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Temperature dependence of the refractive-index dispersion in amorphous germanium at elevated temperatures

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Refractive-index dispersion in amorphous germanium was measured in the vicinity of the optical gap (0.2—1.2 eV) and for the first time at elevated temperatures (25 °C—400 °C). The results at each temperature follow the dispersion of a single oscillator, whose resonance energy and strength decrease linearly with temperature. However, the magnitude of these variations differs markedly (e.g., by a factor of 2 or more, respectively) from temperature derivatives of band gaps or of electron density. It is apparent that in *small gap materials,* such as amorphous germanium, *temperature dependences derived from dispersion do not reflect the temperature dependence of specific interband transitions* (within the framework of the single-oscillator model). A new model is developed which accounts for the temperature dependence of the dispersion by replacing the single oscillator with two other interband electronic oscillators. The stronger of these two, which represents the majority of interband transitions, is located at the maximum of the optical transition strength. Assuming that its oscillator strength is close to unity, and that the temperature derivative of its resonance energy is identical with that of the Penn gap, the parameters of the second oscillator are obtained by fitting to the data. This is a weak oscillator located closely above the optical gap thus representing the low-energy portion of the ϵ_2 spectrum. Moreover, *the temperature derivative of its resonance energy acquires a value similar to that of the optical gap.* In this model the dispersion is sensitive to the location of the weak oscillator due to the low value of its resonance energy and its proximity to the spectral region of interest. The dispersion is similarly sensitive to the location of the low-energy portion of ϵ_2, as obtained by considering its moments. Thus in crystalline germanium, where the weak oscillator and the onset of strong interband absorption lie at higher energies than in amorphous germanium, a smaller temperature derivative of the single-oscillator energy is expected. This prediction is confirmed by experiment. It is concluded that using band-gap derivatives, the two-oscillator model may be utilized to calculate the temperature dependence of the dispersion or vice versa.

I. INTRODUCTION

The relation between ϵ_1 and ϵ_2 (the real and imaginary parts of the dielectric function) has attracted much attention since Penn[1] developed a model that relates the optical dielectric constant to an average energy gap (E_g) and an average oscillator strength. On the basis of polarity trends in the dielectric constant, Phillips[2] has postulated the existence of two kinds of average gaps—the ionic gap and the homopolar gap—their ratio being taken as a definition of a new ionicity scale. One of the first attempts to relate E_g with some specific interband transition has been made by Cardona[3] who demonstrated that for many materials, E_g could be roughly replaced by the energy of the highest peak in the absorption coefficient. Such an approach is required since only one empirical parameter [$\epsilon_1(0)$] is used, i.e., one has to assume some prescription in assigning a value to either the average gap or the oscillator strength. Three different approaches have been tried by various investigators in order to determine trends in interband parameters. The first, taken by Van Vechten,[4] applies a value close to unity to the oscillator strength which is then used to deduce trends in E_g. The second, by Harrison and Pantelides,[5] follows Cardona's assignment of E_g to the highest reflectivity peak and finds empirical trends in the average momentum matrix element [roughly proportional to fE_c (Ref. 6); see below] which are in accord with the linear combination of atomic orbitals (LCAO) models. The third, by Wemple,[7] assigns E_g to E_c, i.e., as obtained from dispersion, and finds empirical trends in the average coordinate matrix element ($\sim f/E_c$). Thus while variations in dielectric constant provide trends in interband transitions (without directly measuring them), the microscopic interpretation is not unique and depends on the actual prescription applied.

A different approach that tried to overcome this limitation utilized the dispersion in the refractive index $n(E)$. Two new parameters, i.e., a new oscillator strength f and resonance energy E_c were determined using the single-oscillator (SO) dispersion formula[8,9] which assumes that a single electronic excitation dominates the subgap dispersion. Thus

$$n^2(E)-1=\frac{f}{E_c^2-E^2}\ , \tag{1}$$

where E is the photon energy. Wemple and DiDomenico[8] and Wemple[10] investigated in this way many materials and found chemical and structural trends in the parameter f/E_c to which they assigned the term "true oscillator strength." Using the moment picture of ϵ_2 which is based on the Kramers-Kronig (KK) relations, they have shown that the main contribution to E_c comes from the low-energy portion of the ϵ_2 spectrum.

