MODELS OF OPTICAL ABSORPTION IN AMORPHOUS SEMICONDUCTORS AT THE ABSORPTION EDGE — A REVIEW AND RE-EVALUATION*)

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Davis-Mott and Tauc models of optical absorption at the absorption edge in the high absorption coefficient region ($\alpha \geq 10^4 \mathrm{cm}^{-1}$) are carefully reviewed with regard to their theoretical foundations, assumptions, mathematical derivations, and results. The full implications of these models are exploited, and it is found that the Davis-Mott model for negligible matrix elements between localised states could account for the cubic power law behaviour of α with photon energy $\hbar\omega$ of some amorphous semiconductors such as a-Si. A fractional power law to find the optical band gap E_{opt}, of the form $[\alpha\hbar\omega \propto (\hbar\omega - E_{\mathrm{opt}})^r; 2 \leq r \leq 3]$ based on Davis-Mott model is proposed in which the index r can be a function of disorder. The Tauc model has further been extended to the case of negligible matrix elements between localised states, in which the same square power law for α vs. $\hbar\omega$ with the same meaning of the optical gap as in the original Tauc model has resulted. A consideration of the case of unequal matrix elements for those transitions between localised states and those between extended states is also included. The meaning of E_{opt} has been re-assessed and it is emphasized that it is an extrapolation of delocalised states to the zero of the density of states rather than a threshold energy for the onset of some kind of optical transitions.

1. Introduction

The optical energy gap, E_{opt} is one of the most important physical parameters in semiconductors, which is usually deduced from the absorption spectrum of the material at the absorption edge; where more or less a rapid rise in the absorption coefficient α with increasing photon energy $\hbar\omega$ occurs in a narrow range of photon energies.

In crystals, it is established that $\alpha(\omega)$ at angular frequency of radiation ω, obeys a simple power law of the form [1]

$$\alpha = C(\hbar\omega - E_{\mathrm{opt}})^r, \tag{1}$$

where r is an index characterising the type of optical transition, it is equal to $1/2$ for direct allowed transitions and 2 for indirect allowed transitions, C is a constant, and E_{opt} is the optical energy gap.

Theoretical models can predict most successfully the behaviour of α with $\hbar\omega$ in crystals, so that there is no confusion concerning the physical meaning of E_{opt}

*) This paper is cordially dedicated to Professor C. A. Hogarth who taught us the Physics of amorphous materials.

deduced from experiment; it is a well-defined threshold energy characterising a real gap in the density of states, and its determination is very crucial to any opto-electronic application of crystalline semiconductors.

In amorphous semiconductors the situation is on shaky grounds, there is a confusion in interpreting optical absorption data at the absorption edge, because there is no well established theoretical model, due to the complexity of the behaviour of electrons in disordered structures.

Althought it is assumed as in crystals, that α obeys a simple power law of the form

$$\alpha\hbar\omega = B(\hbar\omega - E_{\mathrm{opt}})^r. \tag{2}$$

It is somewhat an empirical equation, because it is not based on a firm theoretical model, consequently E_{opt} deduced experimentally is somewhat a vague parameter that has no clear physical meaning, but its variation with preparation conditions, temperature, pressure, etc. conveys a good deal of information about the material of interest [2].

The two major models used to interpret the optical absorption behaviour at the absorption edge in the high absorption region ($\alpha \geq 10^4\mathrm{cm}^{-1}$) in amorphous semiconductors are Tauc [3] and Davis-Mott [4] models.

In this paper, these models are reviewed with respect to their theoretical foundations, assumptions, mathematical derivations, results, and most importantly their full implications have been exploited, where some new conclusions are drawn which may elucidate our understanding of the meaning of E_{opt} according to these models, and may offer us some alternative interpretations of the observed experimental results.

2. Theoretical foundations

All models of optical absorption in semiconductors are based on the Kubo-Greenwood formula for the real part of the frequency dependent electrical conductivity [5], which in amorphous semiconductors is [6]

$$\mathrm{Re}\,\sigma(\omega) = \frac{2\pi e^2\hbar^3\Omega}{m^2}\int N(E)N(E+\hbar\omega)|D|^2\mathrm{d}E/\hbar\omega, \tag{3}$$

where $N(E)$ and $N(E+\hbar\omega)$ are the densities of initial and final states, respectively, $|D|^2$ is the square of the matrix element of the operator $\partial/\partial x$, m the electron mass, and Ω the specimen volume. The integral is calculated over all pairs of initial and final states separated by an energy $\hbar\omega$.

