INT. J. ELECTRONICS, 1993, VOL. 75, NO. 6, 1153-1163

Determination of the optical gap of amorphous materials

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A computational method is applied for the analysis of optical absorption spectra of amorphous materials to obtain both the power index, r, and E_{opt}, the optical band gap, from the theories of Tauc, and Davis and Mott which relate the energy of the incident photon ($\hbar w$) to the absorption coefficient $\alpha(w)$ i.e. $[\alpha\hbar w \sim (\hbar w - E_{opt})^r]$. The present technique proposes the use of the inverse of the logarithmic derivative of optical data. A linear plot of the power law $(\alpha\hbar w)^{1/r}$ or $(n\alpha\hbar w)^{1/r}$ where n is the refractive index of the material is obtained without needing an arbitrary assumption about the exponent involved. Experimental data on SiO, SiO/B_2O_3 and SiO/As_2O_5 amorphous thin films have been re-analysed and much accurate values of r and E_{opt} are reported.

1. Introduction

The optical absorption in solid materials is commonly obtained by the determination of optical absorbance (A) from intensities I_0 and I_t of the incident and transmitted light, respectively, through a material of thickness x. Generally, however, an absorption spectrum is depicted as the variation of absorbance $A = \log_{10}(I_0/I_t)$ as a function of wavelength (λ). The absorption coefficient (α) is a property of the material and depends on the wavelength (or w angular frequency) of the radiation. This coefficient can be defined from the relation:

$$\alpha(\lambda) = x^{-1} \ln I_0/I_t \tag{1}$$

So the absorption coefficient in term of absorbance becomes:

$$\alpha(\lambda) = 2{\cdot}303 A x^{-1} \tag{2}$$

In some cases, and to eliminate the reflection effects, it may be estimated from the absorbance spectra measured for two samples (A_1 and A_2) of the same material at different thicknesses (x_1 and x_2) using the relation (Al-Ani 1984):

$$\alpha(\lambda) = 2{\cdot}303[A_1(\lambda) - A_2(\lambda)]/[x_1 - x_2] \tag{3}$$

For a large number of amorphous materials, glasses and thin films, the absorption coefficient, $\alpha(w) \geq 10^4 \text{cm}^{-1}$ is considered to obey a power law given in the form valid for:

$$\alpha(w)\hbar w = B(\hbar w - E_{opt})^r \tag{4}$$

Where $\hbar w$ is the energy of the incident photon, B is a coefficient assumed to be constant in the optical frequency range and E_{opt} is the optical band gap of the material, the index r signifies the nature of electronic transitions associated with

Received 17 May 1993; accepted for publication by C. A. Hogarth.

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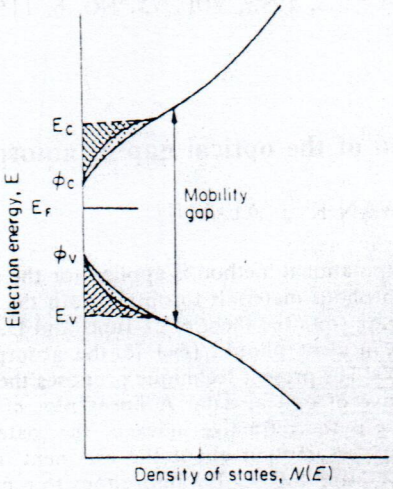

Figure 1. Model of density of states $N(E)$ as a function of electron energy E for amorphous oxide thin films, after Al-Ani (1984) ϕ_c, ϕ_v represent extent of band tailing.

optical processes and takes a value in the range $1 \leq r \leq 3$. Tauc (1966) assumed a density-of-states function with a square root dependence on energy, which is known to be appropriate for crystalline materials, and obtained a quadratic equation, i.e. (4) with $r = 2$.

Davis and Mott (1970) discussed (4) much more extensively and derived the following relation for inter-band transitions in an amorphous semiconductor:

$$(n\alpha\hbar w)^{1/3} = (4\pi\sigma_{\min}/3c)\,[1/(E_e)^2](\hbar w - E_{\text{opt}}) \tag{5}$$

where n is the refractive index of the material, E_e which is an energy interpreted as the range of localized states in the conduction and valence bands (both were assumed to be equal), $\sigma_{\min}$ is the minimum-metallic conductivity and c is the speed of light.

