

OPTICAL PROPERTIES AND ELECTRONIC STRUCTURE OF AMORPHOUS Ge AND Si

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ABSTRACT

The analysis of the infrared absorption bands in amorphous Ge which correspond to transitions between the three branches of the valence band has shown that the valence band wave-functions are delocalized over distances of the order 10^2Å . This is in sharp contrast with the observed low electrical conductivity. Possible reasons for this discrepancy are discussed. A general formula for absorption in amorphous structures is discussed and applied to the analysis of the absorption edges in Ge and Si.

Introduction

This paper is devoted to an attempt to use optical spectra as a means of determining the nature of the electronic wave-functions in amorphous solids. In the first instance, it is useful to consider the infrared absorption spectrum of amorphous Ge as shown in Fig. 1, in particular its low energy region (part I in Fig. 1) which gives us information on the electron states in the valence band, and the absorption edge (part III) from which information on the conduction band states can be deduced. The absorption edge of amorphous Si will also be analyzed.

Valence Band Absorption

In amorphous Ge absorption bands have been observed (1, 2) in the region between 0.05 and 0.5 eV and ascribed to transitions of holes between

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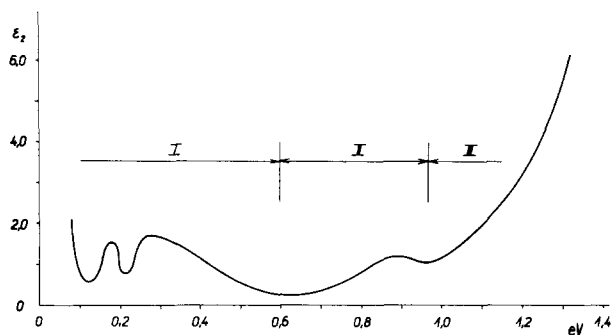


FIG. 1

Absorption in Amorphous Ge.

I. Transitions in the valence band; II. Absorption tail; III. Absorption edge. After Ref. 2.

the three branches of the valence band, similarly as in p-type single crystal Ge. According to these investigations the valence band of amorphous Ge has qualitatively a similar structure as that in crystalline Ge. The spin-orbit splitting deduced from these spectra is 0.2 eV as compared with 0.3 eV in the crystal, and the effective masses m_1 , m_2 are changed

(Table 1). These values were obtained on the assumption that the \underline{k} -vector is exactly conserved during the transitions. An alternative approach is to assume that the changes of effective masses determined from the optical spectra

TABLE 1.

Valence Band Parameters

	ΔE	m_1/m	m_2/m	m_3/m
Crystalline Ge	0.29	0.30	0.04	0.08
Amorphous Ge	0.20	0.46	0.03	0.08

 ΔE spin-orbit splitting m_1, m_2, m_3 effective masses

10^6 cm^{-1} . This means that the valence band wave-functions in amorphous Ge are not too different from Bloch functions. Making use of the uncertainty relation $l \cdot \Delta k \approx 1$ we obtain for the mean free path of the hole $l > 100\text{\AA}$.

are not due to the changes of band curvature but to a non-exact conservation of the \underline{k} -vector (2). In this way we obtain the upper limit of the uncertainty of the \underline{k} -vector to be

This result is corroborated by theoretical considerations. Gubanov (3) expresses the distance between atoms in an disordered chain of atoms as $a(1 + \epsilon\gamma)$ where ϵ is the degree of disorder and γ is randomly variable (with average values $\bar{\gamma} = 0$, $\bar{\gamma}^2 = 1$). He obtains the estimate a/ϵ^2 for the mean free path. X-ray analysis (4) of the atomic correlation in amorphous Ge gives ϵ to be about 10^{-1} which determines the order of magnitude of $l = a/\epsilon^2$

to be 10^2\AA . Also, recent theoretical work by Fletcher (5) indicates that the valence band of Ge is not much changed by the transition from the crystalline into the amorphous state.

It is possible to estimate the hole concentration in amorphous Ge from measurements of the capacitance of amorphous-crystalline p-n junctions (6). These give $N_p \approx 10^{18} \text{ cm}^{-3}$. For $l \approx 2 \cdot 10^{-6} \text{ cm}$ one obtains at room temperature $\sigma \approx 70 \Omega^{-1} \text{ cm}^{-1}$. This calculated conductivity is in sharp contrast with the measured value which, at room temperature, is about $10^{-2} \Omega^{-1} \text{ cm}^{-1}$, that is 4 orders of magnitude smaller. Such a discrepancy is probably a general feature of amorphous materials. In CdGeAs_2 , for example, the conductivity is 6 orders of magnitude smaller in the amorphous state than in the crystalline state. Another difficulty is the disagreement between the sign of the thermoelectric power and of the Hall constant. In the temperature range where the conductivity in amorphous Ge is believed to be due to the holes, the thermoelectric power is positive (7), but the Hall constant is negative and very small (8). Again, this is a feature often observed in semiconducting glasses.