The absorption coefficient $\alpha(\omega)$ is defined in terms of Re $\sigma(\omega)$ by the following relation from electromagnetic theory

$$\alpha(\omega) = \frac{4\pi}{n(\omega)c}\mathrm{Re}\,\sigma(\omega), \tag{4}$$

where $n(\omega)$ is the refractive index of the material. Substituting Eq. 3 into Eq. 4, we obtain

$$\alpha(\omega) = \frac{8\pi^2 e^2 \hbar^3 \Omega}{n(\omega) c m^2} \int N(E) N(E + \hbar\omega) |D|^2 \mathrm{d}E / \hbar\omega. \tag{5}$$

The form of Eq. 5 implies that optical transitions should conserve energy through the convolution of state densities by $\hbar\omega$, but these transitions need not conserve momentum as in crystals, because in disordered solids the uncertainty in the wave vector Δk is of the order of the wave vector itself, so $\vec{k}$-conservation selection rule is relaxed at least at the band edges, and k is not a good quantum number. These transitions are called non-direct, they are in fact direct transitions, but non-vertical and not accompanied by phonon emission or absorption to conserve k as in crystals.

Any modeling effort of interband optical absorption in amorphous semiconductors implies making reasonable assumptions about the functional dependence of $N(E)$ and D on energy E in the region of interest, in order to solve the integral of Eq. 5; which are in these materials neither justified by firm theoretical grounding nor by reliable experimental findings. Therefore, these assumptions are usually based on plausibility arguments or extensions from crystalline theories, and the validity of these assumptions is decided by the degree of fit between theory and experiment with respect to the dependence of α on $\hbar\omega$ (Eq. 2), which has a degree of ambiguity as we shall see.

3. Tauc and Davis-Mott models

There is no fundamental difference between Tauc and Davis-Mott models except for the proposed density of states distributions, so we shall adopt a unified representation.

Figure 1 depicts the density of states distribution according to Mott-CFO model [7]. Three types of optical transitions may contribute to interband absorption, as shown in Fig. 1: (1) transitions between initial and final localised states, (2) transitions between initial localised (extended) and final extended (localised) states, and (3) transitions between initial and final extended states.

The matrix elements for these transitions are related to the spatial overlap between initial and final states wavefunctions. Davis and Mott [4] showed that the matrix elements for transitions between extended states (type 3), and those between weakly localised states and extended states (type 2) have the same value, based on the argument that the enhancement of the normalisation factor of the wave function due to localisation is exactly cancelled by the random phase contribution of all local sites wave functions to the matrix element D, such that it keeps the value of D constant, and is equal to $\pi\sqrt{a/\Omega}$, where a is the average interatomic spacing. Hindley [8] showed that this equivalence comes from his random phase model, so that no break in $\alpha(\omega)$ spectrum occurs at the mobility gap, provided that the one electron approximation is valid and there is no electron-phonon coupling, which is rather doubtful for localised states, but we think that the contribution of electron-electron correlation and electron-phonon coupling may be negligible for

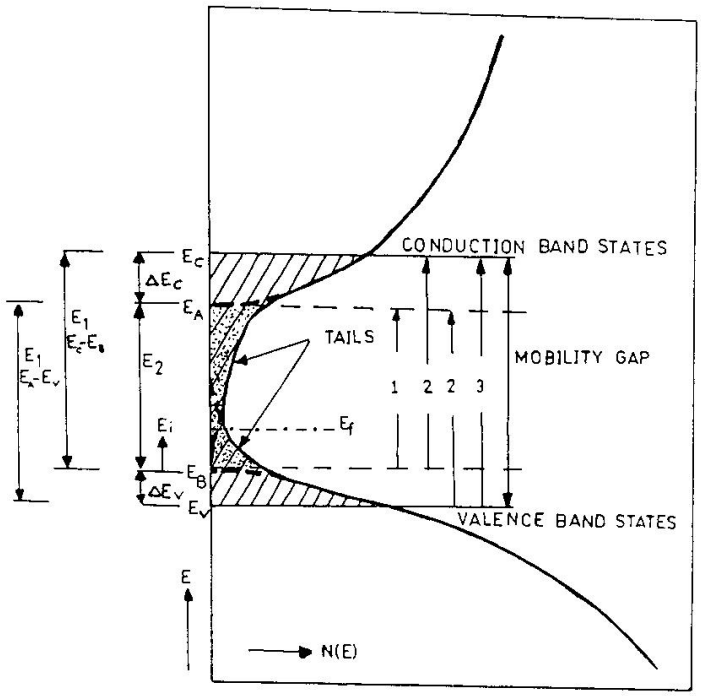

Fig. 1. Density of states $N(E)$ as a function of energy E in amorphous semiconductors according to the Mott-CFO model: *1*, *2*, and *3* are the three possible types of optical transitions, E_1 is the optical gap when $D_{\mathrm{loc}} = 0$, and E_2 is the optical gap when $D_{\mathrm{loc}} = D_{\mathrm{ext}}$, ΔE_c and ΔE_v are the band tails due to disorder.

weakly-localised states which may justify Davis-Mott argument.