Mott and Davis (1979) assumed for (5) in their density-of-states model that:

(*a*) the densities of electron energy states ($N(E)$ in both valence and conduction bands are linear functions of energy $N(E_c) = N(E_V)$;

(*b*) transitions between localized states occcure with the same probability as other transitions, i.e. the same matrix elements.

Davis and Mott (1970) have also derived the following quadratic relation:

$$(n\alpha\hbar w)^{1/2} = (4\pi\sigma_{\min}/c)(1/E_e)(\hbar w - E_{\text{opt}}) \tag{6}$$

Which is based on the assumption that all transitions in which both the initial and final states are localized are negleted.

This is based (Khawaja and Hogarth 1988) on their argument that in the same region of space there will be little chance of finding a localized state derived from both the valence and conduction bands.

Tauc (1970) interprets E_{opt} from an extrapolation of the densities of states deeper in the bands. Davis and Mott (1970) interpreted relation (4) as the transitions from

Material	Function	E_{opt} (eV)	B ($cm^{-1} eV^{-2}$)	References
Ge	$[\hbar^2 w^2 \varepsilon_2]^{1/3}$	0·66	$1·48 \times 10^6$	Vorliček *et al.* (1981) (data after Tomlin *et al.* 1976)
Si	$[\hbar^2 w^2 \varepsilon_2]^{1/3}$	1·30	$1·30 \times 10^6$	Vorliček *et al.* (1981) (data after Thutupalli and Tomlin 1977)
Si	$[n\alpha\hbar w]^{1/3}$	1·20	—	Klazes *et al.* (1982) (data after Thutupalli and Tomlin 1977), (evaporated films)
Si	$[n\alpha\hbar w]^{1/3}$	1·796 ∓0·006	$2·41 \times 10^6$	Klazes *et al.* (1982) (glow discharge films)
As_2S_3	$[\alpha\hbar w]^{1/3}$	2·24	$1·43 \times 10^6$	Khawaja and Hogarth (1988) (data after Kosek and Tauc 1970)
As_2S_3	$[\alpha\hbar w]^{1/3}$	2·25	$5·403 \times 10^5$	Present (data after Kosek and Tauc 1970)
at 296K at 10K	$[n\alpha\hbar w]^{1/3}$	2·25 2·375	$1·2 \times 10^6$ $1·728 \times 10^6$	Present (data after Street *et al.* 1974)
Ta_2O_5	$[n\alpha\hbar w]^{1/3}$	4·06	$5·00 \times 10^6$	Khawaja and Hogarth (1988) (data after Khawaja and Tomlin 1975)
Se	$[\alpha\hbar w]$	2·0	$2·6 \times 10^5$ cm^{-1}	Al-Ani and Hogarth (1984) (data after Chaudhuri *et al.* 1984)
$In_{30}Se_{70}$	$[\alpha\hbar w]$	2·05 1·95	—	Al-Ani and Hogarth (1985 b) (data after Chaudhuri *et al.* 1984)
V_2O_5	$[\alpha\hbar w]^{2/3}$	2·325	$6·822 \times 10^5$ $cm^{-1} eV^{-0·5}$	Al-Ani and Hogarth (1985 a)
70% V_2O_5 30% SiO	$[\alpha\hbar w]^{0·6}$	2·50	$5·165 \times 10^5$ $cm^{-1} eV^{-0·66}$	Al-Ani and Hogarth (1985 a) (co-evaporated films)
30% V_2O_5 70% SiO	$[\alpha\hbar w]^{0·541}$	2·85	$4·103 \times 10^5$ $cm^{-1} eV^{-0·85}$	Al-Ani and Hogarth (1985 a) (co-evaporated films)
V_2O_5/GeO_2 /NiO	$[\alpha\hbar w]^{0·502}$	2·13	—	Ray and Hogarth (1990) (data after Hassan *et al.* 1988)

Table 1. Values of E_{opt} and B for a few amorphous materials re-analysed by different authors.

the localized states at the top of the valence band into the delocalized states in the conduction band (or vice versa). Therefore they interpret E_{opt} as a smaller energy difference between the boundaries of localized states in the valence band and delocalized states in the conduction band, i.e. $E_c - \phi_V$ in Fig. 1, or of localized states in the conduction band and delocalized states in the valence band, i.e. $\phi_c - E_v$ as shown in Fig. 1.

