PHYSICAL REVIEW B VOLUME 7, NUMBER 8 15 APRIL 1973

Refractive-Index Behavior of Amorphous Semiconductors and Glasses

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(Received 28 July 1972)

The refractive-index behavior (magnitude and dispersion) of a variety of optical glasses and amorphous semiconductors is discussed within the same oscillator framework applied earlier to single-crystal refractive-index data. Apart from density differences associated with voids and inefficient packing of disordered atoms, the main quantity of interest turns out to be coordination number as found earlier for single crystals. In tetrahedrally bonded materials (SiO_2, Si, Ge, GaP, GaAs, SiO_x) the refractive-index behavior, as measured by the dispersion energy E_d, is not significantly affected by loss of long-range order, lending considerable support to the view that the particular combination of moments of the ϵ_2 spectrum that determines this oscillator-strength parameter is related solely to short-range interactions. In mixed-oxide glasses the data suggest that admixtures of high-coordination oxides (e.g., BaO or La_2O_3) increase the average cation coordination number above 4 and correspondingly increase the strengths of interband optical transitions. Finally, in semiconductors derived from two-dimensional crystals (As_2S_3) and one-dimensional crystals (Se and Te) it is found that layer-layer and chain-chain coupling, respectively, increase the effective crystalline coordination number above the nearest-neighbor value and that these interactions are largely lost in the amorphous forms. The primary optical effect is a reduction in oscillator strength of lone-pair to conduction-band transitions and a corresponding decrease in E_d.

I. INTRODUCTION

Interest in the optical properties of amorphous semiconductors and glasses has been stimulated by their possible applications as switching elements and optical-transmission media, as well as by their use as passivating materials for integrated circuits. In this paper we will examine the refractive-index behavior (magnitude and dispersion) of several disordered materials and, hopefully, a unified picture will emerge similar in outline to that revealed previously[1] for crystalline solids. Thus, we will focus attention on empirical relationships between refractive indices and the structural and chemical quantities which characterize a material, viz., coordination number and chemical valency. Where possible, comparisons will also be made between amorphous materials and their single-crystal analogs. Finally, we will attempt to relate experimental results to band structure with special attention given to the so-called nonbonded lone-pair valence electrons in such materials as As_2S_3, Te, and Se.

It should be stressed at the outset that bulk properties of disordered materials are more sensitive to preparation techniques than is the case for single crystals, since imperfections such as voids, microcrystallites, and phase separations are not easily controlled or characterized. For example, amorphous films are often composed of disordered atoms interspersed with voids.[2] The void content, at least in amorphous Ge and Si, is strongly dependent on preparation procedures[2] and can range from about 15% in poorly prepared samples to near zero. In the space between voids there is ample evidence[2] that each atom retains its crystalline tetrahedral coordination but that long-range order is destroyed. The above considerations lead us to suspect that any generalizations deduced about the refractive-index behavior of amorphous solids will turn out to be less precise and less reproducible than corresponding generalizations for single crystals.

Rather than present an exhaustive compilation of experimental data, we concentrate on certain restricted classes of amorphous semiconductors and glasses which are either of current interest or which reveal some particularly interesting aspect of the disordered state. These include (i) optical glasses ranging from fused silica to soda-lime silicate glasses to complex glass systems containing many chemical components (e.g., Pb, Ca, and Ba glasses); (ii) the SiO_x system where $0 \leq x \leq 2$; and (iii) the interesting amorphous semiconductors Si, Ge, GaAs, GaP, As_2S_3, Te, and Se.

II. METHOD OF ANALYSIS

The analysis presented here follows closely that given earlier[1] for single crystals. Except in a few cases discussed in Sec. IV, where we make use of moments of ϵ_2 spectra, we focus on fitting refractive-index dispersion data below the band gap to the single oscillator expression

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} , \tag{1}$$

where n is the refractive index for a specified direction of light polarization, E_0 is the energy of the effective dispersion oscillator (typically near the main peak of the ϵ_2 spectrum), E is the photon energy, and E_d is the so-called dispersion energy. The latter quantity measures the average *strength* of interband optical transitions. Its usefulness, which is essentially empirical, rests on the following observations[1] in single crystals.

(i) E_d is very nearly independent of E_0 and consequently provides an independent oscillator-strength quantity which does not depend on the energy scale ("band gap") of the fundamental ϵ_2 spectrum. This contrasts with the commonly used oscillator strength f in the relation

$$n^2 - 1 = \frac{f\Omega_p^2}{E_0^2 - E^2} , \qquad (2)$$

where Ω_p is the plasma frequency of the valence electrons.

(ii) E_d does not depend on the volume density of valence electrons, i.e., internuclear spacings. This result is in marked contrast to the Phillips–Van Vechten dielectric theory,[3] where both the oscillator-strength quantity (Ω_p^2) and the energy-gap parameter (E_g) depend in prescribed ways on internuclear distances.

(iii) Finally, E_d obeys a simple empirical relationship in more than 100 widely different ionic and covalent *crystalline* solids, viz.,

$$E_d = \beta N_c Z_a N_e \text{ eV}, \qquad (3)$$

where

$$\beta = 0.37 \pm 0.04 \text{ eV} \qquad (4)$$

in covalent materials (e.g., C, GaP, ZnS), and

$$\beta = 0.26 \pm 0.03 \text{ eV} \qquad (5)$$

in the more ionic materials (e.g., NaCl, Al_2O_3, TlBr). In Eq. (3), N_c is the coordination number of the cation nearest neighbor[1] to the anion (e.g., $N_c = 6$ in NaCl or $ZnWO_4$ and $N_c = 4$ in Ge), Z_a is the formal chemical valency of the anion (e.g., $Z_a = 1$ in NaCl, $Z_a = 3$ in GaP, and $Z_a = 2$ in Te), and N_e is the total number of valence electrons (cores excluded) per anion (e.g., $N_e = 8$ in NaCl and Ge, $N_e = 10$ in TlCl, $N_e = 12$ in Te, and $N_e = 9\frac{1}{3}$ in As_2S_3).

