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PHYSICAL REVIEW B VOLUME 6, NUMBER 6 15 SEPTEMBER 1972

Pressure Dependence of the Refractive Index of Amorphous Lone-Pair Semiconductors[*,†]

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(Received 22 May 1972)

The pressure dependence of the refractive index (*dn/dP*) of several amorphous chalcogenide semiconductors is reported. *dn/dP* is positive for materials containing group-VI elements in twofold coordination (lone-pair semiconductors), whereas it is negative for tetrahedral semiconductors. Furthermore, *dn/dP* is the same for the amorphous and crystalline phases of a given semiconductor. Although a one-oscillator (Penn) model adequately predicts *dn/dP* for tetrahedral semiconductors, a similar approach does not predict the positive *dn/dP* of lone-pair semiconductors. Local-field corrections appear to be the cause of the positive *dn/dP*. The Lorenz-Lorentz description of the local field predicts *dn/dP* in agreement with experiment for most molecular lone-pair materials. It fails, however, for materials containing large concentrations of group-IV elements. The limitations of the local-field correction in describing *dn/dP* of partially molecular semiconductors is discussed.

INTRODUCTION

The pressure dependence of the refractive index of semiconductors is related to the pressure-induced shifts of the principal interband absorption processes. For tetrahedral semiconductors and compounds of the $A^N B^{8-N}$ type, Phillips[1] describes the principal interband absorption by a single-oscillator model, with an oscillator of energy E_σ, a modified Penn gap.[2] The value of E_σ is actually determined from the refractive index n by

$$n^2 - 1 = (\hbar\omega_p / E_\sigma)^2 , \tag{1}$$

where $\omega_p = (4\pi N e^2/m)^{1/2}$ is the plasma frequency. N is the density of valence electrons participating in the principal interband absorption. The plasma frequency changes with pressure as the reciprocal volume. For group-IV elements the dependence of E_σ on interatomic spacing a follows the empirical relation

$$E_\sigma \propto a^{-2.5} . \tag{2}$$

With this information, Van Vechten[3] calculated the strain dependence of the refractive index. He obtained good agreement with the experimental values for the group-IV elements. One obtains the same value of $(1/n)(dn/dP)$ for the amorphous and crystalline phases of the same substance.

Thus one can use n as a measure of E_σ which is associated with the strength of the chemical bond. The volume dependence of n can test to what extent this association is valid. The simple approach of Phillips and Van Vechten is especially attractive in the case of amorphous semiconductors where the physical properties cannot be described by band theory, and one might hope to relate observed physical properties to the chemical bonding.

Phillips's theory has been limited to $A^N B^{8-N}$ compounds. Most amorphous semiconductors are, however, lone-pair (LP) semiconductors[4]—those containing group-VI elements in twofold coordination. These, of course, are not $A^N B^{8-N}$ materials. The purpose of this work is to determine to what extent n is a measure of bond strength in amorphous LP semiconductors.

This paper reports measurements[5] of the pressure dependence of the refractive index n or of the optical path length nl (l is the sample thickness) of amorphous layers of As_2S_3, As_2Se_3, $GeSe_2$, GeSeTe, and of the alloy glass $Ge_{16}As_{35}Te_{28}S_{21}$. We find that $(1/n)(dn/dP)$ is positive for these materials, whereas it is negative for the tetrahedral semiconductors. Moreover, for several of the chalcogenide materials, $(1/n)(dn/dP)$ is an order of magnitude larger than is observed for tetrahedral semiconductors.

These results cannot be explained by Eqs. (1) and (2). In the following we examine whether the different pressure dependence of the refractive index in the chalcogenide materials is a result of their different electronic structure, or whether the fact that these materials are molecular solids precludes the use of n as a measure of the strength of the chemical bonds.

