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## Optical gap and Urbach edge slope in a-Se

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### Abstract

Good correspondence between the temperature shift of the optical gap and the Urbach edge slope has been found for a-Se. Such coherence, however, does not exist for photoinduced changes of the gap and Urbach edge slope measured at 77 K. The kinetics of photoinduced changes of the gap takes the form of first-order process, while the kinetics of photoinduced changes of Urbach edge obeys stretched exponential form. It is supposed that overheating due to illumination is most probably not responsible for photoinduced changes. Rather an increase in density of localized states at band edges, together with formation of self-trapped exciton-like states could explain the photoinduced changes observed in the gap and Urbach edge slope.

*Keywords:* Optical gap; Urbach edge; amorphous-Se

### 1. Introduction

Amorphous selenium (a-Se), the apparently simple twofold coordinated semiconductor is widely studied and used in applications. Among the properties of interest studied is reversible photodarkening, observed in a-Se only if the material is illuminated below room temperature, in fact, at a temperature close to the that of liquid nitrogen temperature. In connection with these studies, there is also a question whether in a-Se some correspondence between the optical gap ( $E_g$ ) and the Urbach edge slope ( $\sigma$ ) exists, since both quantities are interrelated through the temperature, and  $\sigma$  is usually taken as a measure of some structural disorder, see e.g. Refs. [1,2].

In this communication some our experimental results are summarized, which are addressed to study an interrelation of the optical gap and Urbach edge slope in amorphous selenium.

### 2. Experimental

Two sets of samples were prepared for optical measurements. (i) Bulk samples in the form of thin plan-parallel plates (thickness  $d \approx 0.032$  cm) polished to optical quality on both sides. (ii) Thin films prepared by thermal evaporation (BAE 250T system,  $p \approx 10^{-4}$  Pa, rate of evaporation  $\approx 15$  Å/s) on to glassy substrate (at normal incidence). The thickness of the films was between 0.7 and 1  $\mu\text{m}$ . The films were stored for three months in a dark evacuated

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desiccator in order to relax the material. The optical properties were measured using the Beckman DU-640 UV-VIS spectrophotometer. All the measurements were made in an optical cryostat Cryoson XL 500 fixed in the sample compartment of the spectrophotometer. The optical transmission was measured in the temperature region 76–300 K. The sample illumination was made by a halogen lamp (at  $T \approx 77$  K) equipped with an infrared-cut filter. These measurements were made with helium gas in the inner part of the cryostat in order to minimize any fluctuation of the temperature. The measurements of the spectral distribution of the halogen lamp used indicated a maximum at  $\approx 550 \mu\text{m}$ , i.e. close to the optical gap of a-Se. During illumination, the lamp was fixed in the sample compartment (together with the cryostat) of the spectrophotometer; hence the position of the sample in the beam was always the same.

### 3. Results and discussion

The spectral dependence of absorption coefficient ( $\alpha$ ) in the region of the short wavelength edge in a-Se is usually approximated by [3]:

$$\alpha \hbar \omega = \text{Const.} (\hbar \omega - E_g). \quad (1)$$

However, recent results [4] indicate that for thin films  $(\alpha \hbar \omega)^{1/2}$  versus  $\hbar \omega$  dependence gives better results and hence we evaluated optical gap from<sup>1</sup> [3,5]:

$$\alpha \hbar \omega = B(\hbar \omega - E_g)^2. \quad (2)$$

In Fig. 1 the temperature dependence of the optical gap is shown. The solid curve indicates a fit to our experimental data (solid circles) using Fan's one-phonon approximation [7]:

$$E_g(T) = E_g(0) - A / [\exp(\hbar \omega_0 / K_B T) - 1], \quad (3)$$

where  $E_g(0) = 2.117_4$  eV,  $A = 0.263_4$  eV,  $\hbar \omega_0 = 24$  meV. Within the approximation used the quantity  $\hbar \omega_0$  corresponds to the properly averaged frequency of the phonon spectrum of a-Se. For readers' conve-