It should be noted that the value of the coefficient B in (4) may be obtained from the (slope)^r of the linear region of the plot $(\alpha\hbar w)^{1/r}$ versus $\hbar w$ and its units can be calculated according to $cm^{-1} eV^{1-r}$.

Early work on a-Ge and a-Si films suggested a square law dependenc of α in the form of (4) (Grigorovici and Vancu 1968, Brodsky *et al.* 1970, Tomlin *et al.* 1976, Thutupalli and Tomlin 1977, Cody *et al.* 1980).

Amorphous thin film	From (10) and (11)		From (10 and (4)			Previous work			References
	r	E_{opt} (eV)	r	E_{opt} (eV)	B	r	E_{opt} (eV)	B (cm^{-1} eV^{-1})	
SiO	1·82	2·30	1·82	2·31	$2{\cdot}74 \times 10^5$ cm^{-1} eV$^{-0{\cdot}82}$	2	2·25	$2{\cdot}401 \times 10^5$	Al-Ani (1983, 1984)
SiO/B_2O_3	1·94	2·80	1·94	2·77	$1{\cdot}80 \times 10^5$ cm^{-1} eV$^{-0{\cdot}94}$	2	2·80	$1{\cdot}932 \times 10^5$	Al-Ani (1983, 1984)
SiO/As_2O_5	2·01	2·55	2·01	2·54	$0{\cdot}79 \times 10^5$ cm^{-1} eV$^{-1{\cdot}01}$	2	2·63	$0{\cdot}900 \times 10^5$	Al-Ani (1983, 1984)

Table 2. Values of r and E_{opt} for amorphous thin films obtained from present method and compared with previous work.

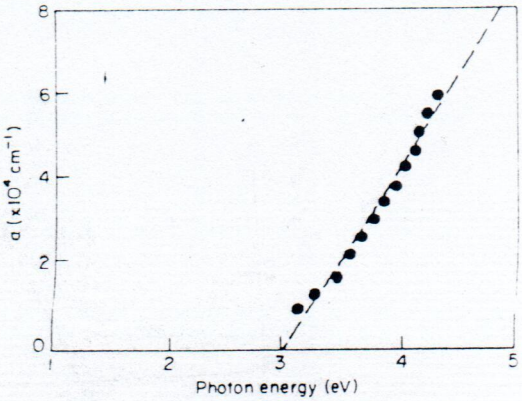

Figure 2. Values of $\alpha(w)$ versus $\hbar w$ for amorphous SiO thin film after, Al-Ani (1983, 1984).

Vorliček *et al.* (1981) have presented (4) in the following form:

$$w^2\varepsilon_2(w) \sim (\hbar w - E_{opt})^r \tag{7}$$

with $(1 \leqslant r \leqslant 3)$ and $\varepsilon_2(w)$ is the imaginary part of permittivity determined from reflectivity measurements in a broad spectral range followed by the Kramers–Kronig dispersion analysis.

They have re-analysed some of the above data as the function $[(\hbar w)^2\varepsilon_2]^{1/3}$ in $(\text{eV})^{2/3}$ versus $\hbar w$ in eV i.e. (7) with $r=3$ for a-Si and a-Ge approximately in the spectral range 1·5–2·3 eV and 0·9–1·7 eV, respectively.

Klazes *et al.* (1982) found E_{opt} of a-Si from $(n\alpha\hbar w)^{1/3}$ as a functrion of $\hbar w$ and concluded that the cubic law gives a better fit in the energy range 1·4–3·2 eV. Using the cube root approximation, they further suggested a single bandgap for evaporated a-Si = 1·2 eV instead of the two values of E_{opt} measured by Thutupalli and Tomlin (1977).

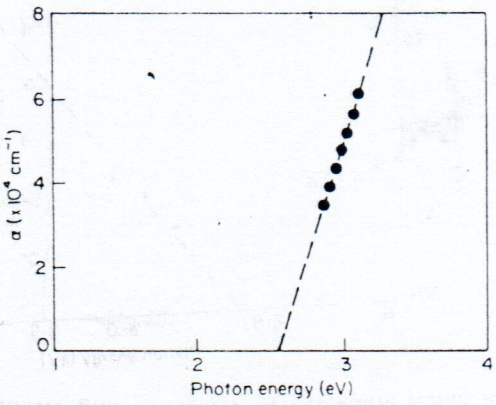

Figure 3. Values of $\alpha(w)$ versus $\hbar w$ for amorphous SiO/B_2O_3 thin film after Al-Ani (1983, 1984).