Our major purpose will be to examine the validity of Eqs. (3)–(5) in disordered solids. It is clear that the coordination number N_c will be central to our discussion, although we should not assume *a priori* that crystalline and amorphous forms of a material necessarily exhibit the same nearest-neighbor coordination. In order to account for voids we use the simplest possible model and assume that voids reduce the average density without affecting the nearest-neighbor coordination in the filled spaces between voids. On the average, however, there may be some small reduction in N_c associated with incomplete or dangling bonds at void boundaries. The primary effect of voids is a reduction in density, and consequently we scale E_d, which is proportional to ϵ_2, by the crystalline-to amorphous-density ratio before drawing conclusions about coordination number. The above considerations are summarized in the proposed relation

$$E_d^a / E_d^x = (\rho^a/\rho^x)(N_c^a/N_c^x) , \qquad (6)$$

where ρ is the density, and a and x refer to amorphous and crystalline forms, respectively.

III. EXPERIMENTAL RESULTS

A. Optical Glasses

We begin this section with a detailed discussion of fused silica (SiO_2) partly because it is a simple chemical system and partly because refractive-index data are available for the single-crystal analog (quartz). The fused silica results have been obtained from the recent index data of Waxler and Cleek.[4] Room-temperature parameter values are given in Table I along with corresponding values in crystalline quartz for both ordinary ray (n_0) and extraordinary ray (n_e) refractive indices. Average values of E_0 and E_d are also tabulated. The value $E_d = 18.1$ eV for crystalline quartz compares with an average $E_d = 18.0$ eV in four other four-coordinated ionic oxides.[1] Note in particular that the oscillator position E_0 is almost exactly the same in both the glassy and crystalline forms, a result that is evident in the uv-reflectivity results of Philipp.[5] Philipp also finds, apart from a small amount of broadening in fused silica, that the detailed structure in the uv-reflectivity spectra of the two materials is identical, leading to the conclusion that optical properties of the SiO_2 system are determined by the SiO_4 tetrahedra and that long-range order is of little consequence. The interband transition strengths, on the other hand, are considerably different with $E_d = 14.71$ eV in fused silica, a value 19% smaller than in crystalline quartz. It should be noted, however, that the density of fused silica is 17% smaller than crystalline quartz even though the Si-O distance remains essentially the same (≈ 1.62 Å). It is tempting, therefore, to attribute the smaller oscillator strength in the disordered form simply to inefficient packing of SiO_4 tetrahedra. Although not easily proved, the *ex-*

TABLE I. Dispersion parameters for fused and crystalline SiO_2. Values of β from Eq. (3) are also given.

	E_d (eV)	E_0 (eV)	β (eV)
Fused SiO_2	14.71	13.38	0.23
Crystal SiO_2 (avg)	18.10	13.33	0.28
Crystal SiO_2 (n_0)	18.04	13.37	···
Crystal SiO_2 (n_e)	18.22	13.25	···

tra 2% reduction in E_d not accounted for by the density decrease may be due to incomplete or dangling bonds characterized by an average Si coordination number slightly less than 4. Robinson[6] has discussed the structure of fused silica in considerable detail and proposes a pentagonal-dodecahedral model which partially fills the volume with a distorted array of SiO_4 tetradedra, although some Si atoms are incompletely bonded to oxygen. The randomness is primarily contained in variations of the Si-O-Si angles associated with distortions of the SiO_4 tetrahedra.

Although the above results suggest that disordered and crystalline forms of SiO_2 are virtually indistinguishable optically when packing-density effects are taken into account, examination of the temperature dependence of the refractive index reveals substantial differences. We can examine the thermo-optic behavior by using Eq. (1) with temperature-dependent parameters E_d and E_0. In differential form Eq. (1) becomes

$$\frac{dn}{dT} = -\frac{(n^2-1)^2}{2n}\left(\frac{dE_0}{dT}\Big/E_d\right)\times\left((1-K)+\frac{(1+K)E^2}{E_0^2}\right), \quad (7)$$

where

$$K = \frac{d\ln E_d}{dT}\Big/\frac{d\ln E_0}{dT} . \quad (8)$$

Values of dE_0/dT and K are given in Table II for fused silica at 293 and 73 °K and for crystalline quartz at 295 °K. The quantity K depends in a rather subtle way on the detailed shape (and its temperature dependence) of the ϵ_2 spectrum. Thus, for a linear energy shift with temperature of the entire ϵ_2 spectrum without distortion, it can be shown that $0 \leq K \leq 1$. The precise value depends on details of the spectral shape. For $K > 1$, it is necessary that the ϵ_2 spectrum change shape as well as shift position with temperature. The value $K = 1$ also forms a boundary between situations where the magnitude of dn/dT increases ($K < 1$) or decreases ($K > 1$) as the photon energy approaches the interband edge. The latter situation also allows for a change in sign of dn/dT as a function of optical wavelength.

Returning to Table II, we note that $K > 1$ in crystalline quartz and $K < 1$ in fused SiO_2. There is also a strong temperature dependence of K in fused silica, although dE_0/dT is independent of temperature to 73 °K. With respect to the "band-gap" temperature dependence, values of dE_0/dT in the two forms of SiO_2 are very similar to magnitudes typical of most solids. It is of interest to note that the larger value of dE_0/dT in fused silica is associated with a very small coefficient of thermal expansion (0.5×10^{-6} °C^{-1}), when compared with crystalline quartz (11×10^{-6} °C^{-1}). It would appear that thermal expansion has very little influence on the thermo-optic behavior of these materials. Much more subtle effects associated with thermal broadening dominate.

In conclusion, we have shown that gross features of the refractive-index behavior of crystalline and disordered forms of SiO_2 are essentially identical when the inefficient packing of atoms in the glassy form is taken into account, while more subtle differences are revealed by comparison of their thermo-optic behavior.

We now ask if other oxide glasses exhibit similarities with fused SiO_2; that is, are they simply loosely packed four-coordinated oxides with values of $E_d \approx 15$ eV and composition-dependent band gaps? Experimental results for a limited assortment of glasses[7,8] are given in Table III. Inspection of Table III leads to the following conclusions.

(i) Apart from the rare-earth glasses [Table III (h)] and very high-Pb glasses [Table III (g)] values of E_d (15.5 ± 10% eV) are very similar to the value found in fused quartz (14.71 eV).

(ii) The optical band gap decreases on addition of other oxides to SiO_2 with the effect increasing in the order CaO, BaO, Na_2O, PbO.

(iii) The optical-transition strengths decrease slightly with the addition of Na_2O but increase somewhat on addition of BaO, CaO, and PbO, with the largest rate of increase occurring for BaO and the smallest for PbO.

(iv) Values of E_d in the La containing glasses[8] (composition unknown) are considerably higher (19.6–21.2 eV) than in the other glasses.

