# OPTICAL PROPERTIES OF AMORPHOUS SELENIUM

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The dielectric constant of amorphous selenium is calculated in the region from 2 to 10 eV using a pseudopotential formalism to calculate "lifetimes" of electrons in the amorphous state. Spicer's "nondirect transition" model is checked and modified to include energy-dependent matrix elements.

In the last few years there has been a growing interest in the interpretation of optical and electrical properties of amorphous semiconductors.[1] Most of the work in this field is more or less concerned with the band-edge region, the occurrence of band tails, and the particular character of electron states in this region (whether they are "localized" or not). The concern of this note will be the form of the optical spectrum of amorphous selenium well above the fundamental threshold, i.e., in the region from 2 to 10 eV. Selenium can serve as a rather promising test model, since there are two well-distinguished regions of optical absorption belonging to two different band triplets,[2] one extending from 2 to 5.5 eV, the other from 6 to 10 eV. Their different behavior on going from the crystalline to the amorphous state is a rather sharp criterion for the validity of any model used to explain disorder phenomena in Se.

The short-range order which is still present in amorphous Se has not up to now been conclusively elucidated. X-ray patterns suggest that there is an appreciable amount of $\mathrm{Se}_8$ rings mixed to more or less distorted Se chains[3]; the respective percentages, however, are as yet unknown.[2,4] Because of the similarity of nearest-neighbor bonding and of the optical spectra of trigonal and $\alpha$-monoclinic selenium we suggest that starting from a solely trigonal short-range order describing the amorphous material will not drastically affect the ideas and results of the following.

We assume a two-particle correlation function

$$f^{\alpha}(\vec{k}-\vec{k}')=\sum_{n\leq N} f_n^{\alpha}(\vec{k}-\vec{k}'-\vec{K}_n)+\sum_{n>N} f_N^{\alpha}(\vec{k}-\vec{k}'-\vec{K}_n)$$

with

$$f_n^{\alpha}(x)=\frac{N}{V}\pi^{-3/2}(\alpha K_n)^{-3}\exp\left(-\frac{x^2}{\alpha^2 K_n^2}\right), \tag{1}$$

where the $\vec{K}_n$ are the reciprocal lattice vectors of trigonal Se, and the parameter $\alpha$ is to be chosen suitably. From Ref. 4 we conclude $\alpha$ is approximately 0.1. Factorizing all more-particle correlation functions into products of two-particle correlation functions, and neglecting "crossed diagrams,"[5] we can factorize the Born series for the Green's function of the amorphous state of selenium in a pseudopotential formalism.[6] The crucial point in this factorization process is the assumption that the pseudopotential $v(\vec{q})$ is flat enough to allow for the approximation

$$v(\vec{q})=v(\vec{K}_n)$$

for all $\vec{q}$ in the Wigner-Seitz cell around $\vec{K}_n$. This approximation replaces the integration over $\vec{q}$ which is inherent in the Born series by a summation over $\vec{K}_n$. Summing up the series leads to a non-Hermitian secular equation of the form

$$\det\left|\varphi_n^{-1}(\vec{k},E+i\Gamma)\delta_{nn'}-v(\vec{K}_n-\vec{K}_{n'})\right|=0 \tag{2}$$

with

$$\varphi_n(\vec{k},E+i\Gamma)=\int d^3k' f_n^{\alpha}(\vec{k}-\vec{k}')[E+i\Gamma-k'^2]^{-1},$$

which for $\alpha\to 0$ yields the well-known Hermitian pseudopotential secular equation of the crystalline case. Using the selenium form factors (and also parts of the computer programs) that Sandrock[7] used, the "band structure" $E=E(\vec{k})$, and the "lifetimes" $\Gamma^{-1}=\Gamma^{-1}(E,\vec{k})$ of the electrons in the system described by formula (1) were calculated. A plot of the reciprocal lifetimes as a function of energy and wave vector is given in Fig. 1(a) (with $\alpha=0.1$).