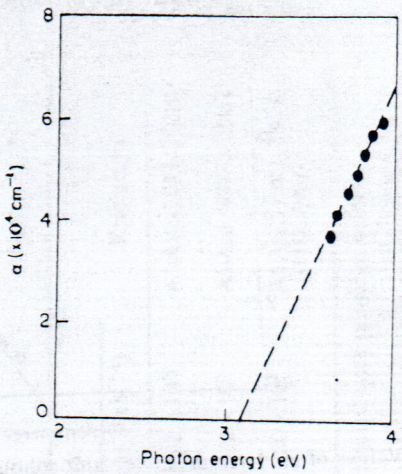

Figure 4. Values of $\alpha(w)$ versus $\hbar w$ for amorphous SiO/As_2O_5 thin film, after Al-Ani (1983, 1984).

Fagen (1970) has reported (Tauc 1974, Mott and Davis 1979) a cubic fit to certain complicated glasses:

$$Si_5Ge_5As_{25}Te_{55}, Ge_{15}Te_{81}Sb_2S_2, Si_{11}Ge_{11}As_{35}P_3Te_{40}, Ge_{16}As_{35}Te_{28}S_{21}$$

Al-Ani and Hogarth (1984, 1985*b*) re-analysed the original data of a-Se and a-$In_{30}Se_{70}$ from previously reported work and found different values of E_{opt} with $r=1$ instead of $r=2$ in (4). Some of the above data are summarized in Table 1.

The choice of $r=3$ instead of 2 for a-As_2S_3 films (Khawaja and Hogarth 1988) displayed some deviation from the linear fit especially in the high region where (4) holds.

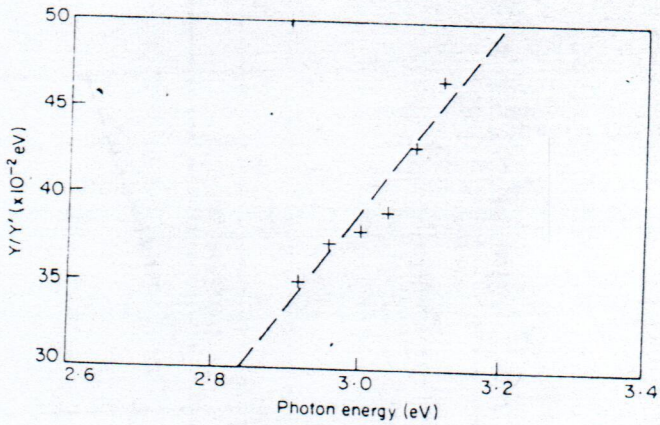

Figure 5. Best square fitting of ratio (Y/Y') versus set of values of $\hbar w$ for amorphous SiO film as obtained from Fig. 2.

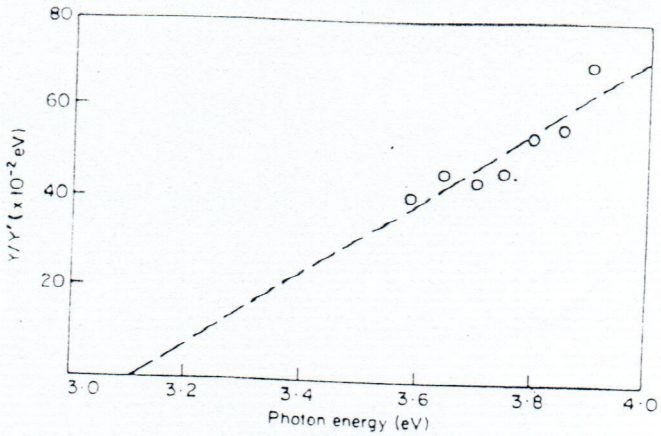

Figure 6. Best square fitting of ratio (Y/Y') versus set of values of $\hbar w$ for amorphous SiO/B_2O_3 film as obtained from Fig. 3.