EXPERIMENTAL DETAILS AND COMPARISON WITH PREVIOUS WORK

The experiments were carried out in an optical pressure vessel using He as the pressure medium. The maximum pressure was 2 kbar. No hysteresis effects were observed. For the As_2S_3 sample,[6] which was 1 mm thick, we measured the shift with pressure of the position of spatially localized interference fringes produced in reflection by a He-Ne laser operating at $\lambda = 3.391\ \mu m$. This is essentially the technique used by Vedam[7] except that we use an InSb photodiode rather than an infrared image converter to count fringes. The four other chalcogenide materials were prepared by radio-frequency sputtering in the form of self-supporting thin films 5–10 μm thick.[8] For these samples we measured the energy shift of the interference fringes at phonon energies well below the absorption edge.

In both cases one measured the pressure shift of the optical path length (nl) which is related to $(1/n)(dn/dP)$ as

$$\frac{1}{nl}\frac{d(nl)}{dP} = \frac{1}{n}\frac{dn}{dP} - \frac{K}{3}\ , \tag{3}$$

where K is the compressibility. The measured values of $(1/nl)[d(nl)/dP]$ are given in Table I for the four materials. Unfortunately, for several materials K has not been measured. The measurement of K is complicated in the case of a-$GeSe_2$ and the amorphous tetrahedral semiconductors because these materials cannot be prepared in bulk form for sound-velocity measurements.

Where values of K were available, $(1/n)(dn/dP)$ was determined and listed in Table I.[9] For comparison, Table I also gives values of $(1/nl)[d(nl)/dP]$, $(1/n)(dn/dP)$, K, and n for amorphous Se,[8] for vitreous and crystalline quartz,[10] for diamond,[11] and for several amorphous and crystalline tetrahedral semiconductors which have been studied by Connell and Paul.[12]

One notices the following general behavior: dn/dP is positive for the chalcogenides and negative for the tetrahedral materials.[13] The compressibility K is large for the chalcogenide semiconductors and small for the tetrahedral semiconductors. On the other hand, no clear trend can be identified in the values of n for the various materials. The values of $(1/n)(dn/dP)$ for the amorphous and crystalline phases of the tetrahedral semiconductors are similar. Connell and Paul[12] conclude from this fact that dn/dP is determined by short-range order.[14]

The fact that the pressure coefficient of n is positive for the chalcogenide semiconductors but negative for the tetrahedral materials means that the volume dependence of the chemical bond is different for the two classes of materials if n is related to the bond strength as in Eq. (1). Let us examine this possibility next.

ONE-OSCILLATOR MODEL

As mentioned above, the approach of Phillips and Van Vechten as expressed in Eq. (1) satisfactorily predicts dn/dP for the tetrahedral semiconductors. This approach is effectively a one-oscillator model.

The refractive index n is related to $\epsilon_2(\omega)$, the imaginary part of the dielectric function, by

$$n^2 - 1 = (2/\pi)\int_0^\infty [\epsilon_2(\omega)/\omega]\, d\omega\ , \tag{4}$$

where $\hbar\omega$ is the photon energy. The refractive index n is measured at photon energies small compared with the absorption edge. The factor ω^{-1} in the integrand of Eq. (4) allows us to truncate the integral at some energy $\hbar\omega'$ which is large compared with E_σ. In other words, we assume that n is determined by the valence electrons. If E_σ is well separated from higher-energy excitations, the f sum can also be truncated:

$$\int_0^{\omega'} \omega\epsilon_2\, d\omega = \tfrac{1}{2}\pi\,\omega_p^2\ , \tag{5}$$

where ω_p is determined only by valence electrons. If ϵ_2 is strongly peaked at E_σ, Eq. (4) reduces to Eq. (1).

The success of the one-oscillator model in the case of the tetrahedral semiconductors rests on the fact that the ϵ_2 spectra of these materials contain one broad peak, as shown in Fig. 1(a). One observes, in contrast, two peaks in the ϵ_2 of materials containing group-VI elements in twofold coordination. An example is given in Fig. 1(b).

The reason for the different ϵ_2 spectra is related to the different chemical bonding in tetrahedral semiconductors and those containing group-VI elements in twofold coordination.[4] The valence band of Ge, for example, has an origin different from that of Se. If the states in the solid are con-

TABLE I. Data and calculated parameters for amorphous (a-) and crystalline (c-) materials. K is compressibility, n is refractive index, l is sample thickness, η is defined in Eq. (10).

