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DENSITY OF STATES IN THE GAP, CONNECTED WITH DIPOLE DEFECTS IN THE CHALCOGENIDE VITREOUS SEMICONDUCTORS

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It is shown, that defects with significant dipole moments, which has been found out as a result of quantum chemical modeling of the chalcogenide glassy semiconductors (CGS), give rise to a tail of density of states, slowly falling down deep into the gap. Under some conditions, the exact type of the energy spectrum of the charge carriers is determined in the frame of a potential that describes a dipole field at large distances.

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1. Introduction

Any deviations of the structure of glassy semiconductors from the structure of the appropriate crystals result in the occurrence of states in the gap. In chalcogenide glassy semiconductors the distribution of states in the gap exhibits features specific to discrete [1-3] spectra, and quasi-continuous one [4-6]. As follows from the analysis of the dependence of mobility and conductivity on the electrical field in As_2Se_3 the existence of smooth distribution upon energy of the states near to edges of a valence band is possible. From the analysis of the hole mobility it results the existence of energy levels situated at 0.45 eV from the edge of the valency band.

The nature of these states is not quite clear. It is supposed that local defects, which are related to the changes of chemical bond and coordination, form, as a rule, states, deeply laying in a gap, with enough precisely fixed energy forming a discrete spectrum. In turn, fluctuation in bond lengts, valency and torsion angles results in the formation of gap states, whose density N (E) falls down deep into gap and is characterized by a quasicontinuous spectrum.

However, the local defect, too, in case its geometry is accompanied by significant fluctuations of potential, can form group of the states, distributed enough deep in a gap, and near to the edges of a valence band and conductivity, thus forming a spectrum.

As shown by quantum chemical modeling above mentioned [7], some defects in CGS exhibit significant dipole momentum, which can play a role in the potential fluctuation. Though the quantum chemical modeling allows to define the characteristics only of the levels deeply laying in a gap, the research of fine levels with significant radius of localization by this method is not possible due to the necessity to use large size clusters. The task to define the energy levels E_n of an electron in a dipole field by numerical methods was solved in [8]. Although the dependences E_n on distance between charges that form the dipole were obtained, the kind of density of states of electron in a dipole field is not clear. In [9], the expression for an electron spectrum in the potential $V(r)=-\alpha/r^2$ in quasi-classical approximation $\{E_n = E_0 \exp(-\frac{1}{\lambda} 2\pi n)\}$ was obtained and the wave function corresponding to the exact resolving of the wave equation in such potential was found.

In the present paper is described in dipole approach the analytical solving of the problem of the density of states of the free electron with the effective mass m which moves in a medium with the

permittivity ε, in the dipole field. The equation for E_n, and under some conditions the true type of function N (E) were obtained.

2. The problem

The potential energy of interaction of electrons with two charges is defined by the expression $V_{\text{int}} = -\frac{qe}{\varepsilon r_+} + \frac{qe}{\varepsilon r_-}$, where $r_- = r + d/2$, $r_+ = r - d/2$ and d is the distance between charges. Under the condition $|r| >> |d|$ $V_{\text{int}} \cong -\frac{qe\, dgr}{\varepsilon r^3} = -u(r)$, where $u(r)$ is the part of potential, dependent only on distance, ϑ is the angle between dipoles and r is the vector directed to electron (see figs. 1 and 2).

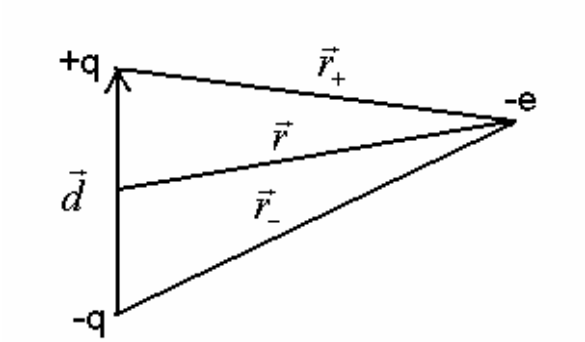

Fig. 1.