Equation 5 becomes now as follows

$$\alpha(\omega) = \frac{8\pi^4 e^2 \hbar^3 a}{n(\omega) C m^2} \int N(E) N(E + \hbar\omega) \mathrm{d}E/\hbar\omega. \tag{6}$$

For transitions between localised states (type 1), two alternative assumptions are usually made, (a) the matrix elements for localised-localised transitions, D_{loc} are equal to the matrix elements for the other two types, D_{ext}, and (b) $D_{\mathrm{loc}} = 0$.

Davis and Mott [4] argued that it is more plausible to neglect all transitions in which both the initial and final states are localised on the argument that in the same region of space there will be little chance of finding a localised state derived from both the valence and condution bands. In their model they used both alternative assumptions, whereas Tauc [3] used only the assumption that all transitions are of equal probability.

These alternative assumptions will affect the way the optical energy gap is de-

fined; it will be equal to $E_A - E_B$, if $D_{ext} = D_{loc}$, and to $E_c - E_B$ or $E_A - E_v$ which-ever is smaller, if $D_{loc} = 0$ (Fig. 1), and hence will affect the limits of the integral in Eq. 6.

If it is assumed that $N(E)$ behaves like some power of E at the extremity of a band, we will have been using the notation of Fig. 1 [4]

$$N_c(E) = N(E_c)\left(\frac{E - E_A}{\Delta E_c}\right)^{r_1},$$
$$N_v(E) = N(E_v)\left(\frac{E_B - E}{\Delta E_v}\right)^{r_2}. \tag{7}$$

If the bands are identical, so that $r_1 = r_2 = r$, $N(E_c) = N(E_v)$, and $\Delta E_c = \Delta E_v (= \Delta E)$; and under the assumption that $D_{loc} = D_{ext}$, we will have [9]

$$\alpha(\omega) = \frac{8\pi^4 e^2 \hbar^3 a}{n(w) c m^2} 2 \int_{E_A - \hbar\omega}^{E_B} [N(E_c)]^2 \left(\frac{(E_B - E)(E + \hbar\omega - E_A)}{(\Delta E)^2}\right)^r \frac{dE}{\hbar\omega}. \tag{8}$$

Let $y = (E_A - \hbar\omega - E)/(E_A - \hbar\omega - E_B)$, then Eq. 8 becomes

$$\alpha(\omega) = \frac{16\pi^4 e^2 \hbar^3 a}{n(\omega) c m^2} [N(E_c)]^2 \frac{(\hbar\omega - E_2)^{2r+1}}{\hbar\omega (\Delta A)^{2r}} \int_0^1 [y(1-y)]^r dy. \tag{9}$$

The integral in Eq. 9 is a standard integral, its solution is $[\Gamma(r+1)]^2/\Gamma(2r+2)$. Then Eq. 9 becomes

$$\alpha(\omega) = \frac{8\pi\sigma_{min}}{n(\omega) c} \frac{(\hbar\omega - E_2)^{2r+1}}{\hbar\omega (\Delta E)^{2r}} \frac{[\Gamma(r+1)]^2}{\Gamma(2r+2)}, \tag{10}$$

where $E_2 = E_{opt} = E_A - E_B$ (Fig. 1) and $\sigma_{min} = (2\pi^3 e^2 \hbar^3 a/m^2)[N(E_c)]^2$ is the minimum metallic conductivity.

Equation (10) is of general validity for any identical initial and final density of states distributions provided that $D_{loc} = D_{ext}$.

Tauc [3] assumed that the density of states distribution is parabolic ($r = 1/2$) as in crystals, and found that $\alpha\hbar\omega \propto (\hbar\omega - E_{opt})^2$ in accord with what was observed at that time for a-Ge.

If we let $r = 1/2$ in Eq. 10, we obtain

$$\alpha\hbar\omega = \pi^2 \frac{\sigma_{min}}{n(\omega) c \Delta E} (\hbar\omega - E_2)^2. \tag{11}$$

According to this model if $\sqrt{\alpha\hbar\omega}$ vs. $\hbar\omega$ is a straight line, then E_{opt} which is obtained from the extrapolation to $\hbar\omega$-axis at $\alpha\hbar\omega = 0$ is equal $E_2 = (E_A - E_B)$, this optical energy gap is considered as the extrapolation of the delocalised states E_c and E_v to the zero of the density of states at E_A and E_B, though it may not be a real zero in the density of states (see Fig. 1).