Material	K (10^{-6} bar^{-1})	$\frac{1}{nl}\frac{d(nl)}{dP}$ (10^{-6} bar^{-1})	$\frac{1}{n}\frac{dn}{dP}$ (10^{-6} bar^{-1})	n	η	$-\frac{1}{2}(n^2+2)$	Ref.[a]
a-$Ge_{16}As_{35}Te_{28}S_{21}$	7.6[b]	5.5 ±1	8.0 ±1.5	3.1 ±0.1[c]	−3.5 ±0.4	−5.8 ±0.4	P
a-As_2S_3	9.3 ±0.4[d]	3.6 ±0.2	6.8 ±0.4	2.41[e]	−2.5 ±0.1	−3.9	P
a-As_2Se_3		4.9 ±0.6					P
a-GeSeTe		2.6 ±0.5					P
a-$GeSe_2$		0 ±0.5					P
a-Se	10.0[f]	7.7	11.0	2.50[g]	−3.9	−4.1	7
c-SiO_2	2.6	−0.19	0.667	1.54	−1.32	−2.18	10
a-SiO_2	2.69	−0.26	0.631	1.46	−1.33	−2.06	10
c-C	0.173		−0.053	2.42	+1.1	−3.92	11
a-Si			−0.05				12
c-Si	1.02	−0.6	−0.3	3.4	+1	−6.8	12
a-Ge			−0.8				12
c-Ge	1.33	−1.4	−1.0	4.0	+2.3	−9.0	12
a-GaP			−0.25				12
c-GaP	1.13	−0.7	−0.3	3	+0.9	−5.5	12
a-GaAs			−0.7				12
c-GaAs	1.34	−1.1	−0.7	3.4	+1.8	−6.8	12

[a] P denotes present work. Numbers correspond to reference numbers in the text.

[b] From 0.1% measurements of longitudinal and transverse sound velocity [D. E. Bowen (private communication)].

[c] K. Murase (private communication).

[d] This value was obtained from Young's modulus and shear modulus furnished by Ref. e.

[e] Servo Corp. of America.

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sidered to be a broadened superposition of molecular states of the constituent bonds, then the valence band of Ge is the bonding (σ) band and the conduction band is the antibonding (σ^*) band. In Se, on the other hand, the valence band is the LP band. The LP band is expected to lie midway in energy between the σ and σ^* bands. Whenever a material contains a group-VI element as a major constituent, the valence band will be the LP band. Thus, the single broad peak in ϵ_2 of Ge is caused by σ to σ^* transitions; the two peaks in ϵ_2 for Se are caused by LP to σ^* and by σ to σ^* transitions, respectively.

TWO-OSCILLATOR MODEL

As we have seen, the assumption leading to Eq. (1)—that ϵ_2 consists of one peak—is reasonably justified in the case of Ge. For Se, Eq. (1) must be modified. To describe the transitions originating from the LP band and from the bonding band we use a two-oscillator model characterized by oscillator strengths f_{LP} and f_σ at energies E_{LP} and E_σ, respectively. Then Eq. (4) yields

$$n^2-1=f_{LP}/E_{LP}^2+f_\sigma/E_\sigma^2 \; . \qquad (6)$$

Again we have assumed that the integral of Eq. (4) can be truncated. Equation (6) relates four unknowns to the single measured quantity n. Let us examine Eq. (6) more closely to see if it can be simplified.