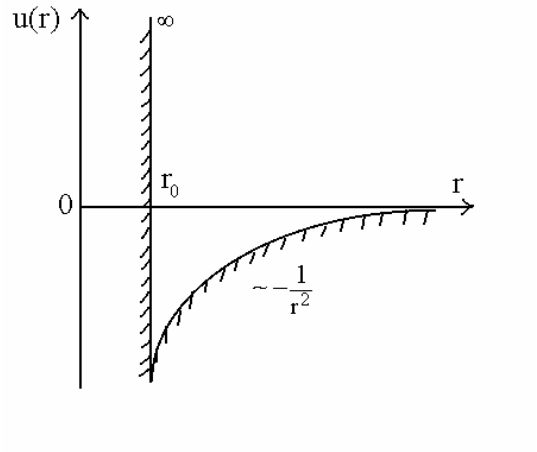

Fig. 2.

For $\alpha_1 = \frac{qe\ d}{\varepsilon}$ the Schrödinger equation for the electron in the model potential for $r>r_0$ is:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2}\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\frac{\partial \psi}{\partial \vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 \psi}{\partial \varphi^2}\right) + \left(\frac{2mE}{\hbar^2} + \frac{2m\alpha_1\cos\vartheta}{\hbar^2 r^2}\right)\psi = 0 \qquad (1)$$

Let us now introduce $\alpha = \frac{2m\alpha_1}{\hbar^2}$ and $E_1 = \frac{2mE}{\hbar^2}$ and express the wave function as the product of an angular and radial part $\psi(\vec{r}) = R(r)\Phi(\vartheta,\varphi)$ where $\Phi(\vartheta,\varphi)$ satisfies to the equation

$$(-\hat{L}^2 + \alpha\cos\vartheta)\Phi(\vartheta,\varphi) = \beta\Phi(\vartheta,\varphi) \tag{2}$$

$\hat{L}^2$ is the operator of a square of the kinetic moment.β represent the values of the angular part of the hamiltonian. The equation for the radial part of the wave function looks as follows

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + \frac{\beta R}{r^2} + E_1 R = 0 \tag{3}$$

3. The solution for the angular part of the Schrödinger's equation

By operating the substitution $x = \cos\vartheta$, $x \in [-1;1]$, the equation (2) can be written as:

$$\left(1 - x^2\right)y'' - 2xy' + \alpha xy = \beta y \tag{4}$$

The following type of solution of the equation (4) can be expressed as a sum of Legendre polynomial:

$$y(x) = \sum_n C_n P_n(x) \tag{5}$$

where $P_n(x)$ satisfies the equation

$$(1-x^2)P_n'' - 2xP_n' = -n(n+1)P_n \tag{6}$$

After substituting (5) in (4), with the consideration of (6) the following recurrent expression for C_n is obtained:

$$C_n\left(\beta + n(n+1)\right) = \alpha\left[\frac{nC_{n-1}}{2n-1} + \frac{(n+1)C_{n+1}}{2n+3}\right], \text{ for } \quad n > 1 \tag{7}$$

where $C_1 = \frac{3\beta C_0}{2\alpha}$

Besides should be satisfied the normalization condition:

$$\sum_{n=1}^{\infty}\left|C_n\right|^2 = 1\cdot \tag{8}$$

At large n the expression (7) can be simplified:

$$C_n n^2 = \alpha\left[\frac{C_{n-1}}{2} + \frac{C_{n+1}}{2}\right] \tag{9}$$

The Taylor formula will be applied:

$$C_{n\pm1} = C_n \pm C_n' + (1/2)C_n'' + \ldots \tag{10}$$

And as a result we shall get

$$C_n'' - \frac{n^2}{\alpha} C_n = 0 \tag{11}$$

The solution of (11) is the function

$$C_n = \sqrt{n}\left[A_1 I_{\frac{1}{4}}\left(\frac{n^2}{2\sqrt{\alpha}}\right) + A_2 K_{\frac{1}{4}}\left(\frac{n^2}{2\sqrt{\alpha}}\right)\right] \tag{12}$$

where *I* and *K* are the modified Bessels functions. Because the condition of convergence to infinite is satisfied only by *K*, finally is obtained the expression for C_n at large *n*:

$$C_n = \sqrt{n} A_2 K_{\frac{1}{4}}\left(\frac{n^2}{2\sqrt{\alpha}}\right) \approx A_2\sqrt{\frac{\pi}{2}}\exp\left(-\frac{n^2}{2\sqrt{\alpha}}\right) \tag{13}$$

In order to find the equation for β, it is necessary to multiply (4) by y^* and make the integration.