The temperature (T) dependence of the refractive-index dispersion has also received some attention. Antoncik[11] and Lukes[12] used a SO formalism to interpret data on Si and Ge associating E_c with the lower-lying reflectivity peak and dE_c/dT with the T derivative of either the direct gap,[11] the indirect gap,[11] or the electrical conductivity gap.[12] Recently a similar approach has been tried by Brodsky and Leary[13] on amorphous silicon. The values of E_c and its T derivative were obtained from those of E_g, and f—which was assumed to be proportional to the electron density—was taken essentially T independent. Obviously this approach disregards the moment picture.[8,10] It should be realized that $n(E)$ is determined by those virtual transitions which weigh heavily the low-energy portion of the ϵ_2 spectrum. Thus f and E_c and particularly their T derivatives are determined mainly by transitions which are close to the onset of strong interband transitions. Moreover, Wemple and DiDomenico[8] have shown that f is not proportional to the electron density. Nevertheless, this approach may apply better to the Penn model [i.e., to $\epsilon_1(0)$] where the oscillator strength can be assumed independent of temperature as was demonstrated by Yu and Cardona.[14] They have shown that in many materials E_2 (the highest reflectivity peak) and dE_2/dT are, respectively, quite close to E_g and dE_g/dT which were calculated from the T dependence of the appropriate pseudopotential parameters. Regarding the moment picture in this case, this assignment is justified since E_g is less sensitive than E_c to the lower-energy portion of ϵ_2 and is also closer to E_2.

In this paper an attempt is made to explore the T dependence of the refractive-index dispersion of amorphous germanium (a-Ge). In Sec. IV it is shown that the T dependence of the SO resonance energy E_c is quite large, and does not fit derivatives obtained by absorption measurements, e.g., the T derivative of the optical gap. Thus, in small-gap materials, it is not possible to calculate the T dependence of the dispersion based on the SO model and the assignment of E_c to a specific interband transition. A new model that invokes two oscillators is therefore introduced (Sec. V). This model accounts reasonably well for both the refractive-index dispersion and its temperature dependence without assuming large derivatives for its resonance energies. Predictions are made regarding the difference in this T dependence between a-Ge and crystalline Ge (c-Ge) which are confirmed by experiment.

II. EXPERIMENTAL

Sample preparation and characterization have been described elsewhere.[15] Essentially, thin films of a-Ge have been evaporated in a vacuum of 10^{-5} Torr onto fused silica substrates held at a temperature of 300 °C. Thickness has been measured with an optical interference microscope while density of 5.15 ± 0.13 g/cm^3 was determined by weighing the sample. The extrapolated room-temperature (RT) value of the long-wavelength refractive index was $n(0)\simeq 4.2\pm0.1$. Both these results are close to values reported[16,17] by Paul, Connell, and Temkin on sputtered a-Ge prepared at and above a substrate temperature of 300 °C. One may thus speculate that our evaporated films have a similar morphology to that of high-quality sputtered films, i.e., that they are homogeneous. Lack of post-deposition oxidation (see below) seems to support such an assumption. The otherwise stable films begin to crystallize in the vicinity of 450 °C as observed by x-ray diffraction and Raman scattering.[15] Thus in our measurements, a temperature of 400 °C was not exceeded, keeping the films safely far from crystallization. An oxide layer—less than 50 Å thick as determined by ellipsometry—which grows on the surface, does not affect the determination of the refractive index and has been ignored. The optical measurements were carried out in two double-beam Beckman spectrometers. Measurements were performed in the normal-incidence transmission mode or in the 20° off-normal reflection mode using a gold-plated mirror as a reference for the latter. A Mettler oven, designed to operate at temperatures up to 400 °C (model FP 52), was used as a sample holder.[15] Temperature was measured to within ~±2 °C using a thermocouple attached to the sample and an internal platinum resistor sensor.

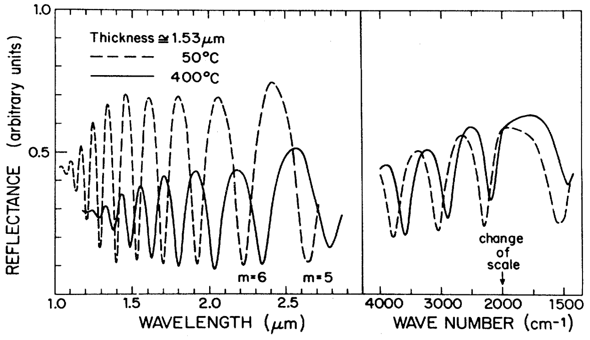

FIG. 1. Recorder trace of reflectance spectra of a-Ge at two temperatures. The order of fringes 5 and 6 is indicated. Relative intensities are of no significance in this figure.