Se has two LP electrons and two bonding electrons per atom. Thus we expect $f_{LP}=f_\sigma$. Since $E_\sigma=2E_{LP}$ as seen in Fig. 1(b), the second term on the right-hand side of (6) contributes about $\frac{1}{5}$ of n^2-1. In all materials except the elements S, Se, and Te, however, there are fewer LP electrons than σ electrons. Thus there are 12 bonding

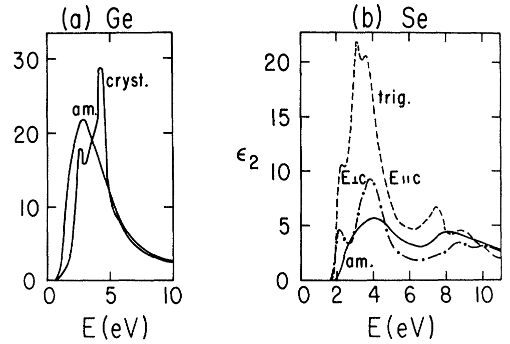

FIG. 1. Imaginary part of the dielectric constant vs photon energy for crystalline and amorphous (a) Ge (Ref. 15) and (b) Se (Refs. 16–18).

electrons per molecule in As_2S_3 but only six LP electrons. In most chalcogenide semiconductors the second term in (6) will contribute appreciably to n^2-1 and cannot be neglected.

It appears from Fig. 1(b) that $E_{LP}=\frac{1}{2}E_\sigma$ for Se. This simplifying assumption may not be valid for other LP semiconductors, especially if they are very ionic.[19] If E_σ is well separated from higher-lying excitations, we may truncate the f sum as in Eq. (5). This gives $f_{LP}+f_\sigma=\frac{1}{2}\pi\omega_p^2$, where ω_p is determined by the total number of bonding and LP electrons which are four per atom in Se. Using this relation,

$$n^2-1=B[(\hbar\omega_p)^2/E_\sigma^2] , \qquad (7)$$

where

$$B=\left(\frac{f_{LP}}{f_\sigma}+1\right)^{-1}\left[1+\left(\frac{E_\sigma}{E_{LP}}\right)^2\frac{f_{LP}}{f_\sigma}\right] . \qquad (8)$$

Since B depends only on the ratios f_{LP}/f_σ and E_σ/E_{LP} it is permissible to assume that B is independent of pressure for the group-VI elements. We discuss this point further below.

When pressure is applied, the sample (assumed isotropic) will undergo strain dl/l. Since Eqs. (1) and (7) are identical except for the factor B, their logarithmic derivatives with respect to strain are identical. After rearranging, this derivative can be written

$$\frac{l}{n}\frac{dn}{dl}\frac{n^2}{n^2-1}=\frac{l}{\omega_p}\frac{d\omega_p}{dl}-\frac{l}{E_\sigma}\frac{dE_\sigma}{dl} . \qquad (9)$$

We define the measured quantity η:

$$\eta=\frac{l}{n}\frac{dn}{dl}\frac{n^2}{n^2-1} . \qquad (10)$$

The model leading to Eq. (9) or (1) then predicts

$$\eta=-\frac{3}{2}-\frac{l}{E_\sigma}\frac{dE_\sigma}{dl} \qquad (11)$$

because $(l/\omega_p)(d\omega_p/dl)=-\frac{3}{2}$.

Equation (11) is the relation Van Vechten[20] used to explain the pressure dependence of the refractive index for the group-IV elements. His procedure is simply the following. He assumes that E_σ depends only on the nearest-neighbor distance for the group-IV elements. In particular, he assumes that it is independent of the principal quantum number. Therefore, a plot of E_σ vs nearest-neighbor distance a for the elements C (diamond), Si, Ge, and Sn gives the pressure dependence of E_σ. He finds $E_\sigma\propto a^{-2.5}$ as shown in Fig. 2. Substituting $(l/E_\sigma)(dE_\sigma/dl)=-2.5$ in Eq. (11) gives $\eta=1.0$. As can be seen from Table I, $\eta=1.0$ is within experimental error of the measured values for diamond and Si. The agreement is not as good for Ge and Sn, but Van Vechten argues that this is a result of the proximity of d states which invalidates the truncation of Eq. (5). Note that η is also positive for GaP and GaAs. The success of the foregoing procedure rests on the equivalence of the measured strain dl/l and the relative change in bond length da/a.