Taking into consideration the relations (5) and (7) the equation for β will be:

$$-\sum_n |C_n|^2 \frac{2n(n+1)}{2n+1} + \alpha\sum_n |C_n|^2 \frac{2}{2n+1}(\beta + (n+1)n) = \beta \tag{14}$$

Then, one obtains

$$(\alpha-1)\sum_{n=0}^{\infty} |C_n|^2 \frac{2n(n+1)}{2n+1} + \alpha\beta\sum_{n=0}^{\infty} |C_n|^2 \frac{2}{2n+1} = \beta \tag{15}$$

Let's define:

$$\begin{aligned} A &= \sum_{n=0}^{\infty} |C_n|^2 \frac{2n(n+1)}{2n+1} \\ B &= \sum_{n=0}^{\infty} |C_n|^2 \frac{2}{2n+1} \end{aligned} \tag{16}$$

From (10) and (11) one gets:

$$\beta = \frac{(\alpha-1)A}{1-\alpha B} \tag{17}$$

From here follows, that at $\alpha = 1$ $\beta = 0$. We must stress, that *B* cannot take in any case values more than 2, then $\alpha < \frac{1}{2}$ $\beta < 0$. Most likely, β becomes negative already at $\alpha < 1$.

Let's consider an opportunity for the existence of positive β.
In case the basic contribution to the sum in (15) is provided by the terms with large *n*, the relation (15) can be simplified:

$$(\alpha-1)\sum_n n|C_n|^2 = \beta \tag{18}$$

or

$$(\alpha-1)\int_0^{\infty} x A_2^2 K_{\frac{1}{4}}^2\left(\frac{x^2}{2\sqrt{\alpha}}\right) dx = \beta \tag{19}$$

If the basic contribution to the integral (19) is produced at large x, it is possible to use the asymptotic development (13). In this case one gets:

$$\beta = (\alpha - 1) A_2^{\,2} \sqrt{\alpha} \tag{20}$$

The relation (20) holds if the maximum of the expression

$$x \exp(-\frac{x^2}{2\sqrt{\alpha}})$$

is achieved at $x >> 1$, That is possible only at $\sqrt[4]{\alpha} >> 1$. For this reason the expression (20) hardly can be used for a numerical estimation of β in the real CGS.

Thus we have obtained, that, in every case, for large values α exist positive β values. It is possible, however to assume from (17), that β becomes positive already at $\alpha > 1$, as follows from (16), that $B < 1$ if C_0 is not abnormally large in comparison with other C_n. It is possible to check up directly, using ratio (7) that this condition is fulfilled at $\alpha \approx 1$ and small β.

4. The solution for the radial part of the Schrödinger's equation

It is known, that the solution of the equation

$$x^2 y'' + x y' + (x^2 - \nu^2) y = 0 \tag{21}$$

are the Bessels functions $J_\nu(x)$, and $Y_\nu(x)$

$$J_\nu(x) = \sum_{k=0}^{\infty} \frac{(-1)^k (x)^{2k}}{k! \Gamma(\nu + k + 1) 2^{2k}} \left(\frac{x}{2}\right)^\nu, \quad Y_\nu(x) = \left(\frac{J_\nu(x)\cos(\pi\nu) - J_{-\nu}(x)}{\sin(\pi\nu)} \right), \tag{22}$$

where

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt \text{ is the } \Gamma \text{ - function} \tag{23}$$