Davis and Mott [4] argued that the assumption in amorphous state that the density of states is parabolic is improbable, although for states beyond E_c and E_v it may be valid. They assumed that $N(E) \propto E$ at band edges; according to Mott [10] he gave reasons for believing that, if fluctuations in the interatomic distance are small, $N(E)$ in the region of localised states should be a linear function of E.

If we let $r = 1$ in Eq. 10, we will obtain the Davis-Mott expression for the cubic dependence of α on $\hbar\omega$

$$\alpha\hbar\omega = \frac{4\pi\sigma_{\min}}{3n(\omega)c(\Delta E)^2}(\hbar\omega - E_2)^3. \tag{12}$$

According to this model, if $\sqrt[3]{\alpha\hbar\omega}$ vs. $\hbar\omega$ is a straight line, then $E_{\text{opt}} = E_A - E_B$ similar to the Tauc model.

This explained the experimental observations for certain multicomponent glasses, and according to Cohen [3] he suggested that in these highly disordered systems, the linear tails in Fig. 1 are important and may extend to an appreciable energy range and are responsible for the observed $r = 3$.

It remained for Davis and Mott to explain what was believed that the square power law holds in most amorphous semiconductors.

They made the more plausible assumption that D_{loc} may be neglected, and gave the following formula

$$\alpha\hbar\omega = \frac{4\pi\sigma_{\min}}{n(\omega)c\Delta E}(\hbar\omega - E_1)^2. \tag{13}$$

The main difference between this expression and the Tauc expression apart from the numerical factor is that here the optical energy gap is $E_1 = E_c - E_B$ or $E_A - E_v$ whichever is smaller (see Fig. 1).

If $D_{\text{loc}} = 0$ and $N(E) \propto E$, Eq. 6 becomes

$$\alpha\hbar\omega = \frac{8\pi\sigma_{\min}}{n(\omega)c(\Delta E)^2} \int_{E_c-\hbar\omega}^{E_B} (E_B - E)(E + \hbar\omega - E_A)\mathrm{d}E. \tag{14}$$

Let $y = (E_c - \hbar\omega - E)/(E_c - \hbar\omega - E_B)$, then Eq. 14 becomes

$$\alpha\hbar\omega = \frac{8\pi\sigma_{\min}}{n(\omega)c(\Delta E)^2}(\hbar\omega - E_1)^3 \left[\int_0^1 y(1-y)\mathrm{d}y + \int_0^1 \frac{E_c - E_A}{\hbar\omega - E_1}(1-y)\mathrm{d}y\right]. \tag{15}$$

The final expression obtained here is

$$\alpha\hbar\omega = \frac{4\pi\sigma_{\min}}{3n(\omega)c(\Delta E)^2}(\hbar\omega - E_1)^2[\hbar\omega - E_1 + 3(E_c - E_A)]. \tag{16}$$

Under the assumption that the linearity of the density of states does not extend appreciably beyond the band edge, it seems plausible to assume that $3(E_c - E_A) > > \hbar\omega - E_1$, and Eq. 16 leads to the Davis-Mott expression (Eq. 13) because $E_c - E_A = \Delta E$.

We shall see that this assumption is in fact unnecessary and the full expression (Eq. 16) with its richer content is more promising than the approximate square power law (Eq. 13).

4. Re-evaluation of the models

It was believed especially in the seventies that in the majority of amorphous semiconductors, including a-Si, the quadratic relation offers the best fit to optical absorption data, except for some multicomponent glasses where the cubic law holds, and a-Se where a linear law holds.

Vorlíček et al. [11], and Klazes et al. [12] found that the cubic law quite significantly offers a better fit than the quadratic law for a-Si for unexpectedly wide photon energy range beyond the absorption edge (0.3–1.3 eV beyond the band gap energy) (Fig. 2).

