ELECTRICAL DC CONDUCTIVITY OF AMORPHOUS SEMICONDUCTORS BY QUASICLASSICAL APPROXIMATION

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The quasiclassical model for the energy spectrum of an electron with randomly shifted bands in a randon potential is suggested. On the basis of this model the expression for dc conductivity is derived. The theoretical results are compared with experimental ones obtained on some chalcogenide glasses and on amorphous Ge and Si.

ЭЛЕКТРОПРОВОДИМОСТЬ АМОРФНЫХ ПОЛУПРОВОДНИКОВ ПРИ ПОСТОЯННОМ НАПРЯЖЕНИИ В КВАЗИКЛАССИЧЕСКОМ ПРИБЛИЖЕНИИ

Рассматривается квазиклассическая модель для энергетического спектра электрона со случайно сдвинутыми зонами уровней энергии в случайном потенциале. На основе этой модели получено выражение для удельной электропроводимости. Проводится сравнение теоретических результатов с экспериментальными данными о халькогенных стёклах и аморфных германии и кремнии.

I. INTRODUCTION

In our recent paper [1] one possible approach to the calculation of the density of states of an electron in a random potential was presented. Starting from the assumption that a one-particle potential can be written as

$$U(\boldsymbol{r}) = U_k(\boldsymbol{r}) + U_p(\boldsymbol{r}) , \tag{1}$$

where $U_k(\boldsymbol{r})$ is a periodical function and $U_p(\boldsymbol{r})$ is a stationary random function (defined by a multigaussian distribution function), the quasiclassical density of states as well as the first and the second quantum-mechanical corrections have been calculated. The results numerically obtained show that in certain ranges of dispersion of the random potential η and the correlation lenght L quantum-mechanical corrections can be ignored. This conclusion is the starting point in the present paper, in which the quasiclassical model with randomly shifted bands is suggested and the expression for dc conductivity is derived. The theoretical results are compared with experimental results obtained on some chalcogenide glasses and on amorphous Ge and Si.

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II. MODEL WITH RANDOMLY SHIFTED BANDS

The density of states is given by the relation

$$g(E) = \frac{1}{2\pi \mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{e}^{\beta E} Z(\beta)\, \mathrm{d}\beta \quad \gamma > 0 . \tag{2}$$

With respect to the above conclusion the statistical sum $Z(\beta)$ is written in a quasiclassical form:

$$Z_0(\beta) = \frac{1}{(2\pi)^3} \iint \exp\left(-\beta[E_n(\boldsymbol{k}) + U_p(\boldsymbol{r})]\right) \mathrm{d}\boldsymbol{k}\mathrm{d}\boldsymbol{r} . \tag{3}$$

Thus the local density of states (per unit volume) we can write

$$g(E) = \lim_{V\to\infty} \frac{1}{V} \frac{1}{2\pi \mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{e}^{\beta E} \frac{1}{(2\pi)^3} \iint \exp\left(-\beta[E_n(\boldsymbol{k}) + U_p(\boldsymbol{r})]\right) \mathrm{d}\boldsymbol{k}\mathrm{d}\boldsymbol{r}\mathrm{d}\beta = \tag{4}$$

$$= \frac{1}{2\pi \mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{e}^{\beta E} \frac{1}{(2\pi)^3} \int \exp^{\left(-\beta[E_n(\boldsymbol{k}) + U_p(\boldsymbol{r})]\right)} \mathrm{d}\boldsymbol{k}\mathrm{d}\beta .$$

For a Gaussian distribution of potential, its mean value is

$$\langle g(E)\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{e}^{-\xi^2/2} \frac{1}{2\pi \mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \mathrm{e}^{\beta E} \frac{1}{(2\pi)^3} \times \tag{5}$$

$$\times \int \exp\left(-\beta[E_n(\boldsymbol{k}) + \eta\xi]\right) \mathrm{d}\boldsymbol{k}\mathrm{d}\beta\, \mathrm{d}\xi .$$