By substituting $x \rightarrow ix$ the equation (20) becomes

$$x^2 y'' + x y' + (-x^2 - \nu^2) y = 0 \tag{24}$$

The solution of (3) will be the functions

$$I_\nu(x) = \frac{J_\nu(ix)}{i^\nu} \qquad \text{and} \qquad K_\nu(x), \tag{25}$$

$$K_\nu(x) = \frac{\pi}{2} \left(\frac{I_{-\nu}(x) - I_\nu(x)}{\sin(\pi\nu)} \right) \tag{26}$$

Let's write the radial part of the Schrödinger's equation (3) as

$$r^2 R'' + 2 r R' + (-|\beta| - |E_1| r^2) R = 0 \tag{27}$$

where $R'' = \frac{\partial^2 R}{\partial r^2}$, $R' = \frac{\partial R}{\partial r}$

Let's make the following substitution:

$$R = \frac{R_1}{\sqrt{r}} \tag{28}$$

After transformations we shall get the equation

$$r^2 R_1'' + r R_1' + (-(\frac{1}{4} - |\beta|) - |E_1| r^2) R = 0 \tag{29}$$

It follows, that the solution (21) is the combination of the following kind

$$R(r) = \frac{1}{\sqrt{r}} (C_1 I_\nu(\sqrt{|E_1|} r) + C_2 K_\nu(\sqrt{|E_1|} r)) \quad \text{, where } \nu = \frac{1}{2}\sqrt{1 - 4|\beta|}$$

.

Let's consider the case of real order, i.e. *Im(ν)=0,*

This condition is fulfilled when:

$$|\beta| \le \frac{1}{4}. \tag{30}$$

The asymptotic functions I_ν and K_ν for large *r* are $I_\nu = \frac{e^r}{\sqrt{2\pi r}}$ and $K_\nu = \sqrt{\frac{\pi}{2r}} e^{-r}$. From these follows that in the solution of the equation must contribute only the K_ν function because I_ν does not fulfil the infinite limit condition. It is also necessary to satisfy the condition $K_\nu(\sqrt{|E_1|} r_0) = 0$ which represents the definition equation for E_{1n}. From the type of function K_ν it follows that $\sqrt{|E_1|} r_0 \approx 1$. For the exacter answer the numerical solution is necessary.

The order of Bessel function will be imaginary:

Now let us discuss the case $|\beta| > \frac{1}{4}$, $\nu = i\frac{1}{2}\sqrt{4|\beta| - 1} = i\lambda$ *Im (λ)=0.* (31)

Because the asymptote to infinity does not depend on ν, we shall consider only K_ν*:*

$$K_\nu(\sqrt{|E_1|} r) = \frac{\pi}{2\sin(i\pi\lambda)} \sum_{k=0}^{\infty} \left(\frac{\sqrt{|E_1|} r}{2}\right)^{2k} \frac{1}{k!} \left(\left(\frac{\sqrt{|E_1|} r}{2}\right)^{-i\lambda} \frac{1}{\Gamma(-i\lambda + k + 1)} - \left(\frac{\sqrt{|E_1|} r}{2}\right)^{i\lambda} \frac{1}{\Gamma(i\lambda + k + 1)} \right) \tag{32}$$

At small *r* from all sum it is meaningful to consider only the term with *k = 0. As Γ(1+iz) = izΓ(iz),*one gets

$$K_\nu(\sqrt{|E_1|} r \to 0) = -\frac{\pi}{2\sin(i\pi\lambda)} \left(\left(\frac{\sqrt{|E_1|} r}{2}\right)^{-i\lambda} \frac{1}{i\lambda\Gamma(-i\lambda)} + \left(\frac{\sqrt{|E_1|} r}{2}\right)^{i\lambda} \frac{1}{i\lambda\Gamma(i\lambda)} \right) \tag{33}$$

Further, we shall take into account the following equalities for Γ function:

$$\Gamma(i\lambda) = \mathrm{Re}(\Gamma(i\lambda)) + i\,\mathrm{Im}(\Gamma(i\lambda)) \tag{34}$$

$$\Gamma(-i\lambda) = \mathrm{Re}(\Gamma(i\lambda)) - i\,\mathrm{Im}(\Gamma(i\lambda)) \tag{35}$$