The refractive index is more accurately determined from the reflectance fringe extrema (Fig. 1) because, in a reflectance spectrum the shift in the extremum position close to the absorption edge is smaller than the corresponding shift in a transmittance spectrum. n was calculated from the wavelength λ_m of the fringe of order m, by formula[17]

$$n=[n_n^2+\sin^2(20°)]^{1/2}\ , \tag{2}$$

where n_n ($=m\lambda_m/2d$) is the refractive index under conditions of normal incidence, d is the film thickness corrected for thermal expansion, and the order m (integer for minima, half-integer for maxima) is determined in a region of small dispersion, using two adjacent reflectance-minima wavelengths. In the calculation of both n_n and n the extinction coefficient κ may be ignored.[18] The absolute error in the refractive index is about 2–3 %, mainly due to error in thickness determination. The relative error using the same sample is about 0.1–0.2 %, as determined by the wavelength accuracy. This error mainly compounds the error in the temperature derivative of the refractive index.

III. RESULTS

Figure 2 shows the refractive index versus photon energy for three temperatures (for the same sample as in Fig. 1) obtained in a cooling run. At photon energies below about 0.5 eV, thermal emission from the sample holder causes asymmetry in the fringe shape (Fig. 1). This, in addition to the higher noise level of the infrared spectrometer, introduces uncertainty in the positions of the broad reflectance maxima. Thus the positions of three maxima (situated approximately near 1850, 2600, and 3350 cm^{-1}) were determined by taking the average value of the wave numbers of two adjacent minima. Consequently, the relative error in the refractive index is about 0.3% in the low-energy spectral region. Similarly, at the high-energy limit the error increases to about 0.4% due to inaccuracy in the reading of the positions of the extrema.

In Fig. 3 the results shown in Fig. 2 and additional data were fitted to a SO model using Eq. (1). While such a fitting cannot be done with sufficient accuracy over a much wider spectral range even if a broadening parameter is introduced,[17,19] it could be performed near and below the optical gap, yielding quite accurate values of E_c and f.[20] In fact, RT values of E_c and f were calculated by Wemple[7] based on refractive-index data by Connell, Temkin, and Paul[17] and yielded values close to our 50 °C results. Notice, however, the temperature dependence of E_c and f which are plotted in Figs. 4(a) and 4(b). At elevated temperatures the oscillator energy E_c and strength f decrease linearly with increasing temperature, and their derivatives, in units of eV/K and eV^2/K, respectively, are

$$\frac{dE_c}{dT} = -(8.5\pm0.8)\times10^{-4} ,$$

$$\frac{df}{dT} = -(4.2\pm0.6)\times10^{-2} .$$

Both derivatives are extremely large. For instance, $(1/f)df/dT \cong -4.7\times10^{-4}$ per K at RT and is much larger than the temperature dependence of the electron density; similarly dE_c/dT is much larger than the T derivative of any interband transition. The reproducibility of the data is demonstrated in Fig. 4(d) where we compare our SO energy data for a-Ge as obtained on three different samples. The closed circles (●) were taken from Fig. 4(a). The open squares (□) were obtained from a transmittance measurement on a similar sample. The (×) symbols were obtained both for cooling and heating from reflectance measurement on a sample prepared at a lower substrate temperature (~200 °C) and annealed at 300 °C prior to measurements. For these three samples the value of dE_c/dT is $(-8.5\pm0.8;\ -9.6\pm1.2;\ -8.8\pm1.2)\times10^{-4}$ eV/K, respectively.

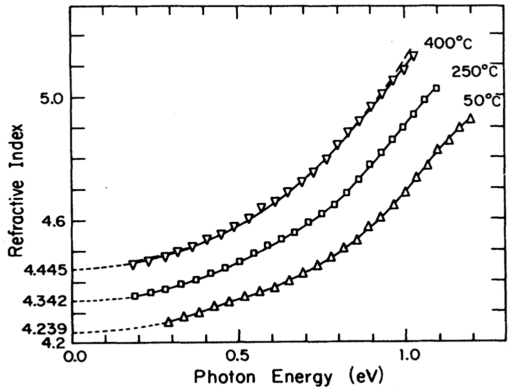

FIG. 2. Refractive-index dispersion spectra of a-Ge at various temperatures. Solid curves represent smooth average of experimental points. Dashed curve at 400 °C is determined according to a single-oscillator analysis (see Ref. 20).

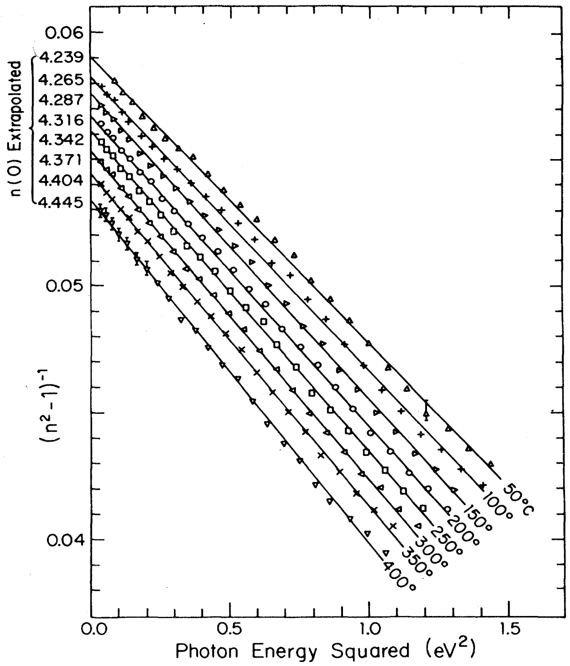

FIG. 3. Single-oscillator analysis of refractive-index dispersion of a-Ge at various temperatures, obtained on the sample shown in Fig. 2. The bars indicate relative error.