This mathematical formulation implies the following interpretation: For every value of the parameter ξ the expression represents the energy of an electron. Thus, for all values of the wave vector $\boldsymbol{k}$ a band is obtained which is shifted from the "crystalline" band by a value of $\xi\eta$. Such a band is formed with a probability equal to $\frac{1}{\sqrt{2\pi}} \mathrm{e}^{-\xi^2/2}$. We wish to point out that all such states are delocalized, and their dynamics in external or some additional (due to the differencies between ideal and real crystals) fields is similar to the dynamics of the Bloch electron. In principle, in a non crystalline matter some localized states can be formed, too. However, their existence can be proved by a precise use of quantum mechanics only. From this

point of view the quasiclassical approximation is very rough; however, it still can provide some basic informations about the nature of non-crystalline matter.

III. DC ELECTRICAL CONDUCTIVITY

For the calculation of the dc electrical conductivity we start from the model of mutually shifted bands. In the following it is important to realize that the dynamics of an electron is taken similar to that of the Bloch electron.

After applying the effective mass approximation, the conductivity tensor for one kind of carriers can be obtained from the solution of the Boltzmann equation:

$$\bar{\sigma} = -\frac{e^2}{4\pi^3} \int \frac{h^2}{m^{*2}} \boldsymbol{k}\boldsymbol{k}\, \tau(\boldsymbol{k}) \frac{\partial f_0}{\partial E} \mathrm{d}\boldsymbol{k} \,. \tag{6}$$

Here, f_0 denotes the Fermi distribution function.

If the relaxation constant does not depend on the direction of $\boldsymbol{k}$, the relation (6) can be simplified:

$$\sigma = -\frac{16\pi e^2 \sqrt{2m^*}}{3h^3} \int e^{3/2} \tau(\boldsymbol{k}) \frac{\partial f_0}{\partial E} \mathrm{d}\varepsilon \,, \tag{7}$$

where $\varepsilon = \frac{1}{2}\dfrac{(\hbar k)^2}{m^*}$.

In our case, it is $E = E_0 + \varepsilon + \eta\xi$, thus

$$\frac{\partial f_0}{\partial E} = \int_{-\infty}^{\infty} \frac{\partial f_0}{\partial Z}\, \delta(z - E_0 - \varepsilon - \xi\eta)\, \mathrm{d}z \,.$$

After expressing the delta function in integral form, the relation (7) yields

$$\sigma = -\frac{16\pi e^2 \sqrt{2m^*}}{3h^3} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \frac{1}{2\pi\mathrm{i}} \iint \mathrm{e}^{\beta z} \frac{\partial f_0}{\partial z}\, \epsilon^{3/2} \tau(\epsilon) \exp[- \beta(E_0 + \varepsilon + \xi\eta)]\, \mathrm{d}\epsilon\, \mathrm{d}z\, \mathrm{d}\beta \,. \tag{8}$$

The formula (8) represents a conductivity corresponding to a band shifted by $\eta\xi$ from the "crystalline" edge of the forbidden band with the energy E_0.

The mean conductivity is obtained after averaging with respect to ξ

$$\sigma = -\frac{16\pi e^2 \sqrt{2m^*}}{3h^3} \frac{1}{2\pi\mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \int_{-\infty}^{\infty} \int_0^{\infty} \mathrm{e}^{\beta z} \frac{\partial f_0}{\partial z} \exp[-\beta(E_0 - \varepsilon) + \eta^2\beta^2/2] \times \tag{9}$$

$$\times\, \varepsilon^{3/2} \tau(\varepsilon)\, \mathrm{d}z\, \mathrm{d}\varepsilon\, \mathrm{d}\beta \,.$$

This can be calculated only if we know the dominant scattering mechanism and the related relaxation constant. One should here realize that so far only the ideal non-crystalline state has been studied. However, in the real case some additional defects, which cause scattering, are present. For illustration, we shall further consider two types of scattering: scattering on charged centres, and scattering on acoustical phonons, the relaxation constant being $\tau_c = \tau_0^c \varepsilon^{3/2}$ and $\tau_F = \tau_0^F \varepsilon^{-1/2}$, respectively.