It is necessary to reconcile the large delocalization of the valence-band wave-functions, as deduced from the optical spectra, with the low mobility deduced from the electrical conductivity. Because of the optical results, it seems necessary to postulate that in amorphous materials there must be regions within which the valence band wave-functions are not too different from Bloch functions. One would expect their dimensions to be of the order 10^2\AA . It is, of course, not proposed that these regions are crystalline, since this would contradict the results of X-ray analysis. The low conductivity can be caused either by effects at the boundaries of these regions or by the electronic structure within them.

The first possibility was suggested by Stuke (9). The electrical conductivity can be lowered by the necessity of carriers to pass over potential barriers which arise at the boundaries, e.g. from different concentrations of defects or from different internal strains. They may arise from discontinuities of the films produced by evaporation. Because of its wider applicability, another possibility is also of interest: as a result of the fluctuations of the structural parameters, the potential energy to which the carrier is subjected

on its way fluctuates. It is easily shown that in a linear chain of length $l = a/\epsilon^2$, the mean square fluctuation of atomic distances is $\delta a/a \approx \epsilon^2$. These fluctuations lead to a fluctuation of the gap $\delta E_g \approx |VdE_g/dV| \cdot 3\delta a/a$ and to fluctuations of the acceptor concentration $\delta N \approx (\epsilon^2/a)^{3g}$. With $\epsilon \approx 0,1$ and $VdE_g/dV \approx -5 \text{ eV}^{10}$ this gives carrier fluctuations of the order of 10^{17} to 10^{18} cm^{-3} , and barrier heights of the order 10^{-1} eV , capable of explaining the 10^4 room temperature ratio between the calculated and measured conductivities.

Although such barriers may play a role in the electrical conductivity, they do not by themselves explain the difficulty arising from the sign of the Hall constant. Also, the observed very low photo-sensitivity is not compatible with the presence of barriers (8, 11). Another mechanism may be possible, based on the following idea. In the theory of crystals it is customary to consider a certain volume inside the crystal and to construct the wave-functions by imposing some boundary conditions, usually those of Born and Karman. The difference between the energy levels is inversely proportional to the volume chosen but this volume is considered to be only a mathematical device to avoid formal difficulties connected with infinite crystals. Let us assume that in a highly disordered solid the lack of long range order makes it possible to give a real meaning to the basic volume. The material is thus considered to be composed of regions inside which the wave-functions are not too different from Bloch functions, and which are separated from neighbouring regions by some boundary conditions such as the vanishing of the wavefunction. This may again be a mathematical device to describe the finite space correlation in such structures leading to a certain localization of the wave-functions, but the following reasoning will be the same if one considers small crystallites (or macromolecules) fixed in space. If these regions are sufficiently small, the non-zero difference between energy levels will profoundly influence the conduction process. It is possible to estimate these energy differences by considering the regions as potential wells. It is then easily seen that the differences between the energy levels are of the order of $10^{-4} - 10^{-2} \text{ eV}$, for regions of linear dimensions of the order of 10^2 \AA . A typical value of the energy difference at 0.025 eV for linear dimensions 200 \AA and $m^* = 0.5 m$ is about 3 meV . At lower energies it is larger and at higher energies it decreases as

the square root of energy measured from the band edge. One cannot observe such discrete levels in the spectra because the dimensions of the regions fluctuate. As a result of the averaging process, one expects again continuous spectra, as actually observed.

Such a system does not conduct electricity at zero temperature and at low electrical fields if phonon emission is neglected. The electrons present on an energy surface in the \underline{k} -space cannot rearrange themselves under the influence of the field because they cannot change their momentum without changing the energy and, in view of the above argument, successive energy surfaces are far apart. At non-zero temperatures, phonons will allow conduction. The process will become effective with phonons of energies high enough to make transitions between neighbouring energy states possible. We have here a temperature activated conduction process, with some features similar to those of hopping processes. In particular we would expect the model to give small and negative values of the Hall constant for reasons given by Mott and Twose (12). At higher fields there is a certain probability of electronic transitions between the energy surfaces, and these, at a certain field intensity, may lead to a reversible and extremely fast electronic breakdown. This may conceivably explain the electric breakdown observed in semiconducting glasses (13) which has recently attracted attention as a promising electronic switch.