For comparison we also show in Fig. 4(d) the SO energy of c-Ge, as obtained from below RT published data.[21,22] The amorphous value of E_c which is about 15% lower than the crystalline one, reflects the relative shift to lower energies of the low-energy portion of ϵ_2 in a-Ge as compared to c-Ge.[10] The three values which we have calculated using the data of Cardona *et al.*[21] decrease monotonically with temperature resulting in $dE_c/dT \cong -5\times10^{-4}$ eV/K±10%. On the other hand, the results derived from the data of Icenogle *et al.*,[22] indicated by (△), could not be as conclusive. It seems, however, that ignoring their data points at 12.36 μm—as is apparently suggested in the discussion in Ref. 23—the results (○) fit better to those of Cardona *et al.* These results imply that dE_c/dT in the crystal is smaller than in the amorphous case.

IV. DISCUSSION

In this section we are concerned with the temperature dependence of three characteristic energies. The first is the T derivative of the SO resonance energy which is quite

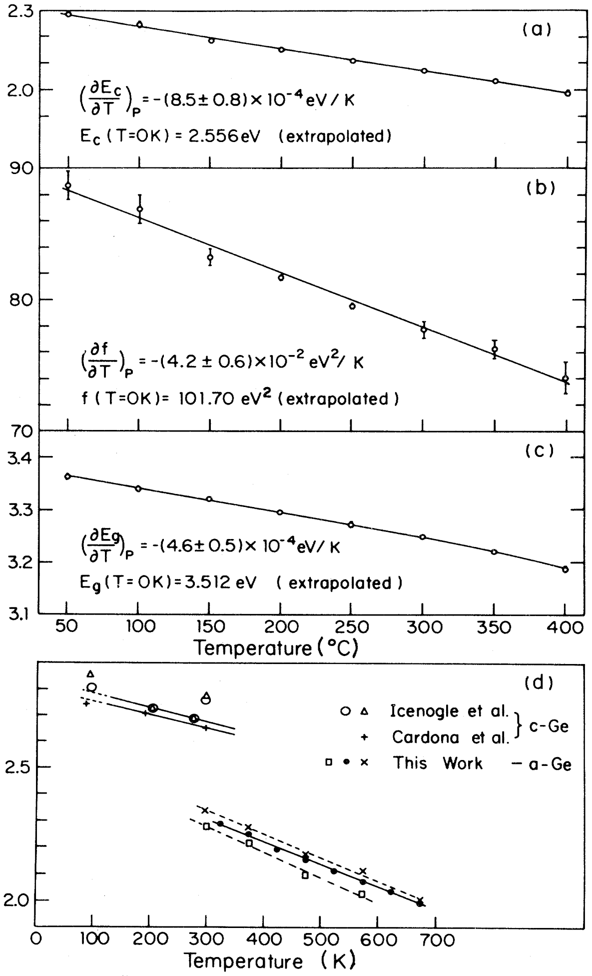

FIG. 4. Single-oscillator parameters vs temperature for the same sample as in Fig. 3. (a) Oscillator energy E_c. (b) Oscillator strength f. (c) Penn gap E_g vs temperature as obtained from the extrapolated dielectric constant (see Sec. IV). (d) Oscillator energy E_c for three amorphous samples as obtained in this work, and for *c*-Ge. ● are points taken from Fig. 4(a); □, present transmittance data on a similar sample; ×, present reflectance data on a sample prepared at a low substrate temperature. The crystalline points were obtained from data of Cardona *et al.* (Ref. 21) and Icenogle *et al.* (Ref. 22). The lines drawn correspond to $dE_c/dT \cong -5\times10^{-4}$ eV/K.