Just as diamond and Si are typical of tetrahedral semiconductors in the pressure dependence of their refractive index, we expect S and Se to be typical of LP semiconductors. In order to test Eq. (11) we need to know how E_σ depends on the nearest-neighbor distance for the elements S and Se. Figure 2 shows that E_σ decreases with increasing a for S and Se, as it does for group-IV elements.

In computing E_σ from Eq. (7) we have assumed $f_{LP}=f_\sigma$ and $E_{LP}=\frac{1}{2}E_\sigma$. These assumptions are reasonable for group-VI elements since there are equal numbers of bonding and LP electrons and the LP band lies midway between the σ and σ^* band.[22] Furthermore, the relative position of the LP band between the σ and σ^* bands is expected to remain the same as a is changed slightly. Therefore, as mentioned above, we assume B is independent of P.

If a is not altered at all by pressure, Eq. (11) predicts $\eta=-\frac{3}{2}$. The experimental values of η for Se and As_2S_3 are about $\eta\approx-3$. Any contribution to Eq. (11) from $(a/E_\sigma)(dE_\sigma/da)$ makes the calculated value of η a smaller negative quantity or positive, as for the tetrahedral materials. Therefore, we are forced to conclude that Eq. (8) is not valid for group-VI elements.

LOCAL-FIELD CORRECTIONS

From the foregoing discussion we conclude that for chalcogenide materials the refractive index

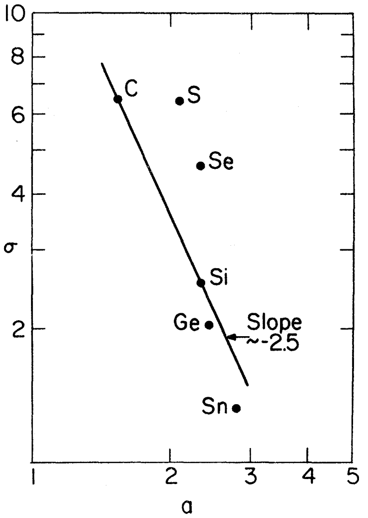

FIG. 2. Log-log plot of $\frac{1}{2}E_\sigma$ (in eV) against nearest-neighbor distance a in Å (c.f. Ref. 21).

cannot be related to the bond strength as in Eq. (8). This is because they are molecular solids. It is well known that trigonal Se and Te are composed of molecular units which are one-dimensional chains; As_2S_3 is composed of two-dimensional layers. Amorphous Se is thought[23] to contain rings (like rhombic S and monoclinic Se) as well as chains, and there is evidence that the layer structure of crystalline As_2Se_3 is preserved in the glass.[24] In all of these materials the bonding within molecular units is predominantly covalent, but the molecular units are held together by weaker Van der Waals forces. On the other hand, Ge is entirely covalent: There are no molecular units.

The compressibilities associated with Van der Waals forces are larger than those associated with covalent bonds. This explains why the chalcogenides have compressibilities an order of magnitude larger than the tetrahedral semiconductors. In materials like Se and As_2S_3, the distance between molecular units will be changed more by pressure than the covalent bond lengths. The application of pressure pushes the molecular units together without appreciably altering their internal coordinates.

Dexter[25] has shown that in a solid held together by Van der Waals forces the refractive index is described quantum mechanically by the Lorenz-Lorentz local-field equation:

$$\frac{(n^2-1)}{(n^2+2)} = \tfrac{4}{3}\pi N\alpha \ , \tag{12}$$

where N is the number of molecular units per unit volume. Their average polarizability α is given by a relation like the right-hand side of Eq. (1) or (6). In the ideal molecular solid, where α does not depend on pressure, we can use Eq. (12) to relate n to the strength of the chemical bond. In that case, logarithmic differentiation of Eq. (12) with respect to dl/l and rearranging yields the prediction

$$\eta = -\tfrac{1}{2}(n^2+2) \ . \tag{13}$$

In Table I are listed $-\frac{1}{2}(n^2+2)$ and measured values of η for the LP as well as the tetrahedral materials. The agreement is remarkably good for some of the LP materials; it is within 5% for Se. Most important, Eq. (13) predicts η to be negative as observed. In contrast, Eq. (13) predicts magnitudes a factor 3–7 too large and a wrong sign for η in the case of the tetrahedral semiconductors.