Although a detailed understanding of the trends noted above would require unavailable structural information, we suggest, tentatively, that the observed increase in E_d with additions of BaO, CaO, PbO, and La_2O_3 is primarily a coordination-number effect; that is, all these cations prefer coordination numbers higher than four. For example, single-crystal BaO, CaO, and PbO are all six-coordinated oxides, while La_2O_3 is seven coordinated. In large groups of six-coordinated *crystalline* oxides, we find[1] that $E_d = 25 \pm 2$ eV, compared with $E_d \approx 18$ eV in several four-coordinated oxides, so that it is not unreasonable to suspect

TABLE II. Thermo-optic parameters for fused and crystalline SiO_2 [see Eqs. (7) and (8)].

Material	$\frac{dE_0}{dT}$ (10^{-4} eV/°C)	K
Fused SiO_2 (293 °K)	−5.4	+0.43
Fused SiO_2 (73 °K)	−5.4	+0.83
Crystal SiO_2 (n_0)	−3.9	+1.45
Crystal SiO_2 (n_e)	−4.7	+1.47

TABLE III. Dispersion parameters for assorted oxide glasses.

(a) $100SiO_2 \times xNa_2O$

x	E_d (eV)	E_0 (eV)
0	14.71	13.38
20	14.4	11.9
30	14.5	11.7
40	14.4	11.5
70	14.2	11.1
100	14.1	10.8

(b) $100SiO_2 \times 20Na_2O \times xPbO$

x	E_d (eV)	E_0 (eV)
0	14.4	11.9
5	14.3	11.0
10	14.1	10.2
20	14.6	9.6
30	14.6	8.9
40	15.0	8.7

(c) $100SiO_2 \times 20K_2O \times xPbO$

x	E_d (eV)	E_0 (eV)
0	14.7	11.9
5	14.1	10.8
10	14.2	10.2
20	14.5	9.5
30	14.5	8.9
40	14.9	8.6

(d) $100SiO_2 \times 20Na_2O \times xCaO$

x	E_d (eV)	E_0 (eV)
0	14.4	11.9
5	14.8	12.0
10	15.0	11.8
20	15.5	11.7
30	15.9	11.6
40	15.8	11.4

(e) $100SiO_2 \times 20Na_2O \times xBaO$

x	E_d (eV)	E_0 (eV)
0	14.4	11.9
5	14.7	11.7
10	15.3	11.7
20	16.0	11.5
30	17.0	11.2

(f) $100SiO_2 \times 10Na_2O \times 10K_2O \times xBaO$

x	E_d (eV)	E_0 (eV)
5	15.0	11.9
10	15.2	11.7
20	15.8	11.4
30	16.4	11.3
40	16.8	11.1

(g) $100SiO_2 \times xPbO \times yK_2O$

x	y	E_d (eV)	E_0 (eV)
0	0	14.71	13.38
10	20	14.2	10.2
20	20	14.5	9.5
40	5	15.3	8.5
50	9	15.5	8.0
70	13	16.2	7.6
95	0	17.4	6.9
123	0	18.3	6.4

(h) Rare-earth glasses (Schott)

	E_d (eV)	E_0 (eV)
LaKN14	21.2	11.7
LaFN2	20.3	10.4
LaSFN3	19.6	9.1

that the observed range of E_d in the listed oxide glasses (14.1–21.2 eV) is primarily a consequence of variations in average cation coordination number. The rare-earth ions, as expected, are the most effective in increasing coordination number whereas PbO is the least effective. Of course, there may also be some undetermined variations in E_d associated with differences in the microstructure and void content (density) of the different glass compositions, although such effects, if present, are not easily elucidated in the absence of detailed structural information.

In summary, variations in the refractive behavior of oxide glasses can be understood as arising principally from changes in the band gap with composition. The relatively small transition-strength changes that do occur, particularly in the rare-earth glasses, are probably a result of differences in the average cation coordination number.

It is of interest to reexamine the dispersion behavior of the oxide glasses from the point of view of lens designers, in light of the trends outlined above. Historically,[9] dispersion has been measured using the reciprocal dispersive power (or Abbe value) ν defined by

$$\nu = (n_D - 1)/(n_F - n_C) , \tag{9}$$

where n_D, n_F, and n_C refer to refractive indices at 5890, 4861, and 6563 Å, respectively. It is easy to show using Eq. (1) that

$$\nu = 0.72 E_0^2 [n_D/(n_D + 1)] \tag{10}$$

or

$$\nu = 0.72 E_d^2 (n_\infty^2 - 1)^2 [n_D/(n_D + 1)] . \tag{11}$$

In Eq. (11) n_∞ is the long-wavelength extrapolation. According to Eq. (10), the Abbe value depends almost exclusively on the band gap E_0 since the refractive-index factor changes only from 0.58 to 0.67 as n_D varies from 1.4 to 2.0. We have plotted Eq. (11) in Fig. 1 for several values of E_0 by taking $n_\infty \approx n_D = n$. The top scale gives the band gap from Eq. (10) with $n_D/(n_D + 1) = 0.63$. The field of existing colorless optical glasses shown in the figure clearly reveals the inherent limitations imposed by available band gaps and transition strengths. The lower boundary in the figure as well as the tail for $\nu > 80$ occurs in glasses containing fluorine. Fluorides are known[1] to exhibit smaller values of E_d and larger band gaps than oxides. Because oxides are limited in band gaps to about 13 eV, values of $\nu > 80$ must necessarily occur in nonoxide systems. The increase in the upper boundary shown in the figure for $\nu < 80$ merely reflects the lower band gaps occurring in glass-forming oxides that prefer coordination numbers above four. We can conclude that existing oxide glasses essentially exhaust the obtainable ranges of n and ν (i.e., $14 < E_D < 23$ eV and $E_0 < 13$ eV). It is of interest that liquids tend to have lower values of E_d than solids[1] (e.g., $E_d \approx 11$ eV in CCl_4 and CS_2) suggesting, according to Fig. 1, that ν will be smaller for a given value of n.