Using these values a dielectric function was calculated according to

$$\mathcal{E}_2(\omega)\sim\int dE\sum_{V,C}\int d^3k\,|M_{VC}(\vec{k})|^2\,\frac{\Gamma_V(\vec{k},E)}{[E-E_V(\vec{k})]^2+\Gamma_V^2(\vec{k},E)}\,\frac{\Gamma_C(\vec{k},E)}{[E+\hbar\omega-E_C(\vec{k})]^2+\Gamma_C^2(\vec{k},E)}, \tag{3}$$

where $M(\vec{k})$ are the isotropic crystalline matrix elements taken from Sandrock[7] as $M_{\mathrm{isotropic}}(\vec{k})=\frac{1}{3}[M_{\parallel}(\vec{k})+2M_{\perp}(\vec{k})]$. The disorder effects are completely incorporated in an energy- and $\vec{k}$-dependent lifetime broadening.

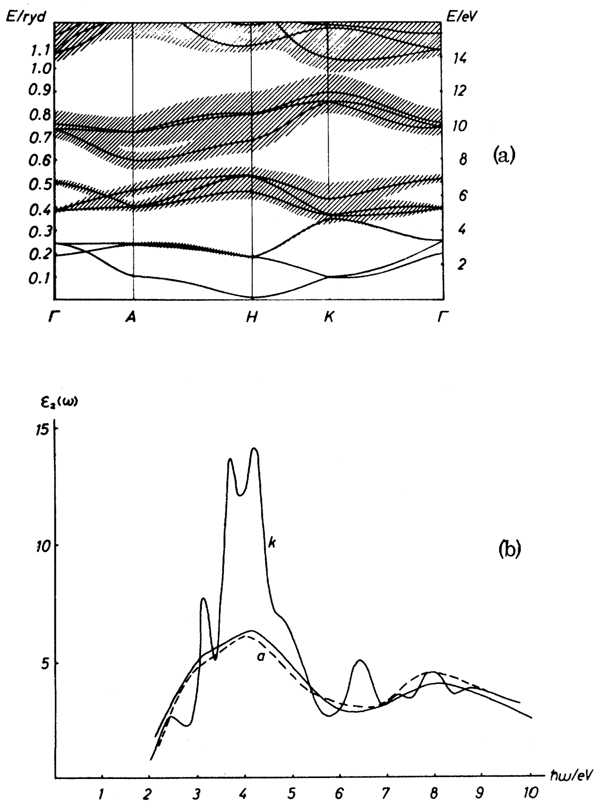

FIG. 1. (a) Electronic "band structure" of amorphous selenium calculated with $\alpha = 0.1$. The imaginary part of $E_n(k)$ is shown as a broadening of the real part. (b) Imaginary part of the dielectric constant. Curve $k$; isotropic spectrum of crystalline Se; curves $a$, spectrum of amorphous Se, calculated (solid line) and experimental (dotted line).

In contrast to Brust's work on amorphous germanium,[8] which is otherwise very similar to the work reported here, the matrix elements are not taken as constant, and the energy and $\vec{k}$ dependence of the lifetimes is not treated as an adjustable parameter, but calculated from Eq. (2). As can be seen from Fig. 1(b) the agreement between our calculated $\mathcal{E}_2(\omega)$ spectrum and experiment is very satisfactory, with the exception of the threshold region. Of course, the neglect of a whole series of diagrams is responsible for this shortcoming. The main feature, however, of the optical spectrum, namely the rather strong decrease of $\mathcal{E}_2$ in the region up to 5.5 eV, and the stability of the second broad peak (from 6 to 10 eV) is borne out of this calculation as a consequence of lifetimes that vary rather strongly with energy. Γ varies from approximately zero in the lower valence band to about 1 eV in the lowest conduction band, the latter value being comparable with those found for amorphous germanium.[8]

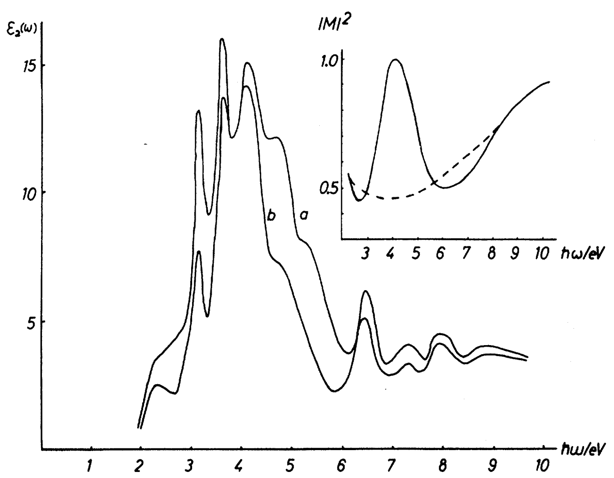

FIG. 2. Dielectric constant of crystalline Se: curve $b$ with pseudopotential matrix elements (Ref. 7), the energy dependence of which is shown in the upper right corner of the figure (solid line); curve $a$, with constant matrix elements.