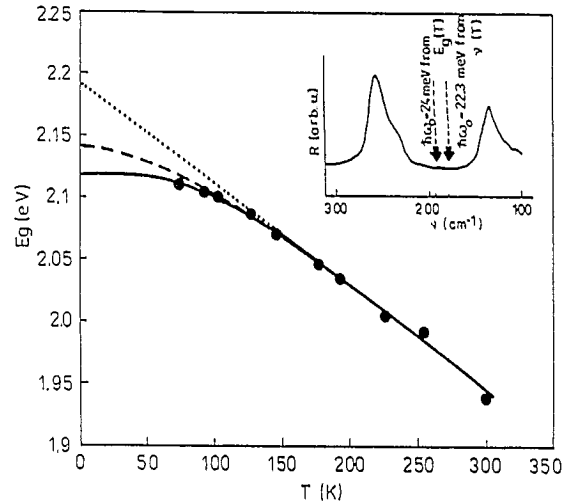


Fig. 1. Temperature dependence of the optical gap ( $E_g$ ) of amorphous Se (full circles). Solid curve – fit to Eq. (3), dashed curve – fit to Eq. (5), dotted line – fit to Eq. (4). Inset – reflectivity ( $R$ ) of glassy Se in far infrared region. The wave numbers corresponding to  $\hbar \omega_0 = 24$  meV (calculated from Eq. (3)) and to  $\hbar \omega_0 = 22.3$  meV (calculated from Eq. (6)) are indicated by heavy arrows.

nience the inset in Fig. 1 shows a typical phonon spectrum of a-Se. The wave number corresponding to calculated  $\hbar \omega_0 = 24$  meV is indicated by a heavy arrow. Similar correspondence between phonons relating to chemical bonds forming the network has been observed e.g. in glassy  $\text{As}_4\text{Se}_2\text{Ge}_1$  [8] and also in glassy  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ ,  $\text{GeSe}_2$ ,  $\text{GeS}_2$ , as well as corresponding quasibinary chalcogenides, (see Ref. [9]). The line in Fig. 1 indicates the fit of our experimental data to the standard linear equation:

$$E_g(T) = E_g(0) - \beta T, \quad (4)$$

while the dashed curve indicates the fit to the Varshni equation [10]:

$$E_g(T) = E_g(0) - \alpha T^2 / (T + B). \quad (5)$$

It is known [11] that, taking the first-order approximation of expansion  $\exp(\theta/T)$  ( $\theta = \hbar \omega_0 / K_B$ ), Eq. (4) results from Eq. (3), where  $\beta = A/\theta$ , and taking the second-order approximation of expansion  $\exp(\theta/T)$ , Eq. (5) results from Eq. (3), where  $\alpha = A/\theta$  and  $B = \theta/2$ . We note that our experimental value  $\beta$  (Eq. (4)) has been found to be  $\beta = 8.2 \times 10^{-4}$  eV K, i.e., close to  $A/\theta = 9.47 \times 10^{-4}$  eV/K and also close to  $\beta = 7.6 \times 10^{-4}$  eV/K found in Ref. [12]. In Fig. 2 the temperature dependence of

<sup>1</sup> We note that this equation has recently been used for calculation of  $E_g$  in a-Se [6].

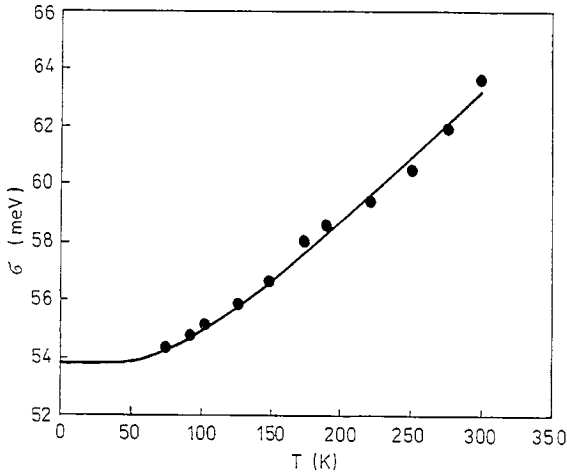


Fig. 2. Temperature dependence of the Urbach edge slope ( $\sigma$ ) (full circles). Solid curve – fit to Eq. (6).