B. Disordered SiO_x System

Use of SiO_x and SiO films for passivating and protective layers has prompted some recent interest in their optical properties. For example, Philipp[5] has shown that the above gap reflectivity data can be understood in terms of a microscopic distribution of Si-Si and Si-O bonds and that these bonds exhibit optical properties very similar to those observed in the amorphous-end members Si and SiO_2. He also suggests that short-range order primarily determines the optical properties. In order to interpolate the optical dielectric constant between Si and SiO_2, Philipp proposes the following form:

$$\epsilon_{SiO_x} \approx (1 - \tfrac{1}{2}x)^2 \epsilon_{Si} + (\tfrac{1}{2}x)\, \epsilon_{SiO_2} , \tag{12}$$

where ϵ_{Si} and ϵ_{SiO_2} are the optical dielectric constants of amorphous Si and SiO_2, respectively, and the quadratic term is an attempt to account for the fact that both the absorption-edge position and absorption strength change with increasing Si con-

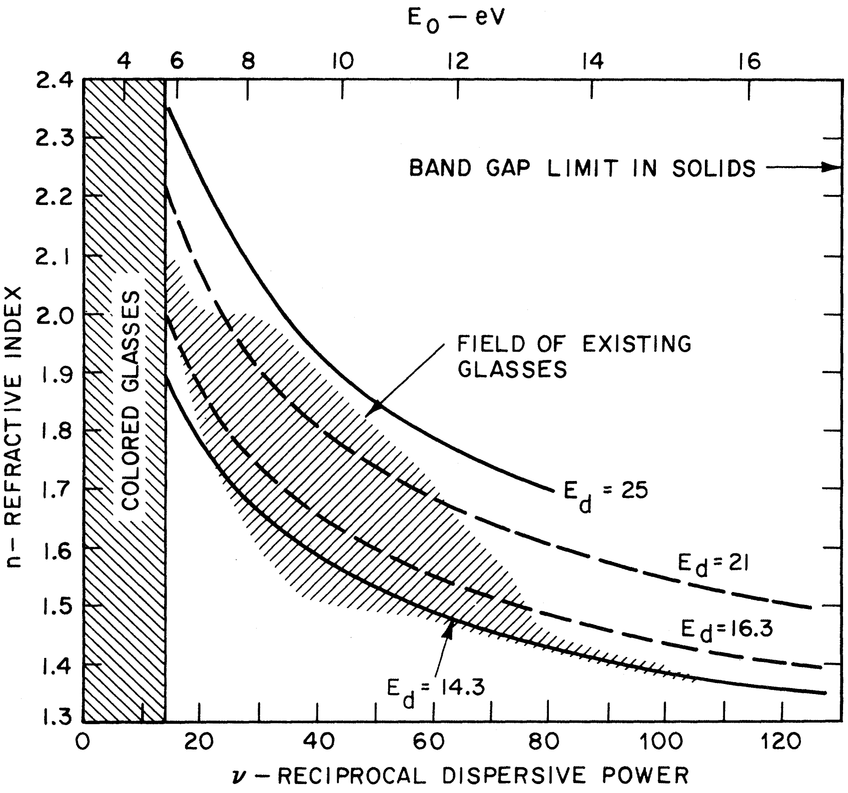

FIG. 1. Refractive index as a function of reciprocal dispersive power ν and oscillator energy E_0 for various values of E_d. The shaded area to the right of $\nu = 14$ gives the field of existing colorless optical glasses, while glasses with $\nu < 14$ would be colored and have been omitted from discussion.

tent. A simple interpolation scheme that falls within the context of the present article would involve *linear* interpolation between the end-member values of E_0 and E_d. Thus, using the values for fused silica shown in Table I and the values $E_d = 38.6$ eV and $E_0 = 3.68$ eV for amorphous Si we assume that

$$E_d(\mathrm{SiO}_x) = 38.6(1 - \tfrac{1}{2}x) + 14.7(\tfrac{1}{2}x) \tag{13}$$

and

$$E_0(\mathrm{SiO}_x) = 3.68(1 - \tfrac{1}{2}x) + 13.38(\tfrac{1}{2}x)\ . \tag{14}$$

The resulting long-wavelength refractive index $n^2 = 1 + E_d/E_0$ is plotted versus x in Fig. 2. The indicated points are taken from the reflectivity data of Philipp.[5] Agreement is fair considering that the actual composition for the $x = 1.5$ point was not accurately known, although no error bars were given.

C. Amorphous Semiconductors

In this section we examine the refractive-index behavior of a few amorphous semiconductors of current interest. Values of E_d and E_0 are given in Table IV along with averages for the crystalline forms. The result for amorphous Si is difficult to analyze in detail because no accurate density information is available for the films used in the measurements, although it should be noted that Chittick[10] reports an approximate density decrease in the amorphous films of 18% ± 6%, which at least overlaps the observed 13% decrease in E_d. Moss and Graczyk[13] find a density decrease of 10–15%, while Brodsky and Stiles[2] have discussed available

TABLE IV. Dispersion parameters and densities (ρ) for several amorphous and crystalline semiconductors.

ρ		E_d (eV)	E_0 (eV)	Ref.
⋯	amorphous Si	38.6	3.7	a
2.33	crystal Si	44.4	4.0	b
5.82	amorphous Te	16	1.4	c
6.25	crystal Te (avg)	37	1.3	d
4.29	amorphous Se	18.6	3.9	e
4.81	crystal Se (avg)	33	3.8	f
3.20	amorphous As_2S_3	22.8	4.7	g
3.42	crystal As_2S_3 (avg)	27	4.5	h

[a] See Ref. 10.

[b] W. Primak, Appl. Opt. 10, 759 (1971).

[c] See Ref. 11.

[d] S. Singh, *Handbook of Lasers* (The Chemical Rubber Co., Cleveland, 1971), pp. 489–507.

[e] W. F. Koehler, F. K. Odencrantz, and W. C. White, J. Opt. Soc. Am. 49, 109 (1959).

[f] I. Gampel and F. J. Johnson, J. Opt. Soc. Am. 59, 72 (1969).

[g] See Ref. 12.

[h] B. L. Evans and P. A. Young, Proc. Roy. Soc. (London) A297, 230 (1967).