Absorption Edge

Figures 2 and 3 show the photon energy dependence of the absorption constant of amorphous Ge (1, 8, 14) and of the imaginary part of the dielectric constant of amorphous Si (15).

In Figs. 4 and 5, an alternative way of showing the energy dependence of absorption is presented. The idea of this plot is to show that there exist regions in which $\pi\omega\sqrt{\epsilon_2}$ is linearly dependent on $\pi\omega$. This is (below) considered as an indication that the transitions are indirect. In such a presentation a tail is clearly distinguished from the rest of the absorption band. In previous measurements (1) this tail had the form of a band and was ascribed to transitions of electrons from acceptors into the conduction band. The results of

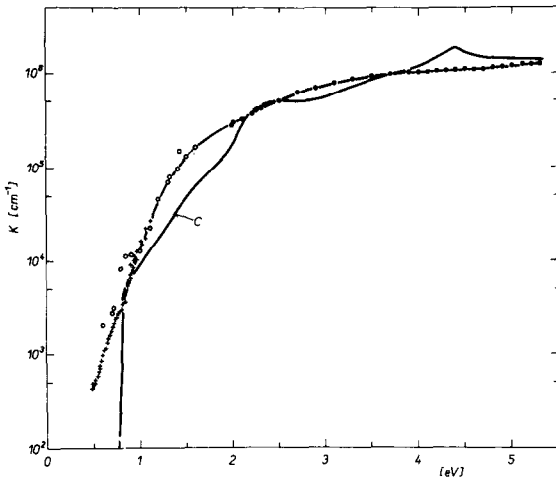


FIG. 2

Spectral Dependence of the Absorption Constant K of Amorphous Ge.

Measurements by Clark (8) +++, by Vancu (1) ooo, by Abrahám (14) ●●●. Curve C corresponds to crystalline Ge.

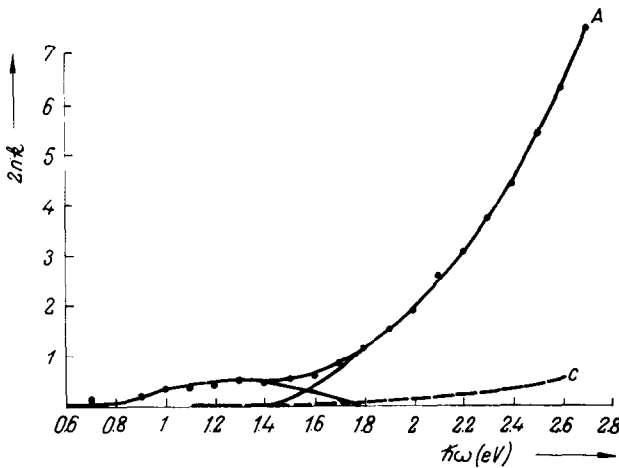


FIG. 3

Absorption in Amorphous Si (curve A), Compared with that in Crystalline Si (curve C). After Grigorovici and Vancu (15).

Clark (8) suggest that it may be due to fluctuations of the energy width of the gap. It is apparent that detailed studies of the temperature dependence of the absorption in the tail could throw more light on its nature.

For formulating the theory of optical transitions in amorphous materials one needs the valence and conduction band wave-functions. We consider the wave-functions in the valence and conduction bands in the crystal with the same short-range order, that is Bloch functions $|v \underline{x}\rangle, |c \underline{x}'\rangle$ where $\underline{x}, \underline{x}'$ are the wave-vectors. When we switch on

the perturbation corresponding to the transition into the amorphous state, the Bloch functions change into some other functions. The basic assumption is that the number of states in the valence band and in the conduction band does not change by this perturbation. Then we can label the wavefunctions in the amorphous body corresponding to $|v \underline{x}\rangle, |c \underline{x}'\rangle$ by indices $\underline{x}, \underline{x}'$ and denote them $|v \underline{x}\rangle_a, |c \underline{x}'\rangle_a$ as linear combinations of the complete

system of the Bloch functions. From the usual one-electron formula for ϵ_2 we obtain

$$\epsilon_2(\omega) = \left(\frac{2\pi e}{m\omega} \right)^2 \frac{2}{(2\pi)^3} \frac{1}{B} \int_{BZ} d^3\mathcal{R} d^3\mathcal{R}' F(\mathcal{R}, \mathcal{R}') \delta(E_c(\mathcal{R}') - E_v(\mathcal{R}) - \hbar\omega) \quad (1)$$

where the integration is performed over the first BZ the volume of which is B.