large, namely, $dE_c/dT \simeq -8.5\times10^{-4}$ eV/K. The second corresponds to the optical gap E_0 which lies close to the onset of strong interband absorption. Its T dependence is given by[24,25] $dE_0/dT = -4.7\times10^{-4}$ eV/K, almost half that of E_c. The third is the T dependence of the Penn gap E_g. This gap is determined experimentally by the dielectric constant $\epsilon_1(0)$ according to the relation[26]

$$\epsilon_1(0)-1=n^2(0)-1=\frac{3}{4}\frac{E_p^2}{E_g^2}\ , \tag{3}$$

where E_p is the plasma energy of the valence electrons which assumes a RT value of 16 eV.[17,27] Its T dependence is determined by that of the coefficient of volume thermal expansion γ, that is $(1/E_p^2)dE_p^2/dT=(1/N_v)dN_v/dT=-\gamma\cong-0.2\times10^{-4}$ per K (N_v being the density of valence electrons).[28] In practice, E_g was obtained from the extrapolated values of $n(0)$ as shown in Fig. 3. This extrapolation ignores contribution to $n(0)$ from free carriers[29,30] or lattice vibrations.[31] The T dependence of E_g is linear up to about 300 °C as shown in Fig. 4(c), with $dE_g/dT=-(4.6\pm0.5)\times10^{-4}$ eV/K.[32]

One observes that $dE_0/dT \cong dE_g/dT$ while dE_c/dT is almost twice as large. It is evident that substitution of each of the first two derivatives for the last may yield erroneous results. It is perhaps worthwhile mentioning that a broadening effect in the ϵ_2 spectrum cannot possibly account for this difference in derivatives as was concluded by considering the moments of ϵ_2. In fact, in order that such an effect yields a T derivative of the resonance energy comparable to that of E_0, a relatively large-T dependence of the broadening has to be invoked. Based on high-temperature pseudo-Brewster measurements, it has been shown that such a large broadening is unlikely to occur in *a*-Ge.[33] Thus it seems that for the purpose of calculating dE_c/dT from interband T derivatives an alternative model is required. This is the subject of the next section.

V. A MODEL FOR THE TEMPERATURE DEPENDENCE OF THE DISPERSION

In deriving the SO approximation [Eq. (1)] for the refractive-index dispersion of semiconductors and insulators,[8] one usually starts with the simplified dispersion formula for bound electrons in an assembly of weakly interacting atoms,[9,34] viz.,

$$\epsilon_1(E)-1=E_p^2\sum_j\frac{f_j}{E_j^2-E^2}\ . \tag{4}$$

Here the important interband transitions which actually depend on wave number have been approximated by individual oscillators,[8] and the sum over these oscillators replaces the sum over empty (conduction-) band states separated by an energy E_j from filled (valence- and core) band states. In Eq. (4), E_j and f_j are the resonance energy and oscillator strength per electron of the jth oscillator.

Consider a model which utilizes only two of these interband electronic oscillators, that is, the dispersion is given by

$$n^2(E)-1=E_p^2\left[\frac{f_2}{E_2^2-E^2}+\frac{f_1}{E_1^2-E^2}\right]\ . \tag{5}$$

Here the oscillator denoted by $j=2$ represents the majority of transitions from the valence to the conduction bands. Its resonance energy E_2 is thus located close to the maximum in the optical transition strength ($E^2\epsilon_2$), and its oscillator strength f_2 derives from the total valence-electron density, i.e., is of the order of unity. The T derivative of E_2 is assumed to equal that of the Penn gap while f_2 is assumed essentially independent of temperature. The other oscillator, denoted by $j=1$, is a much weaker oscillator situated at an energy E_1 in the vicinity of the optical gap, i.e., it represents the low-energy portion of ϵ_2. The purpose of this model is to examine to which extent do parameters of the weak oscillator—which are obtained from dispersion data—compare to the corresponding band parameters. In other words, is E_1 really close to but above the optical gap [$E_0 \cong 1$ eV at RT (Ref. 24)], is f_1 small compared to f_2, is dE_1/dT comparable to dE_0/dT, and does f_1 have a weak T dependence?

The calculation of the parameters of the weak oscillator and their T derivatives is presented in Appendix A. We assumed the following values of the parameters of the strong oscillator: $E_2 = 4.3$ eV, $f_2 = 0.9$, $dE_2/dT = -4.6\times 10^{-4}$ eV/K, and $(1/f_2)df_2/dT = 0$ or -0.2×10^{-4} per K. The parameters of the weak oscillator that were obtained by fitting to the refractive-index data are as follows: $E_1 \cong 1.65$ eV, $f_1 \cong 0.05$, $dE_1/dT \cong -5\times 10^{-4}$ eV/K, and $df_1/dT \cong -0.1\times 10^{-4}$ per K. Thus a close correspondence between the calculated and expected values is obtained. The parameters of the weak oscillator are not very sensitive to changes in the estimate of the strong oscillator's parameters. For any reasonable change of the latter $E_1 \leq \sim 1.8$ eV, dE_1/dT does not increase by more than $\sim 15\%$, and f_1 and df_1/dT are small. Thus it seems that the choice of the strong oscillator's parameters does not limit the generality of some of the conclusions drawn below.