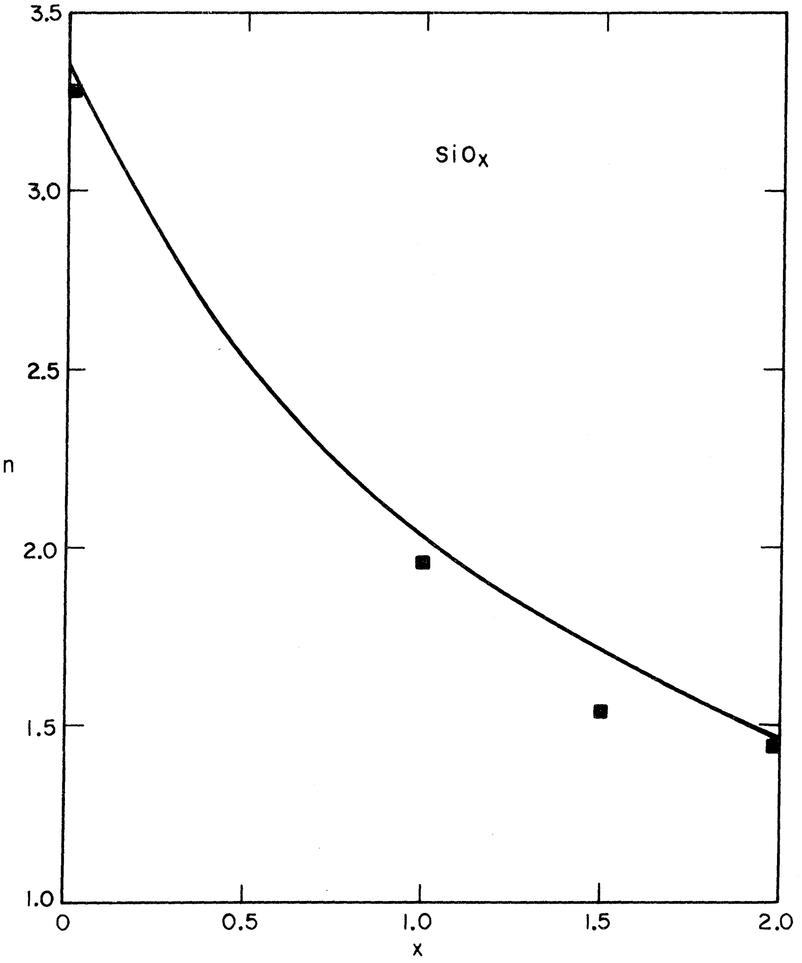

FIG. 2. Refractive index as a function of *x* for the amorphous system SiO_x. The points are taken from Ref. 5.

density information and conclude that the decrease is near 13%. They also conclude that approximately 10% of this decrease is due to voids and the remaining 3% results from inefficient packing of atoms in the "filled" space between voids. The above results suggest that the observed reduction in E_d may be a simple density effect as noted earlier for SiO_2; however, more definite conclusions must await refractive-index dispersion and accurate density measurements on the same film.

The chalcogenide materials listed in Table IV are somewhat more interesting. In the case of Te and Se there is nearly a factor of 2 decrease in E_d in going from crystalline to amorphous forms. The measured ϵ_2 spectra[11] also show a factor of 2 decrease in the vicinity of E_0. In the case of As_2S_3 the decrease is only 16% again in approximate agreement with ϵ_2 spectra.[14] Another point of interest is the slightly larger band gaps in the amorphous forms of all three materials. In order to relate the E_d data to Eq. (3), it is necessary to consider the crystal structure (coordination number). Crystalline (class 32) Te and Se consist of spiral chains of atoms bonded covalently with a nearest-neighbor coordination of two. Adjacent parallel chains are more weakly bonded to one another. Similarly, As_2S_3 consists of two-dimensional layers in which the As coordination number is three. Bonding between layers is relatively weak. If we assume that $N_c = 2$, $Z_a = 2$, and $N_e = 12$ in Te and Se and $N_c = 3$, $Z_a = 2$, $N_e = 9\frac{1}{3}$ in As_2S_3, we find that $\beta(\text{Te}) = 0.77$ eV, $\beta(\text{Se}) = 0.69$ eV, and $\beta(As_2S_3) = 0.48$ eV. These β values are all substantially larger than observed in other covalent crystalline solids, viz., $\beta = 0.37 \pm 0.04$ eV. There is considerable evidence, however, that this discrepancy lies in our choice of too small a coordination number N_c. For example, Levine[15] finds that it is necessary to take $N_c \approx 4$ in Te and Se in order to fit these materials into the widely applicable Philipps–Van Vechten dielectric theory.[3] Furthermore, Hulin[16] as well as Gissler *et al.*[17] have shown that the interaction of a given atom with the four next-nearest neighbors on adjacent chains, when compared with the two nearest neighbors in the same chain, is only about a factor of 2 smaller[18]

TABLE V. Summary of effective coordination numbers in amorphous and crystalline forms of three semiconductors.

	Crystal	Amorphous	Nearest-neighbor N_c
As_2S_3	3.6	3.2	3
Te	4.0	2.1	2
Se	3.3	2.2	2

in Te and a factor of 3 smaller[18] in Se. Thus we might speculate that the effective coordination number is about $2+\frac{4}{2}=4$ in Te and $2+\frac{4}{3}=3.3$ in Se. Using these values for N_c, we find that $\beta(\text{Te}) \approx 0.39$ eV and $\beta(\text{Se}) \approx 0.41$ eV, in agreement with other covalent materials and in essential agreement with one another. In the case of crystalline As_2S_3, we require $N_c \approx 3.6$ rather than $N_c = 3$ in order to fit this material into the general covalent picture with $\beta \approx 0.4$ eV. A value $N_c > 3$ is not surprising in view of the octahedral coordination of those As atoms which "bond" the layers together.[19] Within our present model, the above value of N_c suggests that about 20% of the As atoms act as bonding points between layers. The relatively modest increase in N_c above 3 for crystalline As_2S_3 implies that interactions between layers in As_2S_3 are much weaker than chain-chain interactions in Te and Se. Finally, we should point out other independent evidence that non-nearest neighbors can influence E_d under special circumstances. In the case of solid H_2O (ice) each cation (H^+) is surrounded by two oxygen atoms at distances of 1.0 and 1.7 Å. Using $E_d = 8.7$ eV and taking $Z_a = 2$ and $N_e = 8$, we find that $\beta = 0.54$ eV for $N_c = 1$ and $\beta = 0.27$ eV for $N_c = 2$. These values bracket the covalent value of 0.37 eV and suggest a nonintegral effective proton coordination number of about 1.5 in ice.