$$F(\mathcal{R}, \mathcal{R}') = N \left| \sum_{\ell, \ell'} \sum_{\underline{k}} \langle c \mathcal{R}' | \ell' \underline{k} | v \mathcal{R} \rangle_a p_{\ell \ell'}(\underline{k}) \right|^2 \quad (2)$$

where N is the number of cells in the basic volume, $\sum_{\ell, \ell'}$ is performed over all bands and $\sum_{\underline{k}}$ over the BZ.

$p_{\ell \ell'}(\underline{k})$ is the momentum matrix element in the crystal for the wavenumber \underline{k} between the bands ℓ, ℓ' . In the theory of crystals we usually assume it to be practically a constant p_{vc} independent of \underline{k} . Then, in the crystal, $F(\mathcal{R}, \mathcal{R}')$ reduces to $B |p_{vc}|^2 \delta(\mathcal{R} - \mathcal{R}')$ and leads to the usual formula for ϵ_2 determined by direct transitions. In amorphous materials we shall consider two examples which may correspond to Ge and Si respectively.

(a) The simplest expected change in $F(\mathcal{R}, \mathcal{R}')$ is the broadening of the delta function near $\mathcal{R} = \mathcal{R}'$ as shown symbolically in Fig. 6, curve

b. The reasoning is much simplified if we assume that $|v \mathcal{R}\rangle_a$ and $|c \mathcal{R}'\rangle_a$ are linear combinations of the wavefunctions in the same bands ($\ell = v, \ell' = c$). Then $F(\mathcal{R}, \mathcal{R}')$ obeys

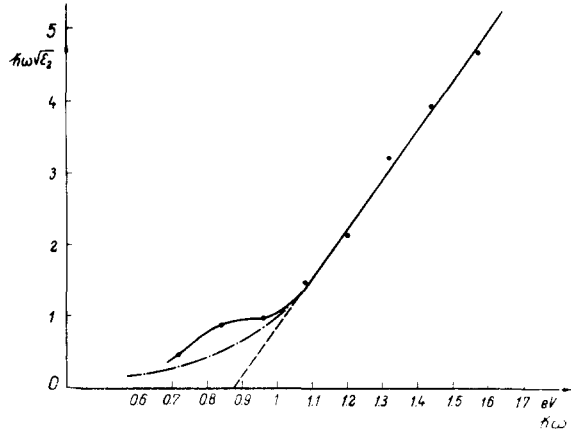


FIG. 4

$\hbar\omega\sqrt{\epsilon_2}$ as a Function of $\hbar\omega$ in Amorphous Ge (1).
Line ---- based on the results of Clark (8).

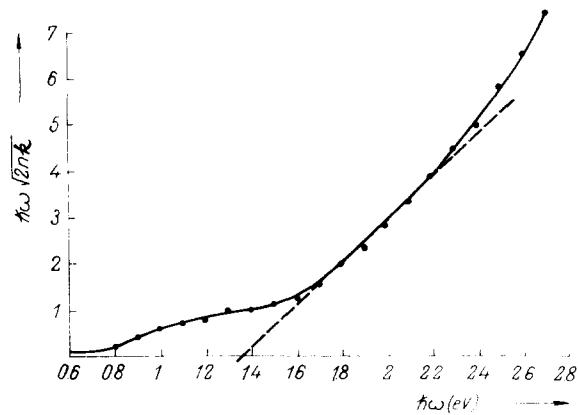


FIG. 5

$\hbar\omega\sqrt{\epsilon_2}$ as a Function of $\hbar\omega$ in Amorphous Si (15).