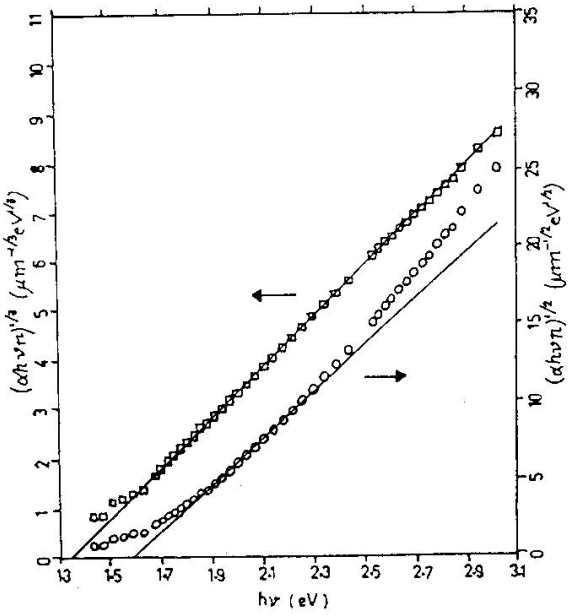

Fig. 2. A plot of $(\alpha\hbar\omega n)^{1/3}$ and $(\alpha\hbar\omega n)^{1/2}$ against $\hbar\omega$ for an a-Si sample [12], sputtered at 200°C in the presence of H_2.

Khawaja and Hogarth [13] found that the cubic law holds better for binary vanadium oxides, and As_2S_3 (Fig. 3) and mentioned that it also holds for many amorphous semiconductors, such as a-Si, a-Ge, Ta_2O_5 and $Ge_{15}Te_{81}Sb_2S_2$, whereas the square law holds for chalcogenide glasses.

Both Klazes at al. [12], and Khawaja and Hogarth [13] explained the cubic fit by a linear distribution of states near the band gap and equal matrix elements for all transitions, based on the Davis-Mott model (Eq. 12). Klazes et al. also made what we think an important statement that the cubic-root approximation

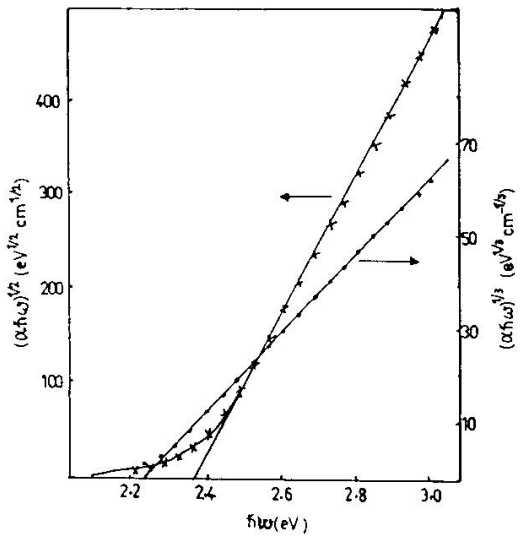

Fig. 3. A plot of $(\alpha\hbar\omega)^{1/2}$ and $(\alpha\hbar\omega)^{1/3}$ against $\hbar\omega$ for a-As_2S_3 [13].

has the practical advantage over the square-root approximation that it defines unambiguously an optical band gap which depends little on the range of photon energies above the band gap where absorption measurements are made.

It may deserve to note that the cubic law for As_2S_3 in Fig. 3 offers a better fit than the square law less significantly than in the case of a-Si in Fig. 2.

We believe that the Davis-Mott model, under the plausible assumption of negligible matrix elements between localised states, has a greater potential to explain experimental observations, through the full expression of Eq. 16.

$$\alpha\hbar\omega = B(\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E). \tag{17}$$

If we plot the cubic root of this function against $\hbar\omega$ for a typical value of ΔE in a-Si, say 0.1 eV (Spear et at., 1981) (Fig. 4), we find that it is linear for a wide range of $\hbar\omega$ values and its extrapolation to $\hbar\omega$-axis is closer to E_2 than to E_1, while the plot of $\sqrt{\alpha\hbar\omega}$ vs. $\hbar\omega$ is not linear, and the extrapolated E value is neither close to E_1 nor to E_2.

The explanation of this behaviour as we found is that the factors $(\hbar\omega - E_1)^2\,(\hbar\omega - E_1 + 3\Delta E)$ and $(\hbar\omega - E_2)^3$ are related by the identity

$$(\hbar\omega - E_2)^3 = (\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E) + 3(\hbar\omega - E_1)(\Delta E)^2 + (\Delta E)^3. \tag{18}$$

Therefore, if $\Delta E \ll 1$, the difference between the two factors $3(\hbar\omega - E_1)(\Delta E)^2 + (\Delta E)^3$ will be very small provided that $\hbar\omega$ is not very large with respect to E_1.