As mentioned above, α is the average polarizability of the molecules in the solid. Using the polarizabilities of Se_2 and Te_2 molecules and Eq. (11), Grosse[26] was able to predict the infrared dielectric constant n^2 of solid Se and Te to within 5%. This is surprisingly good agreement since the "molecules" in solid Se and Te are chains in which the bonding is quite different from that of Se_2 and Te_2.

Thus, the Lorenz-Lorentz equation predicts values of η in fair agreement with experiment for several of the LP semiconductors. In fact, the agreement is better than expected. Dexter argues that the Lorenz-Lorentz equation is valid only when $\frac{4}{3}\pi N\alpha$ is small compared with unity. In Dexter's treatment the local-field correction is the second-order term in a perturbation calculation in which $\frac{4}{3}\pi N\alpha$ is the expansion parameter. $\frac{4}{3}\pi N\alpha$ must be small if higher-order terms are to be neglected. However, Eq. (12) gives a good prediction of dn/dP for Se although it has $\frac{4}{3}\pi N\alpha = 0.64$. It is surprising that the Lorenz-Lorentz equation gives reasonable values of dn/dP for materials with such a large polarizability.

In deriving Eq. (12) Dexter assumes that exchange interactions (i.e., covalent bonds) between molecular units are negligible compared with Van der Waals interactions. In other words, it must be possible to define molecular units which are not covalently bonded in every direction to the rest of the solid. As we have pointed out, this is the case for Se but not for Ge. Consider now alloying Ge into amorphous Se. The transition from a molecular solid to a covalent solid will occur gradually with increasing Ge concentration. At the concentration $GeSe_2$, every Ge is expected to be bonded to four Se atoms and every Se to two Ge atoms. We would expect this composition to contain no molecular units. In that case we expect η positive as for Ge. We have no compressibility data for $GeSe_2$, so η has not yet been determined. However, for the isolelectronic material SiO_2, the relevant data are given in Table I. Although the experimental value of η for quartz is smaller than predicted by Eq. (13), it is negative. One does not usually think of quartz as a molecular solid. However, the structure of α-quartz is very complicated and molecular units composed of spirals of SiO_4 tetrahedra may be present.[27] The fact that the compressibility of α-SiO_2 is twice that of Ge supports our contention that quartz is to some degree molecular. A transition from a partially molecular solid to one containing no molecular subunits must occur as one increases the Ge concentration in an amorphous Ge-Se alloy. Experiments are in progress to observe this transition.

Little has been said in the above discussion about the effects of ionicity on the pressure dependence of the refractive index. It was one goal of Van Vechten's work[3] to understand the different dn/dP observed for ionic and covalent A^NB^{8-N} crystals. Van Vechten points out that while η is negative for the alkali halides ($\eta+\frac{3}{2}$ is positive for all $A^N B^{8-N}$ crystals) it is almost unity (the value for C and Si) even for some very ionic materials. The negative η observed for SiO_2 is probably not, therefore, a result of high ionicity. Rather it appears that just as η depends on ionicity, it also depends strongly on the degree to which the solid is molecular. Even if the solid is only slightly molecular this will be revealed in η because of the small force constants associated with Van der Waals forces.

CONCLUSIONS

Local-field corrections are only understood for the simplest systems. The Lorenz-Lorentz equation adequately describes the refractive index in the extreme tight-binding case: the Van der Waals solid. It is unsatisfactory, however, even for the most ionic alkali halides. Mott and Gurny argue that the failure of the Lorenz-Lorentz equation in this case is due to the nonzero overlap of neighboring ions.[28] Phillips[29] has pointed out that the Lorenz-Lorentz equation fails to describe the refractive index of diamond and Si because of the overlap of the bond charge for neighboring bonds. He suggests that there may be no local-field correction in such materials.