It is important to realize that while the strong oscillator dominates the dispersion (at least at the lower temperatures), i.e., the term with $j = 2$ is the larger term in Eq. (5), the T dependence of the dispersion is dominated by the location of the low-lying weak oscillator. In other words, the proximity of E_1 to the spectral region of interest and the low value of this energy makes the dispersion parameters (e.g., E_c and f) very sensitive to small temperature variations in E_1. Quantitatively, this point is made in Appendix B by comparing dE_c/dT to dE_g/dT using the parameters of the two-oscillator (TO) model. It is shown there that a term proportional to the fourth power of E_1 is mainly responsible for the large difference between dE_c/dT and dE_g/dT. This conclusion is further supported by the moment picture (Sec. I). It has been shown[35] that the difference between the T derivatives of E_c and E_g is mainly accounted for by the variation with temperature of the low-energy portion of the ϵ_2 spectrum, i.e., in the vicinity of the optical gap.[36] Thus the low-energy portion of the ϵ_2 spectrum and the weak oscillator play a similar role to each other as was assumed earlier.

It would be also worthwhile to compare the location of the weak oscillator in *a*-Ge and *c*-Ge. It is noted that E_1 in *a*-Ge is close to but lower than the 2.1-eV crystalline critical point. By identifying the latter with E_1 in *c*-Ge, it becomes clear that E_1(*a*-Ge) should really be smaller than E_1(*c*-Ge) since in *a*-Ge the low-energy portion of the ϵ_2 spectrum (i.e., the onset of strong absorption) lies at a lower energy as compared to the crystalline counterpart. Since in *a*-Ge, the location of E_1 is important in determining the derivative of E_c, it is expected that this increase in E_1 will affect the magnitude of dE_c/dT in *c*-Ge. The latter was calculated assuming $E_2 = 4.4$ eV, $dE_2/dT = -2\times 10^{-4}$ eV/K,[14] and $dE_1/dT = -4.2\times 10^{-4}$ eV/K.[37] The oscillator strengths and their derivatives have been taken from the amorphous case. The resulting dE_c/dT ($= -5.7\times 10^{-4}$ eV/K) in *c*-Ge is much lower than in *a*-Ge, and quite close to the experimental value [Fig. 4(d)].

A final point of interest concerns the relative strength of both oscillators in *a*-Ge. It is noted that f_2/f_1 lies between 12 and 20 (see Appendix A). This is in qualitative agreement with the ratio of $E^2\epsilon_2$ at the energies of both oscillators, namely, about 8–10.[17] Much better agreement is not to be expected, since the TO model does not represent a real ϵ_2 spectrum in *a*-Ge; neither does the SO model. Applied, however, to *c*-Ge, both oscillators obtain an intuitive meaning representing the strongest interband transitions associated with the X and Λ critical points (strong and weak oscillator, respectively). The reason why such a model applies also to *a*-Ge—where there exist no critical points in the density of states—lies probably in the fact that ϵ_1 is not very sensitive to the details in ϵ_2 since both are related by the KK integral.

VI. CONCLUSION

It has been shown that near and below the optical gap, at temperatures above RT, the refractive-index dispersion of *a*-Ge could be fitted to that of a single oscillator. The dispersion parameters, namely, the SO energy E_c and strength f, decrease linearly with increasing temperature. This resonance energy cannot, however, be assigned to any specific energy gap since its temperature derivative is much larger than that of the optical gap or the Penn gap. Similarly, the temperature derivative of the oscillator strength is much larger than that of the electron density.

An alternative model was developed in which the dispersion and its temperature dependence are accounted for, by replacing the single oscillator with two other electronic oscillators, whose resonance energies have temperature derivatives comparable to those of the Penn and optical gaps. The parameters of the stronger of these oscillators were tentatively estimated assuming it represents the majority of interband transitions, while those of the weaker oscillator were obtained by fitting to the data. It was found that the latter is located closely above the optical gap, and that its strength is small compared to that of the strong oscillator. The large relative change with temperature in the location of the weak oscillator (i.e., due to the low value of its resonance energy or its proximity to the spectral region of interest) is mainly responsible for the large temperature derivative of the dispersion parameters. This conclusion is consistent with another method of obtaining E_c, viz., by calculating the moments of the ϵ_2 spectrum. It has been shown[35] that a major part of the temperature dependence of this resonance energy comes from the variation with temperature of the low-energy portion of the ϵ_2 spectrum. Thus the weak oscillator and the low-energy portion of ϵ_2 represent similar entities. It is therefore predicted that in materials where the onset of strong absorption starts at larger energies, or equivalently, where the weak oscillator lies at a higher energy, the magnitude of dE_c/dT is smaller than in *a*-Ge. This prediction was confirmed by examining published data on *c*-Ge. It seems in accord also with results for amorphous and crystalline silicon.[35]

TABLE I. Experimental and calculated room-temperature values of the parameters of the single- and two-oscillator models. The first and second parts present, respectively, the estimated parameters of the strong oscillator and the fitted parameters of the weak oscillator in the two-oscillator model. The last part presents the parameters of the single oscillator E_c, f, and E_g calculated from Eqs. (B1) and (B2), and their derivatives calculated with the aid of Eq. (B3), together with their experimental values.