By using the representation

$$x^{i\lambda} = i\sin(\lambda \ln x) + \cos(\lambda \ln x) \tag{36}$$

One gets:

$$K_\nu(\sqrt{|E_1|}r) \square \frac{\pi i(\mathrm{Re}(\Gamma(i\lambda))\cos(\lambda\ln((\sqrt{|E_1|}r)/2)) + \mathrm{Im}(\Gamma(i\lambda))\sin(\lambda\ln((\sqrt{|E_1|}r)/2))))}{\sin(i\pi\lambda)(\mathrm{Re}^2(\Gamma(i\lambda)) + \mathrm{Im}^2(\Gamma(i\lambda))} \tag{37}$$

From the condition of equality to zero of K_ν in $r = r_0$, where the potential becomes infinite, is obtained the equation for the energy spectrum of the electron in the model potential.

$$\mathrm{Re}(\Gamma(i\lambda))\cos(\lambda\ln((\sqrt{|E_1|}r_0)/2)) + \mathrm{Im}(\Gamma(i\lambda))\sin(\lambda\ln((\sqrt{|E_1|}r_0)/2))) = 0 \tag{38}$$

From this equation, one obtains

$$E_{1n} = \frac{4}{r_0^2}\exp(\frac{1}{\lambda}(-arctg\left(\frac{\mathrm{Re}(\Gamma(i\lambda))}{\mathrm{Im}(\Gamma(i\lambda)}\right) - 2\pi n) \tag{39}$$

The similar expression is obtained in [9] in quasi-classical approximation.

Let us consider the equation (39) for low values of the argument in the Γ function. In this case is valid the following representation, which can be obtained from [10] by maintaining in the developing series only the first order terms.

$$\Gamma(i\lambda) = -\frac{i}{\lambda}\sqrt{\frac{\pi\lambda}{\sin(\pi\lambda)}}\exp(i(0,42 - arctg(\lambda))) \tag{40}$$

Further, if $i\lambda << 1$,

$$E_{1n} = \frac{4}{r_0^2}\exp\left(\frac{1}{\lambda}(0.84\lambda - 2arctg\lambda - 2\pi n)\right) \tag{41}$$

From (40) it follows, that the expression for N (E) will take the form:

$$N(E_n - E_{c(v)}) = \frac{\lambda}{\pi|E_n - E_{c(v)}|} \tag{42}$$

where $E_{c(v)}$ is the edge of the conduction band (valence band).

5. Discussion and conclusion

The expressions for E_n (19) and N(E) (20) are very important. Energy of the ground state, $E_{10}\frac{4}{r_0^2}\exp(-0.58)$, obtained from (40) (we shall remind, that $\lambda \to 0$) is not realistic, if it is not satisfied the condition $\sqrt{|E_1|}r \to 0$.

However, already at $n = 1$ the required condition is observed, and it is possible to use (40) and (41). $\lambda \to 0$ means what β should not strongly exceed 1/4, that means in turn, that α should not

exceed much the value 1. By substituting the fundamental constants, we get $\alpha \cong \frac{5m^*}{\varepsilon m}\mu$, where μ is the dipole moment (Debye) and $\frac{m^*}{m}$ is the ratio of the effective mass of the charge carrier to the electron mass. For CGS typical values of ε are situated in the range 5 - 10, and m^* is lower than m and, therefore, μ should be rather large, in order to appear the states with the density described by the expression (41). So, according to the results of quantum chemical modeling [7], in GeS_2 are formed defects of hypervalent configuration with $\mu \leq 20$ D, that satisfies to a condition of occurrence of such states. One observes that around $\mu \sim 20$D, β can exceed significantly 1/4 and, therefore, the density of states can differ from that given by (41). In this case we must return again to (38) for getting N (E).

Thus, the local defect having significant dipole moment, can appear as a local level caused by change in the character of chemical bond, and, also, as a group of states close to $E_{c(v)}$, with rather wide distribution upon energy, because (41) is a slowly falling down function. This can explain the appearance in the experiment of features characteristic both to discrete and continuous states in the gap.

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