Turning now to results for the amorphous forms listed in Table III, it is necessary first to normalize out any density differences between the disordered materials and their single-crystal analogs. Thus amorphous As_2S_3 is only 7% less dense[20] than crystalline As_2S_3 while E_d is about 16% smaller. The extra 9% reduction may result from a small decrease in the effective As coordination number (from $N_c \approx 3.6$ to $N_c \approx 3.2$) due to a reduction in the number of octahedral bonding points between layers by roughly a factor of 3. The value for amorphous As_2S_3 is not very different from that reported by Varpolin and Porai-Koshits[19] using x-ray radial-distribution analyses. A similar argument can be given for amorphous Te and Se. The 57% decrease in Te includes a contribution of only about 9% due to the density decrease,[21] while only 11% of the total 44% decrease in Se is due to density.[21] We suggest that the remaining large decrease in E_d in Te (48%) and in Se (33%) is due to reduced interaction between chains[11] in the amorphous forms and a consequent tendency for N_c to approach the single isolated chain value of 2. Using this model we find that $N_c \approx 2.1$ in amorphous Te and $N_c \approx 2.2$ in amorphous Se. The above results are summarized in Table V. Apart from trivial density factors, the amorphous forms of these materials differ from their crystalline analogs, within the present model, because interchain coupling is weakened in the case of Te and Se, and interlayer coupling is weakened in As_2S_3. Futhermore, we would suggest that all these materials fall into the same general covalent framework described by Eqs. (3) and (4) with $\beta \approx 0.4$ eV.

IV. ENERGY-BAND CONSIDERATIONS

In the foregoing presentation we have concentrated on essentially three classes of amorphous solids, viz., ionic oxides (SiO_2), covalent materials bonded with directed sp^3 tetrahedral bonds (Si), and covalent materials containing unshared (lone-pair) electrons (Te, Se, As_2S_3). The latter situation has been discussed recently by Kastner.[22] Figure 3 shows schematic energy-level diagrams for these three types of solids. For purposes of comparison, we have forced the energy gaps to be equal. Note that the valence s states lie far below the top of the valence band in SiO_2 and Se, and that the band edge in Se involves transitions between lone-pair p states and antibonding conduction-band states. With these distinctions in mind it is of interest to compare published[2,5,11,14] ϵ_2 spectra for these different classes of materials in both their crystalline and disordered forms. The experimental results are presented in Figs. 4–6 for SiO_2, Si, and Se. The principal feature of the SiO_2 data, as noted earlier, is the presence of the same sharp structure in both crystalline and disordered forms. We have, in fact, omitted the data for amorphous SiO_2 in Fig. 4 since the curve closely mirrors the crystalline results lowered in magnitude by about 20%. It is clear that loss of long-range order has only mildly affected the optical properties and that "localized" excitonic transitions involving individual SiO_4 tetrahedra must dominate. This very simple situation is certainly related to the relatively ionic character of SiO_2. In the case of covalent silicon, sharp structure associated with long-range order found in the single-crystal data is essentially averaged out in the amorphous material, with the resulting ϵ_2 spectrum being more or less a smoothed version of the single-crystal result shifted to lower energy and reduced in magnitude.

The Si results noted above are very much like those reported for amorphous Ge by Donovan *et al.*[23] and for six amorphous III-V compounds

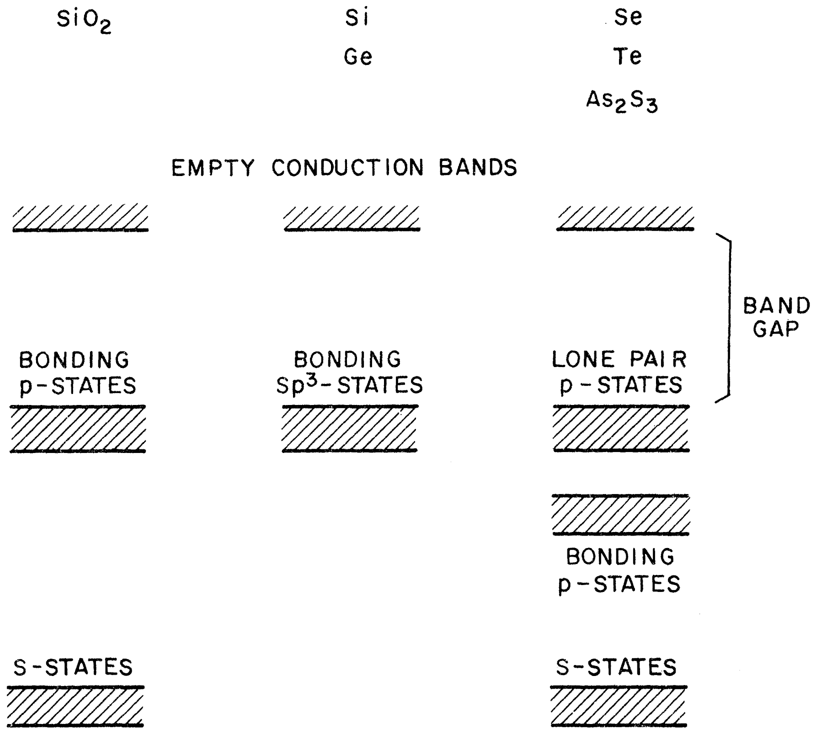

FIG. 3. Schematic band-structure diagrams for the three classes of materials considered (see Ref. 22).

by Stuke and Zimmerer.[24] It is of interest to compute E_d for these other materials from published ϵ_2 spectra using the moment relation[1]