	Strong oscillator						Weak oscillator		
	E_2 (eV)	$\frac{dE_2}{dT}$ (10^{-4} eV/K)	$\frac{1}{E_2}\frac{dE_2}{dT}$ (10^{-4}/K)	f_2	$\frac{1}{f_2}\frac{df_2}{dT}$ (10^{-4}/K)	$\frac{1}{f_2}\frac{df_2}{dT}$ (10^{-4}/K)	E_1 (eV)	$\frac{dE_1}{dT}$ (10^{-4} eV/K)	$\frac{1}{E_1}\frac{dE_1}{dT}$ (10^{-4}/K)
Experiment (single oscillator)									
Calculation (two oscillator)	4.3	−4.6	−1.07	0.9	−0.18	−0.20	1.59	−5.0	−3.15
							±0.01	±10%	±10%
	4.3	−4.6	−1.07	0.8	−0.16	−0.20	1.70	−5.7	−3.35
	4.4	−4.6	−1.04	0.9	0	0	1.63	−5.5	−3.37
	4.4	−4.6	−1.04	0.9	−0.94	−1.04	1.64	−4.8	−2.93

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APPENDIX A: DETERMINATION OF THE PARAMETERS OF THE TWO OSCILLATORS

Estimating the parameters' value of the strong oscillator, those of the weak oscillator have been obtained by fitting to the refractive-index data. (A fit to all four parameters of both oscillators and their derivatives has also been tried but was rather sensitive to the number of data points and to the initial guess of the parameters.) In the estimate we made the following assumptions:

(1) E_2 has been identified with the maximum in the optical transition strength ($E^2\epsilon_2$); thus $E_2 \cong 4.3$ eV at RT (Refs. 17 and 38). It could also be identified with the maximum in the reflectivity which lies close to this energy.[3] Thus E_2 lies at the same energy as in *c*-Ge.

(2) E_2 and E_g—lying quite close to one another ($E_g = 3.375$ eV at RT)—have the same temperature dependence, that is, $dE_2/dT \cong dE_g/dT = -4.6\times10^{-4}$ eV/K.

(3) $f_2 \cong 0.9$. An upper limit to f_2 is obtained noting that the f_j's—the oscillator strengths per electron—are subjected to the effective f sum rule[4] which states that in germanium $\sum_j f_j \cong 1.25$ (due to the contribution to the effective electron density from 3*d*-core electrons this sum is greater than 1). However, the TO model takes into account only two of the lower lying of these oscillators and neglects others. Thus $f_2+f_1<1.25$. [This is justified since the other oscillators, which lie at higher energies, make a negligible contribution to the refractive index—owing to both the $1/E_j^2$ factor and their lower strength as may be seen from Eq. (4)—but make a finite contribution to the f sum.] With regard to a lower limit, it may, in principle, be possible to determine that fraction of the f sum which mainly contributes to the refractive index, by comparing the quantities $\epsilon_{0\,\text{eff}}(E)$ and $n_{\text{eff}}(E)$.[39] These determine which fraction of the dielectric constant and the sum of the oscillator strengths, respectively, has been exhausted up to energy E. Compare Figs. 17 and 18 in Ref. 38 where at 10—12 eV $\epsilon_{0\,\text{eff}}$ almost saturates and n_{eff} obtains about 70—80% of its maximum value. Since $\epsilon_{0\,\text{eff}}$ saturates slowly this yields a lower limit to f_2+f_1 of about $(0.7\text{—}0.8)\times1.25 \cong 0.9\text{—}1.0$. Indeed, Schwidefsky found that for fitting exactly the dielectric constant of amorphous Si using four oscillators, a value of $\sum_j f_j \cong 0.7$ was needed.[19] This corresponds to a value of about $0.7\times1.25 \cong 0.9$ of the f sum in our case. Within these limits we have arbitrarily assumed that $f_2=0.9$ or 0.8 and performed calculations for both values.

(4) f_2 is essentially independent of temperature. This may be assumed since f_2 does not differ much from $\sum_j f_j$. The values $(1/f_2)df_2/dT=0$ and $-\gamma$ have been used in the fitting.