When we recalculated the published data for a-As_2S_3 (e.g. Kosek and Tauc 1970, Street *et al.* 1974) we have found that they all fit (4) with $r=3$ much better than with $r=2$. Examples are also presented in Table 1.

For the effective use of those amorphous materials in electronic devices, the value of E_{opt} must be calculated as accurately as possible. We present a new procedure for finding the value of E_{opt} for a non-crystalline material.

2. Method and calculation

Making the substitution that:

$$Y = \ln (I_o/I_t)\hbar w$$

(4) can be written as:

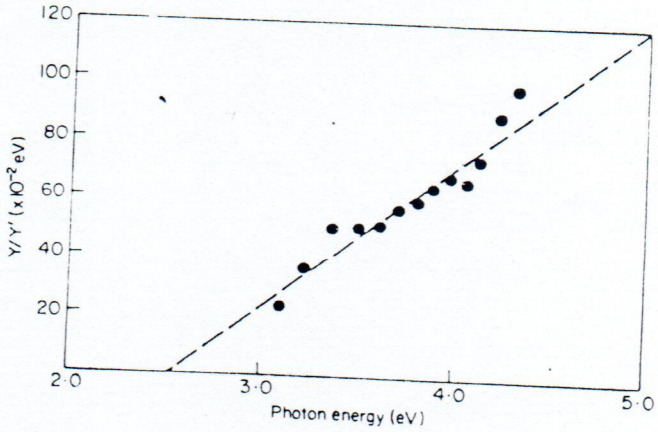

Figure 7. Best square fitting ratio (Y/Y') versus set of values of $\hbar w$ for amorphous SiO/As_2O_5 film as obtained from Fig. 4.

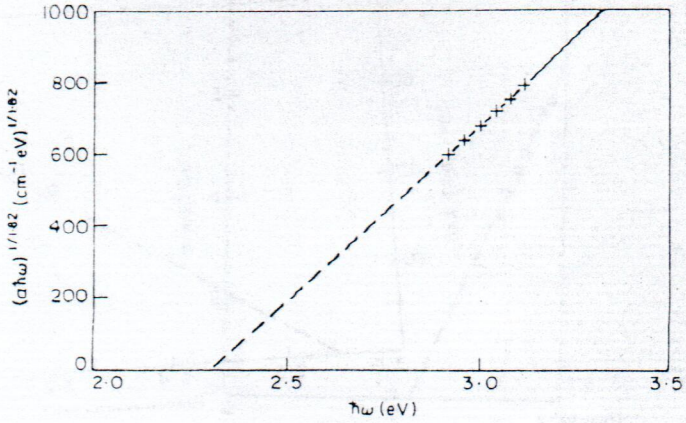

Figure 8. Variation of function $(\alpha\hbar w)^{1/r}$ versus $\hbar w$ for a-SiO film. Value of $r = 1{\cdot}82$ (Table 2).

$$Y = \beta[\hbar w - E_{\text{opt}}]^r \tag{8}$$

where $\beta = xB$ is another constant and is thus dimensionally different from the constant B.

Taking the derivative of Y with respect to $\hbar w$ i.e. (Y') from (8) we find the following new equation:

$$\frac{Y}{Y'} = \frac{\hbar w - E_{\text{opt}}}{r} \tag{9}$$

In the present work we have used the lagrangian interpolation polynomial to find the derivative. We then plot the function Y/Y' against $\hbar w$ and applying the best square fitting to find the best line passes through the points. The best line is chosen by taking the maximum cross correlation coefficient (maximum chi-square) of the points.

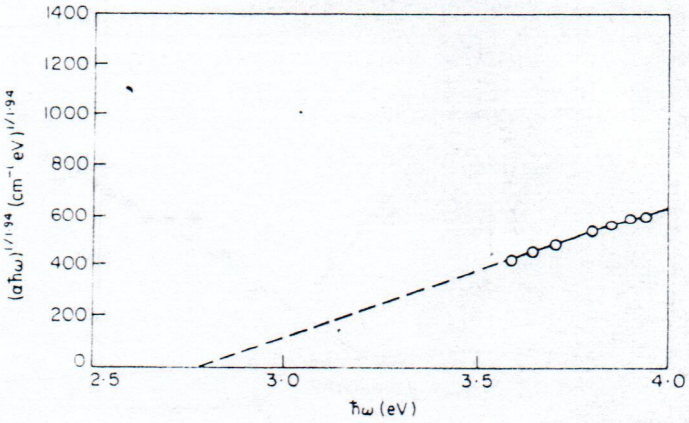

Figure 9. Variation of function $(\alpha\hbar w)^{1/r}$ versus $\hbar w$ for a-SiO/B_2O_3 film. Value of $r = 1{\cdot}94$ (Table 2).