$$E_d^2 = M_{-1}^3/M_{-3}\,, \tag{15}$$

where the rth moment M_r is defined by

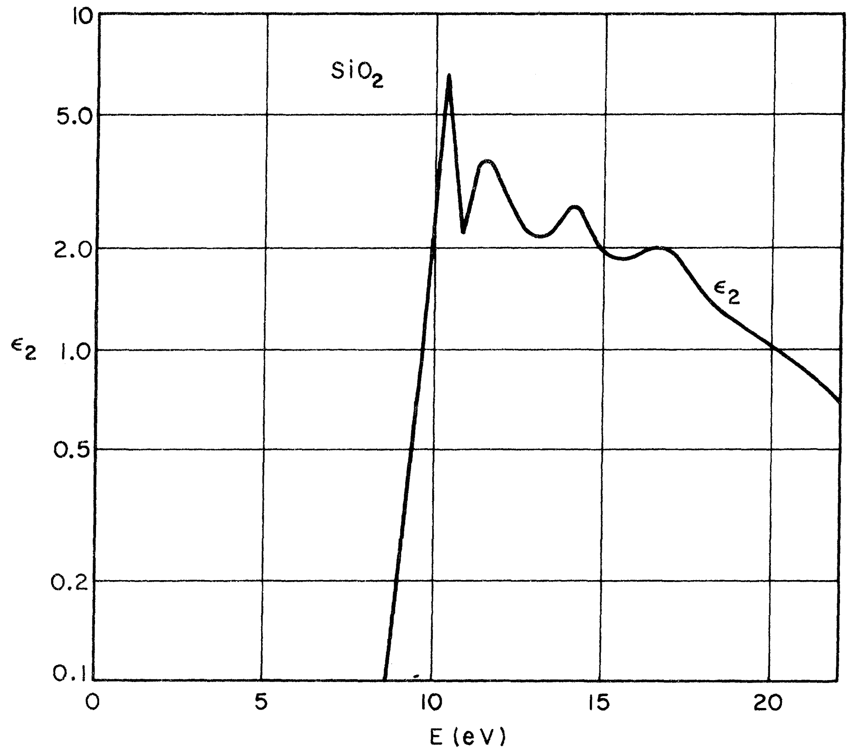

FIG. 4. Loss part of dielectric function for crystalline SiO$_2$ (Ref. 5). The curve for amorphous SiO$_2$ essentially mirrors this curve about 20% lower in magnitude.

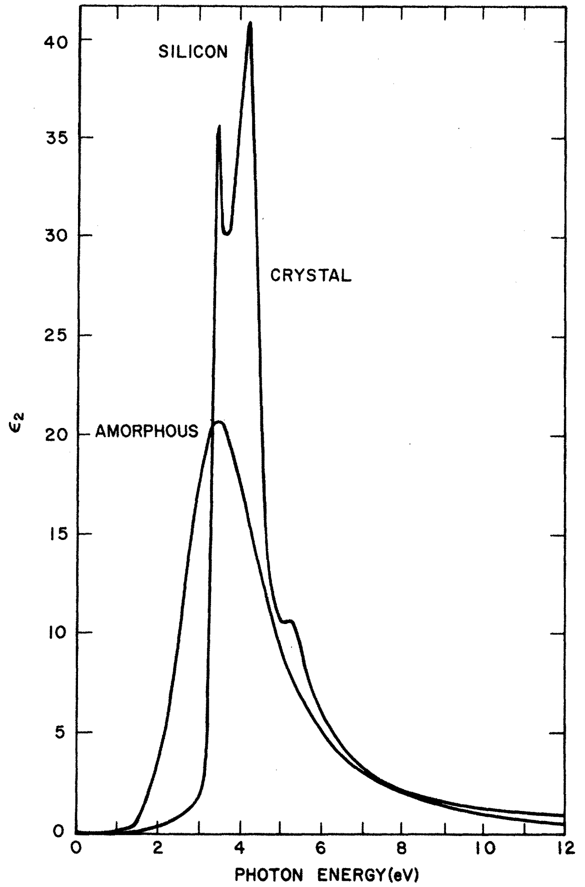

FIG. 5. Loss part of dielectric function for crystalline and amorphous Si (Ref. 2).

$$M_r = (2/\pi)\int_{E_g^*}^{\infty} E^r \epsilon_2(E)dE\,; \tag{16}$$

E is the photon energy and E_g is the band gap. Results are given in Table VI. We have omitted InP, GaSb, InSb, and InAs from the tabulation because plots of ϵ_2/E^3 vs E for these materials show a lack of convergence at low energies resulting, presumably, from experimental errors. In low-band-gap materials, the moment M_{-3} is very sensitive to the values of ϵ_2 near the gap. Returning to Table VI, we note that the value $E_d \approx 34$ eV obtained from the ϵ_2 spectrum of amorphous Si is somewhat less than the value $E_d = 38.6$ eV obtained from refractive-index dispersion data on different films (see Table IV). A more detailed comparison cannot be made at present because precise density information is not available. It is possible, perhaps, that the surface oxide contamination on Si described recently by Philipp[26] affects the reflectivity data and contributes to the low value of E_d. More definite conclusions are possible for amorphous Ge. The low-density (87% of crystalline) films[22] deposited at room temperature yield a value $E_d = 35$ eV which, when corrected for density, give $E_d = 40 \pm 1$ eV compared with $E_d = 41$ eV in crystalline Ge. In films[23] deposited at 250–300 °C,[25] the absorption edge is shifted upward from 0.6 to 0.8 eV resulting in a lower value of M_{-3}, and the density is near that of crystalline Ge. For this material $E_d = 39 \pm 1$ eV, which is very close to the crystalline value. Similarly, for both GaP[24] and GaAs[24] $E_d = 34$ eV in their amorphous forms, but density corrections yield $E_d = 37 \pm 3$ eV nicely overlapping the crystalline values of 37 eV. Note, however, the very large reduction in E_0 in amorphous GaP when compared with GaAs, Ge, or Si. The above results lend considerable support to the view that E_d is a measure of oscillator strength that is largely independent of the long-range order in tetrahedral diamond-type compounds. The ϵ_2 spectrum changes its shape and magnitude so as to keep E_d constant, and in particular this requires smaller peak values of ϵ_2 in amorphous material if the band gap is shifted to lower energy.

A qualitatively different situation from that in Si and Ge exists in Se (and also in Te and As_2S_3), where the two main peaks at 4 and 8 eV are preserved in amorphous material, but the strength of the lower-energy peak markedly decreases. This peak is associated[22] with transitions between filled lone-pair p states and empty antibonding p states (see Fig. 3). Within the framework of our coordination model, we would conclude that the strengths of these lone-pair transitions depend rather strongly on interchain and interlayer coupling, whereas their energy positions are relatively independent of these interactions. Some experimental support for this view is provided by the photoelastic data of Galkiewicz and Tauc,[12] who find that the quantity $K = d\ln E_d/d\ln E_0 \approx 44$ in amorphous As_2S_3, where the indicated fractional changes are associated with pressure-induced dilatation. Thus, transition strengths are much more strongly affected by strain in this material than transition energies. For comparison it should be noted that $K \approx -0.51$ in GaAs.[12]

TABLE VI. Summary of dispersion parameters obtained using moments of ϵ_2 spectra.