the Urbach edge slope ( $\sigma(T)$ ) is shown by open circles. The values of  $\sigma(T)$  were calculated by linear regression of  $\ln(\alpha)$  versus  $\hbar\omega$  dependence ( $\alpha = \alpha_0 \sim \exp[(\hbar\omega - E_g)/\sigma(T)]$ ) measured at the same temperatures as those at which thin films were measured. Neither the origin nor the temperature dependence of the Urbach edge seems to be a definitively solved problem. Here we use Cody's expression [2] for the slope of Urbach edge in the form:

$$\sigma(T) = \frac{\hbar\omega_0}{\sigma_0} \left( \frac{1}{2} + \frac{x}{2} + \frac{1}{\exp(\hbar\omega_0/K_B T) - 1} \right). \quad (6)$$

The first term in parentheses corresponds to zero-point contribution and the second one to a structural disorder contribution to the slope of the Urbach edge. A quantity  $\sigma_0$ , the Urbach edge parameter, could be taken as a material constant. The solid curve in Fig. 2 represents the fit of our experimental data to Eq. (6), where  $\hbar\omega_0 = 22.3$  meV,  $\sigma_0 = 1.75$  and  $x = 7.4$ . This means that at the limit  $T \rightarrow 0$ , a zero-point phonon contribution is close to  $\approx 6.4$  meV, while a structural disorder contribution to the Urbach edge slope is close to  $47.1$  meV<sup>2</sup>. Combining Eqs. (3) and (6) we obtain:

$$E_g(T) = E_g(0) - A(1+x)/2 + (A\sigma_0/\hbar\omega_0)\sigma(T). \quad (7)$$

<sup>2</sup> Assuming that  $x$  is independent or very weakly dependent on the temperature in the measured temperature region.

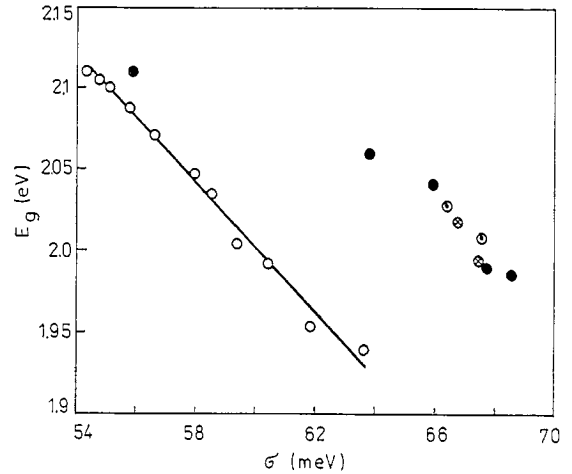


Fig. 3. Optical gap versus Urbach edge slope. Open circles – experimental values from  $E_g(T)$  and  $\sigma(T)$  dependences. Solid line – fit to Eq. (7). Full circles and combined circles correspond to photoinduced changes of  $E_g$  and  $\sigma$  at  $T \approx 77$  K. For the meaning of combined circles, see text.

In Fig. 3 our experimental  $E_g(T)$  and  $\sigma(T)$  data are fitted by the solid line to Eq. (7). Using  $E_g(0)$ ,  $\hbar\omega_0$  and  $A$  values calculated from the  $E_g(T)$  fit (Eq. (3)), we obtain  $\sigma_0 \approx 1.8$ ;  $x = 7.2$ , i.e., values close to those obtained from the  $\sigma(T)$  fit (Eq. (6)). Hence, both the optical gap and Urbach edge slope seem to be interrelated through the electron–phonon interaction. We note that a correlation between  $E_g$  and  $\sigma$  follows also from Skettrup's model of the Urbach edge [13]; it was observed e.g. for certain chalcogenide glasses [1] and as well for a-Si(H) [2]. The results of photoinduced changes of the optical properties of both bulk samples and thin films induced by illumination at 77 K are summarized in Fig. 4 as kinetics of evaluation of the optical gap (crosses), slope of  $(\alpha\hbar\omega)^{1/2}$  versus  $\hbar\omega$  dependence (full circles) and slope of Urbach edge (open circles). Dashed curves represent the fit using Eqs. (8)–(10) to our experimental data:

$$E_g(77, t) = E_g(77, 0) - [E_g(77, 0) - E_g(77, t \rightarrow \infty)] \times [1 - \exp(-kt)], \quad (8)$$

$$\sigma(77, t) = \sigma(77, 0) + [\sigma(77, t \rightarrow \infty) - \sigma(77, 0)] \times \left\{ 1 - \exp[-(kt)^n] \right\}, \quad (9)$$

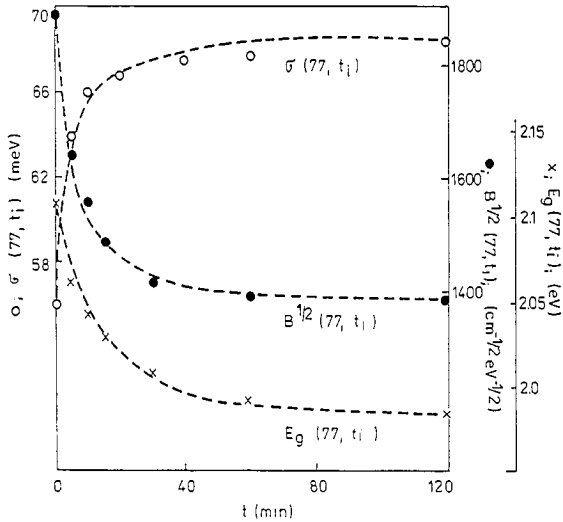


Fig. 4. Time dependence of photodarkening – crosses –  $E_g$ , full circles –  $B^{1/2}$ , open circles –  $\sigma$ .

$$B^{1/2}(77, t) = B^{1/2}(77, 0) + [B^{1/2}(77, t \rightarrow \infty) - B^{1/2}(77, 0)] \times \{1 - \exp[-(kt)^n]\}. \quad (10)$$

The following parameters were obtained from the fits:  $k(E_g(77, t)) = 72.83 \text{ min}^{-1}$ ,  $E_g(77, t \rightarrow \infty) = 1.985_9 \text{ eV}$ ,  $k(\sigma(77, t)) = 0.21 \text{ min}^{-1}$ ,  $\sigma(77, t \rightarrow \infty) = 68.6 \text{ meV}$ ,  $k(B^{1/2}(77, t)) = 0.2 \text{ min}^{-1}$ ,  $B^{1/2}(77, t \rightarrow \infty) = 1383.9 \text{ cm}^{-1/2} \text{ eV}^{-1/2}$ ,  $n = 0.5$ . From Fig. 4, a considerable difference is evident between the kinetics of photoinduced change of  $E_g(77, t)$ , which is close to the first-order process, and the kinetics of photoinduced changes  $B^{1/2}(77, t)$  and  $\sigma(77, t)$ , both of which are stretched exponential forms with the same values of parameters  $n$  and  $k$  (see Eqs. (9) and (10)). The dependence of the gap ( $E_g(77, t)$ ) versus Urbach edge slope ( $\sigma(77, t)$ ) is shown by full circles in Fig. 3. The “combined” circles have to be taken with same caution because  $\sigma(77, t)$  values (○) or  $E_g(77, t)$  values (⊗) were calculated from Eqs. (8), (9). A considerable change is evident in  $E_g$  versus  $\sigma$  dependence induced by illumination in comparison with that which is induced by change of the temperature only (open circles). We suppose this difference indicates that photoinduced darkening is most probably not due to a local overheating in the illuminated area of the sample. If we take for further consideration a nearly saturated photodarkened state