If we plot the factors $(\hbar\omega - E_2)^3$, $(\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E)$, and $3\Delta E(\hbar\omega - E_1)^2$ against $\hbar\omega$ for $\Delta E = 0.15$ eV (Fig. 5), we find that $(\hbar\omega - E_1 + 3\Delta E)(\hbar\omega - E_1)^2 \approx$

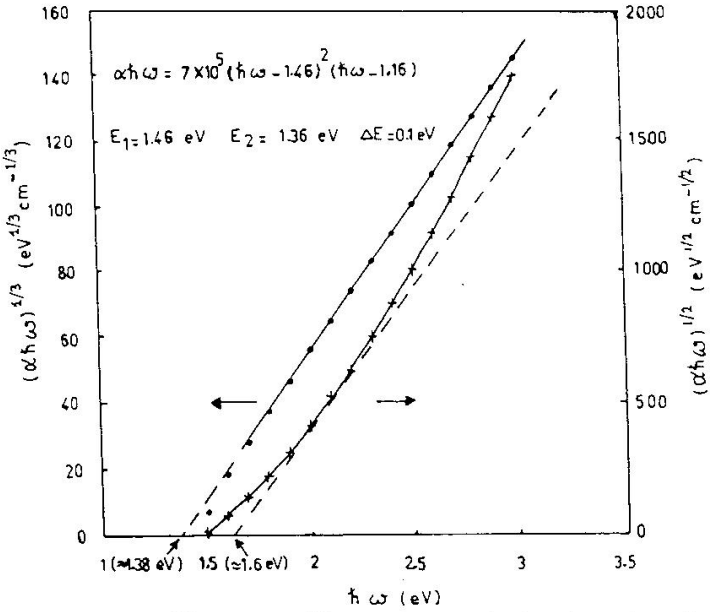

Fig. 4. A plot of $(\alpha\hbar\omega)^{1/3}$ and $(\alpha\hbar\omega)^{1/3}$ against $\hbar\omega$ for the function $\alpha\hbar\omega = 7\times10^5 \times (\hbar\omega - 1.46)^2\,(\hbar\omega - 1.16)$ [$E_1 = 1.46\,\mathrm{eV}$, $E_2 = 1.36\,\mathrm{eV}$, $\Delta E = 0.1\,\mathrm{eV}$].

$\approx (\hbar\omega - E_2)^3$ for a wide range of high $\hbar\omega$ values, but it does not approach the assumed approximate value of $3\Delta E(\hbar\omega - E_1)^2$ for any range of $\hbar\omega$ values.

Therefore, we suggest that Eq. 16 and hence the Davis-Mott model for linear density of states and $D_{\mathrm{loc}} = 0$, has the potential to explain the cubic power law without recourse to the less plausible assumption that $D_{\mathrm{loc}} = D_{\mathrm{ext}}$.

This leads us also to suggest that the best fit power law according to this model is not exactly cubic or square, but may be fractional, and we propose the following:

$$\alpha\hbar\omega = B(\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E) \approx B'(\hbar\omega - E_{\mathrm{opt}})^r, \quad 2 < r < 3, \tag{19}$$

where E_{opt} deduced from the extrapolation to $\hbar\omega$-axis of the best fit straight line to $\hbar\omega$-axis for some fractional index r, is not necessarily equal to E_1 or E_2, but generally will be closer to E_2 if r is very close to 3, this is expected when the range of localised states ΔE is sufficiently small (i.e., $\Delta E \lesssim 0.1\,\mathrm{eV}$).

To avoid any arbitrary assumption of the index r, we can make use of the method proposed by Al-Ani [14].

The plot of the function

$$\frac{\alpha\hbar\omega}{\mathrm{d}(\alpha\hbar\omega)/\mathrm{d}\hbar\omega} = \frac{\hbar\omega - E_{\mathrm{opt}}}{r} \tag{20}$$