		Amorphous		Crystalline		
	ρ^a/ρ^x	E_d (eV)	E_0 (eV)	E_d (eV)	E_0 (eV)	Ref.
Si	$\cdots$	34	3.1	44.4	4.0	2
Ge	0.87 ± 0.02	35	2.3	41	2.7	23
Ge	1.0 ± 0.03	39	2.6	41	2.7	25
GaP	0.85-1	34	3.1	36.8	4.6	24
GaAs	0.85-1	34	2.9	36.7	3.7	24

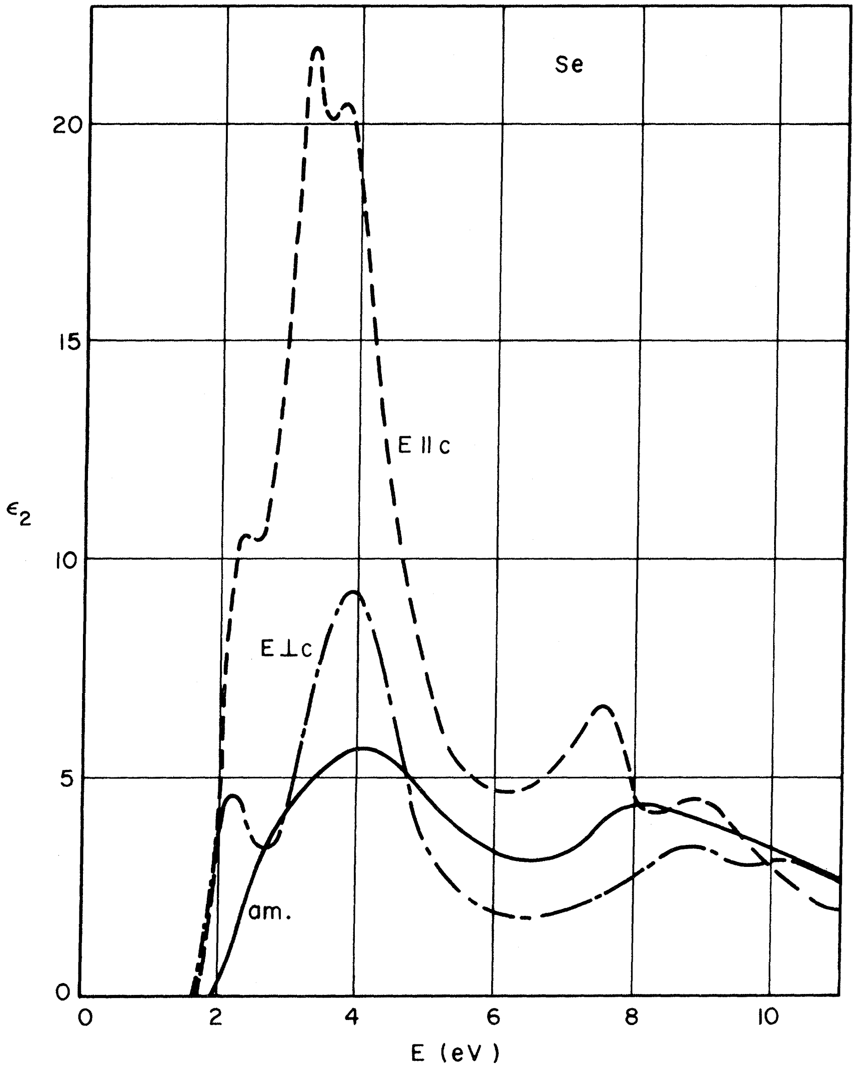

FIG. 6. Loss part of dielectric function for crystalline and amorphous Se (Ref. 11).

V. CONCLUSIONS

We have suggested that the refractive-index behavior of amorphous solids can be understood within the same general framework established earlier for crystalline solids with the same value of β. Apart from important, though not always reproducible, density differences associated with inefficient packing of disordered atoms, the main quantity of interest is coordination number. In tetrahedrally bonded materials, whether ionic (SiO_2) or covalent (Ge), the results indicate that the refractive-index behavior, as measured by the dispersion energy E_d, remains largely unaffected by loss of long-range order. That is, the nearest-neighbor environment remains largely intact, and it is this environment which dominates the optical properties. In the mixed oxide glass systems we suggest that the observed variations in transition strengths E_d result primarily from changes in the average nearest-neighbor coordination number produced by admixtures of high-coordination oxides (e.g., BaO or La_2O_3). Finally, in two-dimensional crystals (As_2S_3) and one-dimensional crystals (Te and Se), it is proposed that layer-layer and chain-chain bonding, respectively, increase the effective coordination number above the nearest-neighbor value and that these interactions are effectively lost, or at least greatly reduced, in the amorphous forms. The primary optical effect is a reduction in oscillator strength of lone-pair to conduction-band transitions.

ACKNOWLEDGMENTS

The author wishes to thank Professor J. Tauc for informative discussions on the optical properties of amorphous semiconductors and M. DiDomenico, Jr. and S. Knight for helpful comments on the manuscript.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 8 15 APRIL 1973

Electronic Properties of an Amorphous Solid. III. The Cohesive Energy and the Density of States*

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(Received 21 July 1972)

The effect of topological disorder on the cohesive energy and the electronic density of states of amorphous Si and Ge is investigated. The methods used include moment expansions and various exactly soluble models that include the Bethe lattice and Husimi cactus lattices, for which an extremely compact derivation of the density of states is presented. An isolated topological defect in a diamond cubic lattice is also studied. The question of the existence of square-root band edges in topologically disordered systems is examined. A review of recent experimental evidence, relating to the shape of the density of states, is given.

I. INTRODUCTION

In the tight-binding approach to the electronic properties of amorphous semiconductors such as *a*-Si, one can distinguish two aspects of the lack of long-range order that characterizes these materials. First there is the random variation in the size of matrix elements which represent interactions between neighboring orbitals. Second there is the random character of the topological network defined by the bonds between neighboring sites. The present paper concludes a series[1,2] of three in which the topological aspect of disorder is treated in isolation by defining a simple model Hamiltonian, appropriate to amorphous Si or Ge, in which only nearest-neighbor interactions are considered and the variation in the size of the interactions is neglected. The model, which is described more fully in the first two papers of this series,[1,2] can have no pretension to anything like a complete description of an amorphous semiconductor. It merely elucidates the relationship between band structure and topological properties.

The previous papers[1,2] were chiefly devoted to the demonstration that, for such a model, various properties of the density of states are independent of the details of structure, provided that it is everywhere tetrahedrally coordinated, so they obtain for periodic and nonperiodic systems alike. These include the existence of a gap in the density of states,[1–3] the attainment of various bounds,[1,2] and the existence of two δ functions in the density of states.[1,2] (If the overlap parameters V_1 and V_2 are given values appropriate to Si or Ge, the gap is between valence and conduction bands and the δ functions are at the top of each band.[4,5]) The purpose of the present paper is to consider properties that are *not* independent of the structure. These