We further tried to check the nondirect-transition model[9] to calculate the optical spectrum of amorphous Se. To clarify the question of whether the usual assumption of constant matrix elements is justified or not we calculated the combined density of states $n_{c0}(\omega)$ of crystalline Se. By dividing $\omega^2\mathcal{E}_2(\omega)$ through $n_{c0}(\omega)$ we got the averaged crystalline matrix element as a function of energy, Fig. 2, showing a rather sharp structure at about 4 eV. As a detailed investigation of the band structure[7] and the combined density of states shows, the respective band-to-band transitions mainly originate from the top plane of the Brillouin zone ($H$-$M$-$Z$ plane in the nomenclature of Ref. 7). Inspection of the nearly free-electron model of Se suggests that the pronounced maximum of matrix elements at 4 eV is due to umklapp enhancement.[10]

If we now assume that the $\vec{k}$ selection rule is totally relaxed in the case of amorphous Se we are led to calculate the convolution of the densities of states of the valence and the conduction band. Using constant matrix elements we find rather good agreement as to the smearing out of the structure of $\mathcal{E}_2(\omega)$, but not as to the relative height of the two distinct peaks of the spectrum, Fig. 3. On the other hand one can show that structure in the energy dependence of the averaged crystalline matrix element which belongs to transitions in a small region of the Brillouin Zone (BZ) vanishes in the amorphous case,[11] whereas structures stemming from large por-

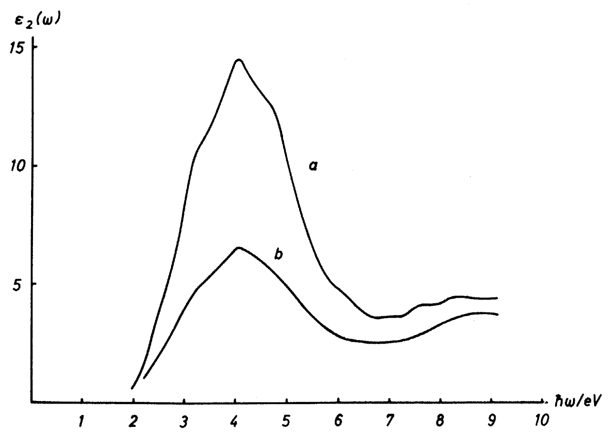

FIG. 3. Convolution of the densities of states of the valence and conduction bands of Se, with (curve *a*) constant matrix elements, (curve *b*) energy-dependent matrix elements as taken from Fig. 2 (dotted line).

tions of the BZ are almost conserved. This results in an averaged matrix element for amorphous selenium which is shown in Fig. 2 as a dashed line.[12] The dielectric constant calculated with these matrix elements as

$$\mathcal{E}_2(\omega)=\omega^{-2}|M^{\rm eff}(\omega)|^2\int dE\,n_V(E)n_c(E+\hbar\omega)$$

yields a very satisfactory agreement with the experimental spectrum, see Figs. 1(b) and 3. Once more one should mention that there is no description of tails, especially because we have assumed the densities of states in the single bands to be the same as in the crystal. This assumption is supported as to the conduction band by recent synchrotron-radiation measurements by Cardona.[13] The modified nondirect-transition model described above has been extended to amorphous germanium and silicon.[11]

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[5] See, e.g., F. Yonezawa, Progr. Theor. Phys. 31, 357 (1964), where a classification of the diagrams is given, which are relevant in the description of disordered systems.

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[10] J. C. Phillips, Solid State Phys. 18, 55 (1966).

[11] K. Maschke and P. Thomas, to be published; this "damping" of umklapp-enhanced matrix elements has a close connection to the large imaginary parts of the energy, which result from Eq. (2) in the region of Bragg reflection as a consequence of the particular form of $\varphi_n$.

[12] As a matter of fact one should take into account explicitly the $f$-sum rule. That would lead to a slight increase of matrix elements for higher energies in still better accordance with experiment.

[13] M. Cardona, to be published.