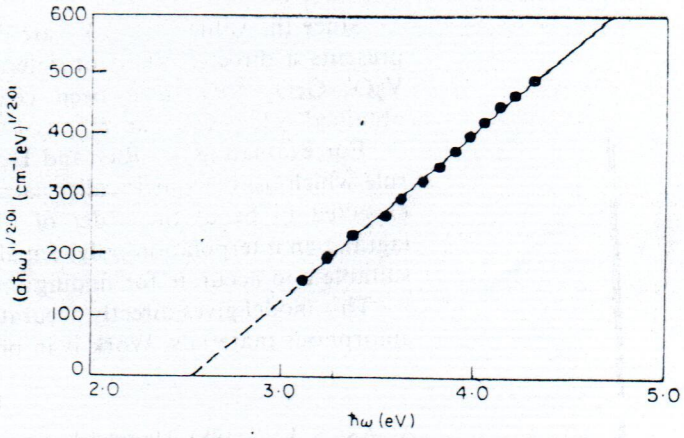

Figure 10. Variation of function $(\alpha\hbar w)^{1/r}$ versus $\hbar w$ for a-SiO/As_2O_5 film. Value of $r=2{\cdot}01$ (Table 2).

Next we find r from the slope as follows

$$r=(\text{slope})^{-1} \tag{10}$$

From the slope and intercept with the ordinate we calculate the energy E_{opt} where:

$$E_{opt}=\frac{\text{extrapolated intercept (at } Y/Y'=0)}{\text{slope}} \tag{11}$$

3. Results and discussion

The experimental data have been taken from Al-Ani (1983, 1984). Figures 2–4 display the variation of $\alpha(w)$ against $\hbar w$ for three samples SiO, SiO/B_2O_5 and SiO/As_2O_5 amorphous thin films. Figures 5–7 show the dependence of the function (Y/Y') (see (9)) on $\hbar w$. The best straight lines are drawn through the points using the method of linear regression. Using (10) and (11) the new values of r and E_{opt} for those samples are computed and listed in Table 2. The old values are also included. Furthermore, using the new value of the exponent r (10) we have plotted the function $(\alpha\hbar w)$ versus $\hbar w$ in Figs 8–10 according to (4) and using the least square method the extrapolated intercept with the abscissa at $Y/Y'=0$ to give the new theoretical value of the optical energy gap (Table 2).

The uncertainty in the values of r and E_{opt} will depend on the numerical technique used for finding the derivative Y'. Our method, however, gave the maximum chi-square of the points $(\gamma^2)=0{\cdot}999$ as presented in Figs 8–10. This is essential for finding E_{opt} at $\alpha(w)\geqslant 10^4\,\text{cm}^{-1}$. But, the fitted values of r showed clearly that they are different form the Tauc (1966) and Davis and Mott (1970) values 1, 2, or 3. In the absence of further information it is not easy to suggest much about the density of states function but the results obtained herein demonstrate the complexities of the optical absorption edges in those amorphous materials. So, in amorphous solids: $N(E)\propto E^r$, where r is not necessarily equal to the values 1, 2 or 3 and could well take fractional values depending on the material under examination.

Since the values of (Y/Y') are determined from measured absorbance data, this presents a direct method of determining both r and E_{opt}. Glass samples such as V_2O_5-GeO_2-NiO have been considered by Ray and Hogarth (1990). They obtained values of r and E_{opt} as 1·99 and 2·13 eV, respectively.

For evaluating Y', Ray and Hogarth (1990) preferred the mid-point difference rule which uses symmetrically placed interpolating points. In their view the error is expected to be of the order of the square of the interval between points. The lagrangian interpolation polynomial which has been attempted herein is found to be suitable and accurate for finding these parameters.

This model gives directly accurate values of r and E_{opt} and it is recommended for amorphous materials. Work is in progress on other samples.

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