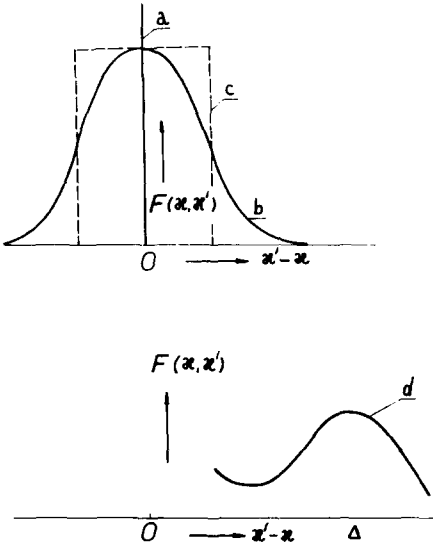


FIG. 6

$F(\underline{x}, \underline{x}')$ Factor, Plotted Schematically Near $\underline{x} = \underline{x}'$.

For simplicity, it is assumed to be a function of $\underline{x} - \underline{x}'$ only.

(a) Its form in the crystal: a delta function. (b) The broadening caused by the transition into the amorphous state.

(c) Approximation of the actual form as discussed in the text.

(d) The form expected in Si.

the following sum rule

$$\int_{BZ} d^3 \underline{x} d^3 \underline{x}' F(\underline{x}, \underline{x}') = B^2 |p_{vc}|^2. \quad (3)$$

Let us consider a particularly simple case that $F(\underline{x}, \underline{x}')$ is a constant F_0 in a certain part B_0 of BZ and zero in the rest.

From equ. (3) we determine F_0 to be $B |p_{vc}|^2 / B_0$. In the range in which this assumption holds, equ. (4) gives:

$$\epsilon_2(\omega) = \left(\frac{2\pi e}{m\omega} \right)^2 \frac{(2\pi)^3}{2} \frac{1}{B_0} |p_{vc}|^2 \int dE g_c(E) g_v(\hbar\omega - E). \quad (4)$$

This means that ϵ_2 is determined by the convolution of the densities of states in the valence and conduction bands $g_c(E)$, $g_v(E)$ for which energy is conserved. If we assume that, as in the crystal, $g_v(E) \sim E^{1/2}$, $g_c(E) \sim E^{1/2}$ we obtain $\omega^2 \epsilon_2 \sim E^2$, in accord with the experimental result shown in Fig. 4 for amorphous Ge. If we further assume that the absorption edge in amorphous Ge corresponds

to the direct $\Gamma_{2'} \rightarrow \Gamma_{25'}$ transitions in the crystal and that the corresponding densities of states are roughly the same, we can estimate B_0 to be about 10^{21} cm^{-3} ($\approx 10^{-4} B$). As the valence band wavefunctions are practically Bloch functions, B_0 gives the reciprocal volume containing the \underline{k} vectors with which the conduction band wavefunctions are constructed. Using the uncertainty relation, we can say that the electronic states are represented by wavepackets extending over a volume $(2\pi)^3 / B_0 \approx 10^{-19} \text{ cm}^3$ (as compared with the valence band wavefunctions which according to our previous considerations extend over volumes two orders of magnitude larger).

(b) With amorphous Si the situation is more difficult because it is very probable that the transitions at the edge correspond to phonon-aided indirect

transitions $\overline{\Gamma}_{25'} \rightarrow \Delta_1$ in the crystal rather than to direct transitions which in crystalline Si take place at a much higher energy. In amorphous Si the intensity of this absorption (Fig. 3) is much enhanced relative to the crystalline absorption (the slope of the linear portion in Fig. 5 is about 14 times higher than the slope in the crystal). In the present context, this means that $F(\mathcal{K}, \mathcal{K}')$ has a non-zero value for $\mathcal{K} \equiv \overline{\Gamma}$, $\mathcal{K}' \equiv \Delta$ (Fig. 6, curve d). In the linear combinations describing the function $|c_{\mathcal{K}'}|_a$ at $\mathcal{K}' = \Delta$, there must be admixed also crystalline wave-functions with $\mathcal{K} = 0$. If $F(\mathcal{K}, \mathcal{K}')$ can be again represented near the maximum by a constant value, one would again expect the linear dependence of $\hbar\omega\sqrt{\epsilon_2}$ vs. $\hbar\omega$ over a relatively small energy interval, as actually observed (Fig. 5).

An alternative description of these transitions has been suggested by Grigorovici (15). He ascribed the enhancement of the absorption as due to frozen-in phonons of a certain effective temperature. Corresponding to the observed factor 14, the effective temperature should be about 5600°K which is very roughly in accord with the effective temperature estimated from X-ray studies of the disorder.

The large enhancement of indirect transitions observed in amorphous Si suggests the necessity to consider such transitions also in Ge. They were neglected in the above arguments but may in fact play an important role because of the high densities of the states involved.

Acknowledgement

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