It is worthy of note that the success of Van Vechten's procedure in the case of group-IV elements tells us little about local-field corrections in those materials. Although he shows that n depends quite simply on nearest-neighbor distance, there may be local-field corrections which also depend on nearest-neighbor distance. The volume dependence of n yields information about local-field corrections only if the local fields are determined by coordinates which change more under pressure than the bond lengths.

If local-field corrections are not understood in Ge and Si—the completely bonded extreme—it is not surprising that the problem remains unsolved for cases like As_2S_3 or SiO_2 which are only partially molecular. There have been attempts to extend local-field arguments to partially tight-binding cases. The most common approach[30] is to assume the full Lorenz-Lorentz correction as given by Eq. (12). Then any deviation from the prediction of Eq. (12) is attributed to a change in α with pressure. This takes into account the fact that if the molecular units are large and complex, their internal coordinates will be altered somewhat by stress. Such an approach seems reasonable for solids in which the molecular units are not too large. However, when molecular units are of macroscopic dimensions it follows from the arguments of Phillips and Mott and Gurny that the Lorenz-Lorentz correction is itself invalid.

Throughout the preceding discussion we have not distinguished between amorphous and crystalline materials. Indeed, it appears that dn/dP is quite insensitive to long-range order. Connell and Paul pointed this out in the case of the tetrahedral semiconductors. Fused quartz and α-quartz have $(1/n)(dn/dP)$ equal within 6%. It appears, then, that local-field corrections as well as microscopic polarizability depend only on short-range order.

So far we have discussed the effects on n of only two kinds of coordinates: the bond length or nearest-neighbor distance and the intermolecular distances. When stress is applied to a solid, bond angles can also change. In anisotropic materials, bond angles will change even under hydrostatic pressure. This will be the case for many LP semiconductors. We need, therefore, a greater understanding of the relation between local-field corrections and bond angle in order to utilize n as a measure of bond strength for LP semiconductors.

In summary, the Lorenz-Lorentz local-field correction predicts results in reasonable agreement with experiment for molecular solids. In this case, Eq. (12) can be used to relate n to the strength of the chemical bond. For the tetrahedral materials, on the other hand, Phillips's theory is appropriate. However, for solids which are only partially molecular, a better theory of local-field corrections is necessary before we can relate n to the strength of the chemical bond.

ACKNOWLEDGMENTS

The author is indebted to Professor H. Fritzsche for his guidance and encouragement throughout all phases of this work, and to M. Paesler for his assistance in sample preparation. The generosity of Energy Conversion Devices, Inc. in furnishing samples of several materials is gratefully acknowledged.

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*Submitted in partial fulfillment of the requirements for the Ph. D. degree at The University of Chicago.

†Work supported by Air Force Office of Scientific Research, Office of Aerospace Research, USAF, under Contract No. AF F44620-71-C-0025. We have also benefited from support of Materials Sciences by the Advanced Research Projects Agency at The University of Chicago.

‡Fannie and John Hertz Foundation Fellow.

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Theory of Photon-Drag Effect in Polar Crystals*

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(Received 7 April 1972)

The theory of the photon-drag effect in polar crystals is considered using Fröhlich's model for the electron-phonon interaction. An equation is derived for the electric field generated by this effect. Numerical examples are given for CdS crystals.

I. INTRODUCTION

Recent advances in high-intensity laser technology have made it possible for us to observe many new and interesting phenomena in some semiconductors. Among these are the multiple-photon absorption process, harmonic generation, self-induced transparency, and photon-drag effect.[1-4] The photon-drag effect arises from the transfer of momentum from photons to the free carriers (either holes or electrons) through photon-electron-phonon interactions.[4,5] As a result of the transfer of momentum, a net flow of charge appears in the direction of propagation of the electromagnetic wave (i.e., a current or photovoltage effect can be observed).

The mathematical basis of the photon-drag effect arises from the first-order terms of the matrix element of the free-carrier–photon–phonon interaction when the matrix elements are expanded in terms of the wave vector of the photons.

The photon-drag effect was experimentally observed by Danishevakii *et al.*[4] and by Gibson *et al.*[5]