Let us denote

$$\langle \varepsilon^r \rangle = -\frac{16\pi^2 e^2 \sqrt{2m^*}}{3h^3} \frac{1}{2\pi\mathrm{i}} \int_{\gamma-\mathrm{i}\infty}^{\gamma+\mathrm{i}\infty} \int_{\infty}^{\infty} \mathrm{e}^{\beta z} \frac{\partial f_0}{\partial z} \exp[-\beta E_0 + \eta^2\beta^2/2] \times \tag{10}$$

$$\times \int_0^{\infty} \varepsilon^{3/2+r}\, \mathrm{e}^{-\beta\varepsilon}\, \mathrm{d}\varepsilon\, \mathrm{d}z\, \mathrm{d}\beta \,.$$

After performing integration over β, the relation (10) can be rewritten as

$$\langle \varepsilon^r \rangle = \frac{16\pi e^2 \sqrt{2m^*}}{3h^3} \frac{2\Gamma(r + 5/2)}{\sqrt{2\pi}\,\eta} (kT)^{r+5/2} \int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2 u^2\right] \times \tag{11}$$

$$\times\, \mathscr{F}_{r+1/2}\left(u - \frac{E_0 - E_F}{kT}\right) \mathrm{d}u \,,$$

where

$$\mathscr{F}_v(v) = \frac{1}{\Gamma(v+1)} \int_0^{\infty} \frac{x^v}{1 + \mathrm{e}^{x-v}}\, \mathrm{d}x \,.$$

When taking the relaxation constant in the form $\tau(\varepsilon) = \tau_0 \varepsilon^r$, the mean conductivity is

$$\langle \sigma \rangle = \tau_0 \langle \varepsilon^r \rangle \,. \tag{12}$$

For carriers scattered on acoustical phonons the relation (12) becomes

$$\langle \sigma \rangle = \frac{16\pi e^2 \sqrt{2m}}{3h^3} \frac{2}{\sqrt{2\pi\eta}} (kT)^2 \int_{-\infty}^{\infty} \exp[-1/2(kT/\eta)^2 u^2]\, \mathscr{F}_0\left(u - \frac{E_0 - E_F}{kT}\right) \mathrm{d}u \,. \tag{13}$$

The summation of electron and hole contributions yields the total conductivity

$$\langle \sigma^F \rangle = \frac{32\sqrt{\pi e^2}}{3h^3}\frac{(kT)^2}{\eta}\int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2 u^2\right]\left[\tau_{oe}^F \sqrt{m_e^*}\,\mathscr{F}_0\left(u-\frac{\Delta E}{2kT}-\frac{\delta E}{kT}\right)+\right. \tag{14}$$

$$\left. + \tau_{op}^F \sqrt{m_p^*}\,\mathscr{F}_0\left(u-\frac{\Delta E}{2kT}+\frac{\delta E}{kT}\right)\right] \mathrm{d}u\,,$$

where $\Delta E = E_c - E_v$, $\delta E = \Delta E/2 - (E_c - E_F)$.

Analogically, for scattering on charged centres one obtains:

$$\langle \sigma^c \rangle = \frac{64\sqrt{\pi}\,e^2}{h^3}\frac{(kT)^4}{\eta}\int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2 u^2\right]\left[\tau_{oc}^c \sqrt{m_e^*}\,\mathscr{F}_2\left(u-\frac{\Delta E}{2kT}-\frac{\delta E}{kT}\right)+\right. \tag{15}$$

$$\left. + \tau_{op}^c \sqrt{m_p^*}\,\mathscr{F}_2\left(u-\frac{\Delta E}{2kT}+\frac{\delta E}{kT}\right)\right] \mathrm{d}u\,.$$