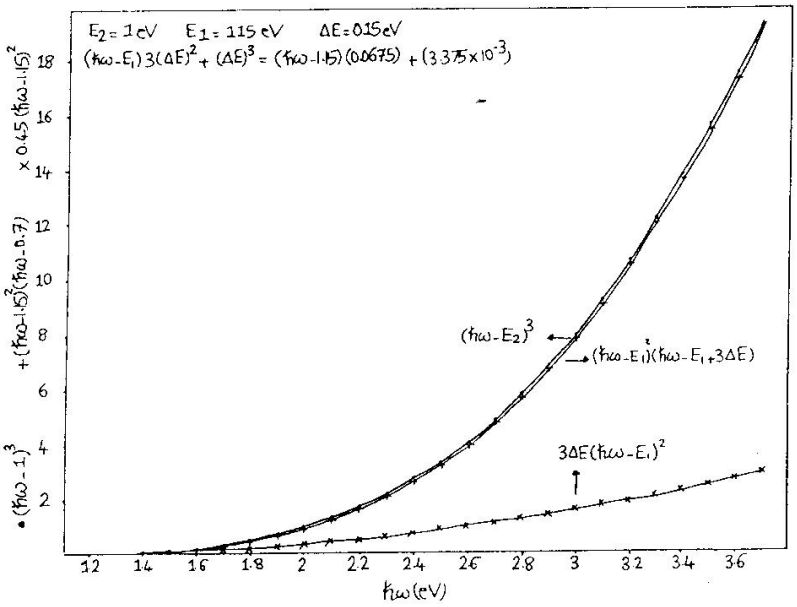

Fig. 5. A plot of the functions $(\hbar\omega - E_2)^3$ $(\cdot)$, $(\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E)$ $(+)$, and $3\Delta E(\hbar\omega - E_1)^2$ $(\times)$ against $\hbar\omega$ for $\Delta E = 0.15\,\mathrm{eV}$, $[E_2 = 1\,\mathrm{eV}$, $E = 1.15\,\mathrm{eV}]$.

against $\hbar\omega$ gives immediately the value of E_{opt} from the extrapolation to $\hbar\omega$-axis at

$$\frac{\alpha\hbar\omega}{\mathrm{d}(\alpha\hbar\omega)/\mathrm{d}\hbar\omega} = 0,$$

and the value of the index r from the inverse slope.

Moreover, we can relate Eq. 20 to Eq. 16 as in the following:

$$\frac{\alpha\hbar\omega}{\mathrm{d}(\alpha\hbar\omega)/\mathrm{d}\hbar\omega} = \frac{\hbar\omega - E_{\mathrm{opt}}}{r} \approx \frac{(\hbar\omega - E_1)(\hbar\omega - E_1 + 3\Delta E)}{3(\hbar\omega - E_1 + 2\Delta E)}. \tag{21}$$

So r may become a measure of disorder ΔE, but is not expected to be a sensitive one, however, we think that this point deserves further investigation.

These new prospects in the full expression of the Davis-Mott model for $D_{\mathrm{loc}} = 0$, tempted us to derive the expression for the case of parabolic density of states under the same assumption of negligible matrix elements for transitions between localised states; in this case, Eq. 6 becomes

$$\alpha\hbar\omega = \frac{8\pi\sigma_{\mathrm{min}}}{n(\omega)c\Delta E} \int_{E_c - \hbar\omega}^{E_B} \sqrt{E + \hbar\omega - E_A}\sqrt{E_B - E}\,\mathrm{d}E. \tag{22}$$

Let

$$y = \frac{E_c - \hbar\omega - E}{E_c - \hbar\omega - E_B},$$

then

$$\alpha\hbar\omega = \frac{8\pi\sigma_{min}}{n(\omega)c\Delta E}(\hbar\omega - E_1)^2 \int_0^1 \sqrt{1-y}\sqrt{y + \frac{E_c - E_A}{\hbar\omega - E_1}}\,dy \tag{23}$$

and we get the following expression

$$\alpha\hbar\omega = \frac{\pi^2\sigma_{min}}{2n(\omega)c\Delta E}(\hbar\omega - E_1 + \Delta E)^2, \tag{24}$$

which most surprisingly leads to the same expression of Tauc apart from a factor of 1/2 because $\Delta E = E_1 - E_2$, i.e.,

$$\alpha\hbar\omega = \frac{\pi^2\sigma_{min}}{2n(\omega)c\Delta E}(\hbar\omega - E_2)^2. \tag{25}$$

Thus E_{opt} is not the expected threshold energy $E_1 = E_c - E_B$ but $E_2 = E_A - E_B$, which confirms what was stated before, that it is the extrapolation of delocalised states to the zero of the density of states.

We now consider the case of unequal matrix elements, i.e., $D_{loc} = D_{ext}$ for completeness. It has been pointed out by Spear et al. [15], that, although the matrix elements D_{loc} may be negligibly small, but this may not apply for states close to the mobility edge, one would not expect an appreciable change in the spatial overlap of states above and below E_c (or E_v). Guided by Spear's work, we can write Eq. 6 for the case of $D_{loc} = D_{ext}$, $N(E) \propto E$, and $\hbar\omega > E_1$:

$$\begin{aligned}\alpha\hbar\omega = {} & \frac{8\pi\sigma_{min}}{n(\omega)c(\Delta E)^2}\frac{|D_{loc}|^2}{|D_{ext}|^2}\int_{E_A-\hbar\omega}^{E_c-\hbar\omega}(E + \hbar\omega - E_A)(E_B - E)dE \\ & + \frac{8\pi\sigma_{min}}{n(\omega)c(\Delta E)^2}\int_{E_c-\hbar\omega}^{E_B}(E + \hbar\omega - E_A)(E_B - E)dE,\end{aligned} \tag{26}$$