( $t = 120 \text{ min}$ ) then it follows from Eq. (3) that to reach a change of the gap from  $E_g(77, 0) = 2.109_7 \text{ eV}$  to  $E_g(T, 120) = 1.985_8 \text{ eV}$ , the thin film should be overheated by illumination at  $T \approx 77 \text{ K}$  to  $T = 253 \text{ K}$ . At the same time, however, if the structural term is not depending on the temperature, the bulk sample should be overheated (by illumination for 120 min at  $T = 77 \text{ K}$ ) to 408 K to reach  $\sigma(T, 120) = 68.58 \text{ meV}$ . This is hardly probable since such temperature exceeds the softening temperature of Se by about 85 K and we did not observe any indication of the flow of material in the illuminated area of the sample. Moreover, after some time at room temperature, the Urbach edge slope “relaxed” back (with an error  $\pm 2 \text{ meV}$ ) to nearly virgin value. If the overheating of the bulk is close to the estimated overheating of the thin film (i.e. it is close to  $T \approx 253 \text{ K}$ ), then the quantity  $X$  should be temperature dependent which, however, disagrees with our experimental results, see Fig. 3, open circles and line. Hence, we suppose that photoinduced changes of the gap and Urbach edge slope are not connected with overheating or, in other words, these changes are not connected with some local increase of temperature. Of interest is the similar kinetics of photoinduced changes of  $B^{1/2}$  and  $\sigma$ , see Fig. 3. Both quantities can be taken as some measure of disorder [3]. Since in the Mott–Davis interpretation  $B^{1/2}$  is inversely proportional to  $\Delta E$  [3] (i.e. it is proportional to the width of localized states at band edges), a decrease of  $B^{1/2}$  values induced by illumination indicates an increase of localized states at the band edges. This seems to be consistent with the observed increase of Urbach edge slope ( $\sigma$ ). Hence darkening induced by illumination is accompanied by an increase of localized states at the band edges. We speculate that suitable defects responsible for observed photodarkening are, however, self-trapped exciton (STE)-like states. The role of STE in the process of photodarkening of amorphous chalcogenides was proposed by Street [14] and discussed in connection with possible models of photodarkening by Elliott [15]. According to Street, the band edge localized states could be those states which bind an exciton. Once the STE is created, e.g. by bond switch (see Fig. 3a in Ref. [15]), the photodarkening can occur because optical transitions proceed between the ground state and the self-trapped exciton state. In this case, as pointed out by Elliott

[15], the photo-created charged defects ( $\text{Se}_3^+$ ,  $\text{Se}_1^-$  centre, see e.g. Ref. [16]) could increase the magnitude of an internal electrical microfield<sup>3</sup> which according to Dow–Redfield’s model of Urbach edge [18] results in a broadening of the Urbach edge (i.e. to an increase of  $\sigma$  due to illumination), which we observed. It could also be possible that STE occur at centers where p lone-pair electronic states of Se atoms interact strongly [19]. Such a situation can also occur if dihedral angle distortions give rise to localized states in the gap close to band edges [20], the process proposed by Nagels et al. [4] as a possible origin of photoinduced darkening in a-Se.

#### 4. Conclusion

(1) The temperature shift of the gap of a-Se was found to be well described within Fan’s one-phonon approximation.

(2) The temperature shift of the Urbach edge slope of a-Se was found to be compatible with Cody’s relation. Consequently, both quantities  $E_g(T)$  and  $\sigma(T)$  are interrelated through the temperature and phonon field with energy  $\hbar\omega_0$  close to 22.3–24 meV.

(3) The evaluation of photoinduced darkening of the gap has been observed close to first-order kinetics, while photoinduced change of the parameter  $B^{1/2}$  (slope of  $(\alpha\hbar\omega)^{1/2}$  versus  $\hbar\omega$  dependence) was found to obey stretched exponential form. The stretched exponential form with the same parameters ( $k$ ,  $n$ ) also obeys the evaluation of photoinduced change of the Urbach edge slope.

(4) It is supposed that photoinduced phenomena in a-Se are most probably not due to a local over-

heating. Rather an increase of localized states at band edges and creation of self-trapped exciton-like states could be responsible for observed photodarkening in a-Se.

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<sup>3</sup>We note that these microfields penetrating the illuminated spot can enhance a decrease of the gap by  $\Delta E = eFR$ , where  $F$  is the internal electrical field and  $R$  is the distance between centers [17].