For a full determination of conductivity we must know the temperature dependence of the Fermi level shift $\delta E = \delta E(T)$. It can be determined from the electrical neutrality condition

$$n = p\,. \tag{16}$$

The concentration of electrons — n and holes — p can be calculated from the density of states (5), using again the effective mass approximation:

$$n = \pi m_p^{*3/2}\left(\frac{kT}{h^2}\right)^{5/2}\int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2 u^2\right] \mathrm{F}_{1/2}\left(u-\frac{\Delta E}{2kT}+\frac{\delta E}{kT}\right) \mathrm{d}u\,, \tag{17}$$

$$p = \pi m_p^{*3/2}\left(\frac{kT}{h^2}\right)^{5/2}\int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2 u^2\right] \mathrm{F}_{1/2}\left(u-\frac{\Delta E}{2kT}+\frac{\delta E}{kT}\right) \mathrm{d}u\,. \tag{18}$$

Putting (17) and (18) into (16) an equation for δE is obtained:

$$\int_{-\infty}^{\infty} \exp\left[-\tfrac{1}{2}\left(\frac{kT}{\eta}\right)^2\right]\left\{m_e^{*3/2}\,\mathscr{F}_{1/2}\left(u-\frac{\Delta E}{2kT}-\frac{\delta E}{kT}\right)-\right. \tag{19}$$

$$\left. - m_p^{*3/2}\,\mathscr{F}_{1/2}\left(u-\frac{\Delta E}{2kT}+\frac{\delta E}{kT}\right)\right\} \mathrm{d}u = 0\,.$$

IV. NUMERICAL ANALYSIS AND DISCUSSION

The expressions (14), (15) were numerically evaluated, using the temperature dependence of the Fermi level shift $\delta E = \delta E(T)$ numerically calculated (from

(19)), too. In Figs. 1 and 2 the families of $\ln\sigma$ vs $1/T$ curves for both types of scattering are shown. No essential qualitative differences were obtained when the ratios m_e^*/m_p^* and τ_{oe}/τ_{op} were varied within the interval 0.1—5. Figs. 1 and 2 yield a qualitative conclusion that in the high temperature region the conductivity approaches the values corresponding to some fictitious crystalline state characterized by the one-particle potential U_k. For small values of η and high temperatures the temperature dependence of conductivity gives practically a constant thermal activation energy (estimated as $d\ln\sigma/d\,(1/T)$) over a wide range of temperature. Some small deviations at low temperatures should be observed. The "intrinsic" behaviour of dc conductivity through the whole measured temperature range is shown by most chalcogenide glasses (they are reviewed in [2]). Some small deviations from the straight line (in $\ln\sigma$ vs $1/T$ plot) at low temperatures are evident, e. g. from the experimental results obtained on amorphous As_2Te_3 [3], on glasses $CdTl_xAs_2$ and $DcGe_xAs_2$ [4]. For a fixed value of temperature the value of

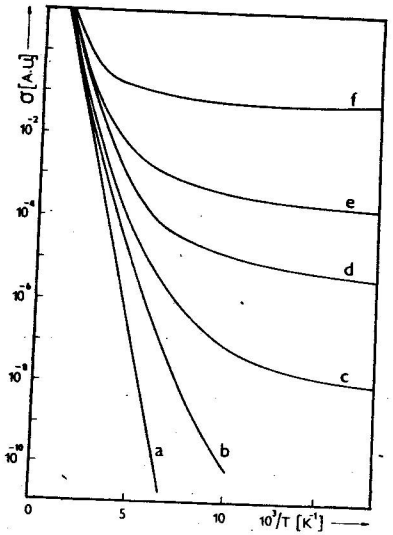

Fig. 1. The electrical dc conductivity vs $1/T$ for scattering on acoustical phonons, using various values of parameters η and $E = 0.8$ eV. The curves (a) to (f) were calculated (from 14) for the following values of η : 0.01, 0.05, 0.06, 0.07, 0.08 and 0.1 eV.