where the first integral is for transitions between localised states, and the second is for transitions between extended states (types *2* and *3* in Fig. 1). The first integral $\int_{E_A-\hbar\omega}^{E_c-\hbar\omega}$ can be divided into two already solved integrals $\left(\int_{E_A-\hbar\omega}^{E_B} + \int_{E_B}^{E_c-\hbar\omega}\right)$, therefore the final expression is

$$\begin{aligned}\alpha\hbar\omega = {} & \frac{4\pi\sigma_{min}}{3n(\omega)c(\Delta E)^2}\frac{|D_{loc}|^2}{|D_{ext}|^2}[(\hbar\omega - E_2)^3 - (\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E)] \\ & + \frac{4\pi\sigma_{min}}{3n(\omega)c(\Delta E)^2}(\hbar\omega - E_1)^2(\hbar\omega - E_1 + 3\Delta E).\end{aligned} \tag{27}$$

If ΔE is small and/or $|D_{\rm loc}|^2/|D_{\rm ext}|^2 \ll 1$, the first integral is vanishingly small, and this justifies the negligence of absorption due to localised states in the high absorption region.

For parabolic density of states distribution, the general expression is,

$$\alpha\hbar\omega = \frac{\pi^2}{2}\frac{\sigma_{\rm min}}{n(\omega)c\Delta E}\left(\frac{|D_{\rm loc}|^2}{|D_{\rm ext}|^2}+1\right)(\hbar\omega - E_2)^2. \tag{28}$$

It is a straightforward matter to show that the two special cases when $D_{\rm loc} = D_{\rm ext}$ and $D_{\rm loc} = 0$ result from the general expressions of Eqs. 27 and 28.

There is one reservation about the general expressions when $\hbar\omega$ is larger than the mobility gap (i.e., $\hbar\omega > E_1 + \Delta E$), the contribution from transitions between localised states, i.e., the first term should vanish, and this is not implied in these expressions, but this further justifies the negligence of this contribution in the region of photon energies of interest in experimental investigations of the absorption edge, where the linearity of the plot $\sqrt[n]{\alpha\hbar\omega}$ vs. $\hbar\omega$ starts at about 0.1 eV or more beyond the band gap energy (see Figures 2 and 3).

5. Conclusions

1. We associate the cubic dependence with linear density of states distributions for both cases; $D_{\rm ext} = D_{\rm loc}$, and $D_{\rm loc} = 0$, though not in a perfect manner for the second case, but as ΔE is small in many amorphous semiconductors, such as a-Si, a-Ge and As_2S_3 [16] this approximation may apply to them, though to varying degrees depending on ΔE, this possibly explains the different degrees of significance of fit to the cubic law compared to the square law a-Si (Fig. 2) and As_2S_3 (Fig. 3).

2. We associate the strict square power law dependence with parabolic density of states distributions, and an imperfect square power law dependence may be associated with linear density of states distribution for large enough degree of disorder ΔE. In this we depart from the previous conclusion that the strict square power law dependence may result either from parabolic density of states according to the Tauc model or from the Davis-Mott model for the case of $D_{\rm loc} = 0$ (Eq. 13).

3. $E_{\rm opt}$ deduced experimentally, may not coincide with any threshold energy for the onset of some kind of optical transitions, but may be an extrapolation to the zero of the density of states (though not a real zero) as in the parabolic case $[N(E) \propto \sqrt{E}]$; or an extrapolated energy (E_2) augmented by the degree of disorder (ΔE), as in the linear case $[N(E) \propto E]$ when $D_{\rm loc} = 0$; even for the case of $D_{\rm loc} = D_{\rm ext}$, we speculate that only weakly localised states may contribute significantly to optical absorption, and $E_{\rm opt}$ is still an extrapolated energy E_2 to the zero of the density of states.

4. The dependence of α on $\hbar\omega$ for the Davis-Mott model when $D_{\rm loc} = 0$ may be approximated as a fractional power law, where the magnitude of the index r

may be a rough measure of disorder ΔE, and may be deduced experimentally from

$$\frac{\alpha\hbar\omega}{\mathrm{d}(\alpha\hbar\omega)/\mathrm{d}\hbar\omega}$$

vs. $\hbar\omega$ plot.

5. Experimental measurements of the absorption coefficient should be of high accuracy, and cover a fairly wide range of photon energies beyond the absorption edge, say $\approx 1.5\,\mathrm{eV}$, to assess more certainly the exact dependence of α on $\hbar\omega$, hence, choose the model which fits best the experimental data.

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