our approximation, (2) and (3) give

$$\frac{1}{\delta^{(p)}(y)} = 1 - \frac{8 \pi^2 n}{3} \sum_{s \geq 2} \frac{s_{2s}}{x_m} \times$$

$$\left[ \frac{(y^2 + \lambda^2)^{s}}{y^2 + s_{2s} \lambda^2 / p_2} + \frac{16 \pi^2 n}{9} \frac{s_{2s}}{x_m} \right]^{-1}$$

(5)

where $\lambda = 3/2 x_m^2$, $x_m$ is the value of $x$ which minimizes $\delta_{1s}(x)$ in (4) and $s_2 = \delta_{2s}(x_m) - \delta_{1s}(x_m)$.

3. Stability of the insulating side. — For a given value of the impurity concentration, we have to search for a minimum of $\delta_{1s}(x)$ occurring for a finite value $x_m$. In order to be associated to a stable state, this minimum must be lower than

$$\delta_{1s}(\infty) = - \frac{\pi^2}{48} n x_m^2$$

which corresponds to the extended state (uniform electron density) $\delta_{1s}(\infty)$ is the energy of the bottom of the conduction band.

The calculation is made self-consistent by an iterative procedure: initial (e. g. hydrogenic) values of $x_m$, $s_2$, and $p_2$ are inserted into (1), (2) and (3) to give a new set of parameters etc... Owing to the self-consistency requirement, the system of equations (1)-(3) may or may not possess a set of consistent solutions. Indeed, with our criterion, we find a stable ground state for $n < n_c$; $n_c$ defines the critical impurity concentration for the transition. We find $n_c = 0.61$...
or \( a_0 N_{i}^{1/3} = 0.21 \), a value which is close to the one obtained when the transition is approached from its metallic side [1, 6]: \( a_0 N_{i}^{1/3} \approx 0.25 \). Results of the calculation are plotted on figure 1 (a). We see that for \( n = n_i, \epsilon_{1s} \) is non-vanishing; this means that, within the framework of our model \( (T = 0, \) no disorder effect), the transition is a \textit{first-order} one. This results stems from the cooperative character of the polarization mechanism: the polarization term \( \delta V^{(p)} \) leads to a reduction of \( \epsilon_{1s} \) which in turn increases \( \delta V^{(0)} \). We emphasize the necessity to perform the variational calculations in a coherent way: a non self-consistent procedure would give not only a higher value of \( n \) but a second-order transition.

4. Dielectric-constant enhancement. — With the set of parameters \((x_m, \delta_2, p_2)\) used in the above discussion, one may calculate from (5) the static dielectric constant \( \epsilon(0) \) or the quantity \( C = (\epsilon(0) - 1)/(\epsilon(0) + 2) : \)

\[
C = \frac{2^{-13/2}}{3^{1/2}} \frac{x_m^2}{\epsilon_{2p} - \epsilon_{1s}} n. \tag{6}
\]

As \( n \) increases, we see (Fig. 1b) an increase of \( z(0) \) which is enhanced by a factor of about 3 at the transition. More precisely, plotting \( C \) as a function of \( n \), one finds for \( n \lesssim 0.3 \) an increase faster than the linear one predicted by the Clausius-Mossotti relation. Apart from the small variation of \( x_m \), a linear increase of \( C \) with \( n \) would follow from (6), assuming a constant energy denominator (or equivalently a constant polarisability \( a^0 \) in (2)); instead the energy difference decreases with \( n \), as illustrated in figure 2, leading to the non-linear increase of \( C \). The cooperative character of the transition mechanism \( s \) responsible for this behaviour and also for the fact that \( \epsilon(0) \) does not diverge at the transition in contradistinction to the divergence associated with a continuous transition [7].

Our result agrees with a recent experimental study [2] of the static dielectric constant for P-, As- and Sb- doped Si, at concentrations lower than but close to the critical concentration for the transition. These measurements have been performed at the limit of vanishing frequency and extrapolated down to the lowest temperatures to avoid any (real) excitation of carriers. They show a marked deviation from the Clausius-Mossotti relation with just a threefold increase of \( \epsilon(0) \) at the transition. Although our model is not readily applicable here, owing to the non-hydrogenic character of donors in P-, As- and Sb- doped Si, these data give a strong support to our theory.

5. \( D^- \) state formation and \( \epsilon_{1s} \) vanishing. — Using our variational method and keeping the insulating state as the ground state, we may characterize the \( D^- \) excited state. To estimate the variational energy \( \epsilon_D \), of the system of two electrons in the singlet state, we take as trial wave function a product of one-electron-wave functions \( \phi(r) = (\pi b^3)^{-1/2} \exp(\ -r/b) / \), then in reduced units

\[
\epsilon_D = -\frac{2 \pi}{\bar{z}} \int_0^\infty \left[ m(y) \ -\frac{1}{2} \int_0^\infty \left| \frac{\phi(y)}{\epsilon_D^{(0)}} \right|^2 y^2 dy \right] dy
\]

where \( m(y) \) is the Fourier transform of \( | \phi(r) |^2 \) and \( z = b/a_0 \). In (7), the first term corresponds to the kinetic energy of the two electrons, the second to the interaction of both electrons with the charged center and with neutral donors and the third term describes the interaction between the two electrons. In a one-electron diagram, we plot as a function of donor concentration (Fig. 3) the energy \( \epsilon_{1s}, \) of the first electron bound to the donor center (ground state) and that \( (\epsilon_D - \epsilon_{1s}) \) of the second electron bound to the same center (excited state). The difference of these two energies corresponds to the intradonor correlation energy \( U, \) \( U = \epsilon_D - 2 \epsilon_{1s} \). At the limit of vanishing concentration, the variational calculation gives the standard values \( b = 1.455 \) \( a_0 \) and \( \epsilon_D = -0.945 \) \( \text{eV} \). We then use elementary tight binding formulation to describe the formation of the bands \( D^0 \) and \( D^- \) which are associated with the first and the second bound states. We define two transfer integrals:

\[
T^0(R) = \langle \psi_{1s}(r) | V_{eff}(r) + J(r) | \psi_{1s}(r - R) \rangle \tag{8}
\]

\[
T^-(R) = \langle \phi(r) | V_{eff}(r) + J(r) | \phi(r - R) \rangle
\]
where, as for \( V^{\text{eff}} \), \( L^{\text{eff}} = L^0 + \delta L \) and

\[
L^0(r) = -\frac{e^2}{\kappa} \left( \frac{1}{b} + \frac{1}{r} \right) \exp(-2r/b)
\]

is the potential due to both the charged center and the other bound electron. To the first approximation, the bandwidths \( W^0 \) and \( W^- \) (in reduced units) are then

\[
W^0 \simeq 2 \frac{N}{\mathcal{M}} \int_{|\mathbf{R}^0| \geq \delta} d^3 R T^0(\mathbf{R}) .
\]

It is worth pointing out that the wave functions and effective potentials in (8) are those deduced from the variational calculation; the bandwidth estimate thus fully incorporates the effect of electron-electron correlations. From (8) and (9), we have calculated the bandwidths \( W^0 \) and \( W^- \) as a function of donor concentration. In the one-electron diagram (Fig. 3) are plotted the position of band extrema. These results correspond to the scheme of closure of an effective gap between two bands, separated by the correlation energy (Mott-Hubbard scheme). The above calculation shows that this closure does take place for a donor concentration close to the critical value \( n_\text{c} \). However the underlying assumption is that the insulating state itself remains stable; the formation of an effective gap is a consequence of the very existence of the insulating state, so that the gap closure cannot be taken as a M-I transition criterion. This point was not apparent in the discussion of the Hubbard Hamiltonian given by Berggren [11] in which the possibility of a ground-state instability was ruled out because only intraatomic correlations were taken into consideration.

Should we identify the conducting activation energy \( \varepsilon_2 \) to the effective gap between \( D^0 \) and \( D^- \) bands and the activation energy \( \varepsilon_1 \) to the energy difference between the bottom of conduction band and the top of \( D^- \) band

\[
\left( \varepsilon_{1s}(\infty) - \varepsilon_{1s} - \frac{W^0}{2} \right),
\]

we would see that, in agreement with experiments [8, 9, 10], \( \varepsilon_2 \) strongly decreases as \( n \) increases and tends to vanish near \( n_\text{c} \), whereas \( \varepsilon_1 \) remains finite [9]. We likewise understand from figure 3 why \( \varepsilon_2 \) has been observed only in a restricted donor concentration range near \( n_\text{c} \). Our calculation differs from the Berggren’s one [11] in that accounting explicitly for interdonor-electron correlations, we get (i) a value of intradonor correlation energy \( U \) which decreases when \( n \) increases and (ii) unequal values of bandwidths \( W^0 \) and \( W^- \).

A more detailed discussion of the \( D^0 \) and \( D^- \) impurity-band properties will be given elsewhere.

6. Thermodynamical analysis of the M-I transition. — Up to now, we have limited ourselves to discuss the stability of the insulating ground state at \( T = 0 \). In order to fully describe the phase transition and to discuss the finite temperature situation, we have to estimate the free energy of both insulating and conducting subsystems which are specified by the concentrations \( n_b \) and \( n_t \) of bound and free carriers, taking into account the mutual interactions. The free energy of the whole system has then to be minimized with respect to \( n_T \) where

\[
n_T = \frac{n_T}{n_b + n_t}.
\]

This method which is an extension of the one proposed by Falicov and Kimball [12] brings out that the activation energy of \( n_T \) is in general distinct from the binding energy of the localized state. To this end, one needs to calculate the effective potential of the binding center including the response of both bound and free carriers:

\[
V^{\text{eff}}(q) = \frac{V^0(q)}{e^{\delta q(q)} + e^{\delta q(q)} - 1}
\]

where \( e^{\delta q(q)} \) is the polarization term given by (3) and where the screening term \( e^{\delta q(q)} \) is obtained from an expression like (2) in which the eigenstates are conduction band states. In the same way, one needs to calculate all terms like \( J(r) \) in (1), which describe the various interactions between species (neutral and ionized donors).

Taking all the above terms into consideration enables us to solve the paradox raised by Prest and Pettengill [13] who had stated that the self-consistency conditions prevent the occurrence of the transition in a simple screening model. More generally the
thermodynamical analysis becomes possible only once it is realized that the transition takes place between a plasma-like system of carriers correlated to charged impurities and a neutral system made up of polarizable and interacting atom-like species.

7. Conclusion. — To summarize, we have analyzed the M-I transition in doped semiconductors using a method which gives due consideration to correlations between both free and bound carriers and to interactions. This method enables us to describe the transition approached from its insulating side as well as from its metallic side to predict some phenomena which are observed in the neighbourhood of the transition — namely the dielectric-constant enhancement and the \( \varepsilon_2 \) vanishing — and ultimately to outline a thermodynamical analysis of the transition. Our method may be extended in particular to account for the effect of disorder or of exchange or to describe more complex electronic structures.

Note added in proof: An accurate description of the D\(^-\) state requires a more complex wave function than the one we have used, especially to calculate the binding energy (see e.g. Bethe, H. and Salpeter, E., in *Handbuch der Physik*, vol. 35 (Springer Verlag, Berlin) 1957, p. 240). We do not believe however that the use of a better wave function would strongly modify the bandwidth \( W^- \), so that the conclusions of our § 5 are essentially unchanged.

References