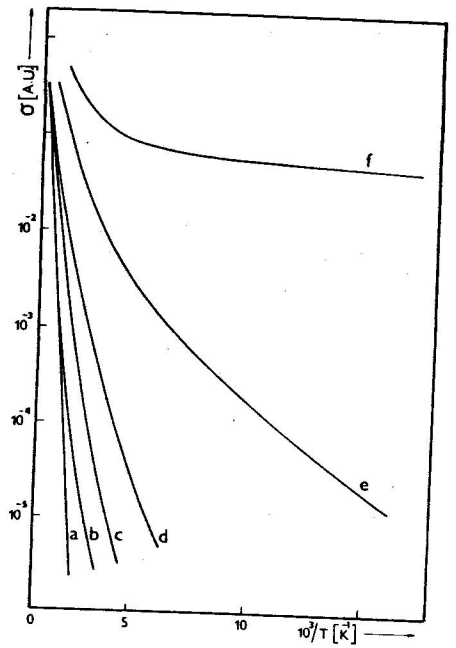

Fig. 2. The electrical dc conductivity vs $1/T$ for scattering on charged centres using various parameters η and $E = 0.8$ eV. The curves (a) to (f) were calculated (from (15)) for the following values of η : 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 eV.

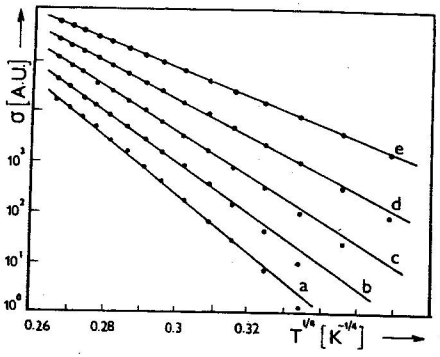

Fig. 3. The electrical dc conductivity vs $T^{-1/4}$ for scattering on charged centres at low temperatures for different values of η ((a) — 0.062 eV, (b) — 0.064 eV, (c) — 0.066 eV, (d) — 0.068 eV, (e) — 0.07 eV). The numerical computations were carried out with the parameters $\Delta E = 1.1$ eV, $m_p^*/m_e^* = 3$, $\tau_{op}/\tau_{oe} = 1$.

effective activation energy increases with decreasing η, whereas the conductivity decreases. Assuming that the decrease in η is due to annealing, these facts are in a qualitative agreement with the experimental results obtained on some chalcogenide glasses [5—7]. Annealing treatment on amorphous Ge and Si [8—10] gives also such a display of conductivity curves as in Figs. 1, 2. For a given value of η and of other parameters a certain low temperature exists, in which the theoretical results behave like $\sigma \sim \exp(T_0/T)^{1/4}$ with $T_0 \in 7 \times 10^6 \div 10^8$ K. Such behaviour is generally observed on amorphous Si and Ge [8—12]. However, some principal problems arise if one would attempt to interpret these experimental results within the framework of our simple model. Neglecting quantum-mechanical corrections the states in the gap are delocalized. On the other hand, the $T^{-1/4}$ law was proposed by Mott [13], who assumed the model of hopping electrons between the localized states near the Fermi level. On the idea of localized states near the Fermi level other more rigorous theoretical approaches are based, too (e. g. [14, 15]). The experimental results in papers mentioned above are interpreted in this sense. The simultaneous measurements of dc conductivity and ESR at various annealing stages show a good correspondence if the ESR spectra are interpreted in the sense of localized states near the Fermi level [16]. Consequently we feel that the interpretation of low temperature dc conductivity of amorphous Ge and Si on the basis of our simple model is somewhat schematical. But a qualitative agreement between the model and the experimental results indicates that experimental observation of the $T^{-1/4}$ law only does not provide sufficient evidence for localized states near the Fermi level.

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Received May 19th, 1977