The parameters of the weak oscillator and their temperature derivatives obtained by the fitting are shown in the three upper rows of the calculation in Table I. The errors in these parameters indicate the limited accuracy of data and fitting procedure. On the other hand, the various calculations—some of which are not shown in the table—indicate that the parameters of the weak oscillator are not very sensitive to changes in the estimated parameters of the strong oscillator (e.g., see the fourth row of the calculation). Particularly, E_1 and dE_1/dT are not sensitive to changes in E_2 and f_2, while f_1 and df_1/dT remain small in all calculations. Using the TO parameters we calculated in the remainder of the table the SO parameters E_c, f, and E_g and their temperature derivatives. The agreement between calculated and experimental results is fairly good. It is very good for E_g which is obtained at $E=0$, since in this limit the truncation of the single- and two-oscillator series becomes exact (see Appendix B).

APPENDIX B: A RELATION BETWEEN THE PARAMETERS OF THE SO AND TO MODELS

Both the SO and the TO models describe the dispersion in the refractive index and their parameters could be relat-

TABLE I. (*Continued.*)

	Weak oscillator			Single oscillator					
	f_1	$\frac{df_1}{dT}$ $(10^{-4}/\mathrm{K})$	$\frac{1}{f_1}\frac{df_1}{dT}$ $(10^{-4}/\mathrm{K})$	E_c (eV)	$\frac{1}{E_c}\frac{dE_c}{dT}$ $(10^{-4}/\mathrm{K})$	f (eV^2)	$\frac{1}{f}\frac{df}{dT}$ $(10^{-4}/\mathrm{K})$	E_g (eV)	$\frac{1}{E_g}\frac{dE_g}{dT}$ $(10^{-4}/\mathrm{K})$
Experiment				2.305	−3.70	89.3	−4.7	3.375	−1.36
(single oscillator)				±0.015	±10%	±1.3	±15%	±0.010	±10%
Calculation	0.0453	−0.03	−0.65	2.62	−3.45	116	−4.15	3.360	−1.47
(two oscillator)	±0.0010	±40%	±40%	±0.09	±15%	±4	±30%	±0.015	±10%
	0.0669	−0.14	−2.1	2.53	−3.40	109	−4.15	3.360	−1.43
	0.0534	−0.13	−2.45	2.58	−3.30	114	−4.10	3.355	−1.38
	0.0540	0	0	2.60	−3.55	115	−4.80	3.355	−1.25

ed to each other. To this end we expanded both Eqs. (1) and (5) in a power series in E^2 and truncated these series after the E^4 term.[40] Assuming a unique expansion and comparing terms of equal order one obtains

$$f \cong \frac{(f_2+C_1E_2^2)^2}{f_2+C_2E_2^4}E_p^2\,, \tag{B1}$$

$$E_c^2 \cong \frac{f_2+C_1E_2^2}{f_2+C_2E_2^4}E_2^2 \cong \frac{1}{3/4}\frac{(f_2+C_1E_2^2)^2}{f_2+C_2E_2^4}E_g^2\,, \tag{B2}$$

where $C_1=f_1/E_1^2$ and $C_2=f_1/E_1^4$. In the right-hand side (rhs) of Eq. (B2), use was made of the fact that in the long-wavelength limit Eqs. (1), (3), and (5) become identical. Taking the derivative of the rhs of Eq. (B2) one obtains

$$\frac{1}{E_c}\frac{dE_c}{dT}-\frac{1}{E_g}\frac{dE_g}{dT}=\frac{1}{2f}\frac{df}{dT}+\frac{\gamma}{2}\cong\frac{f_2}{f_2+C_1E_2^2}\left[\frac{1}{f_2}\frac{df_2}{dT}+\frac{C_1E_2^2}{f_2}\left[\frac{1}{C_1}\frac{dC_1}{dT}+\frac{2}{E_2}\frac{dE_2}{dT}\right]\right]$$
$$-\frac{f_2}{2(f_2+C_2E_2^4)}\left[\frac{1}{f_2}\frac{df_2}{dT}+\frac{C_2E_2^4}{f_2}\left[\frac{1}{C_2}\frac{dC_2}{dT}+\frac{4}{E_2}\frac{dE_2}{dT}\right]\right]\,. \tag{B3}$$

Substitution of the RT values of the TO parameters in the rhs of Eq. (B3) yields a value of ~ -2×10^{-4} per K as compared to -2.3×10^{-4} per K obtained by direct substitution of the SO parameters in the left-hand side, where the RT values $E_c=2.305$ eV and $E_g=3.375$ eV were used. It is evident that the derivative of the $C_2=f_1/E_1^4$ term, owing to its strong dependence on E_1, is the dominating term in the rhs of Eq. (B3). This confirms the large contribution of the weak oscillator to the T dependence of dispersion due to its location.

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