TEMPERATURE COEFFICIENT OF THE REFRACTIVE INDEX

OF DIAMOND- AND ZINCBLENDE-TYPE SEMICONDUCTORS

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Abstract

We have calculated the temperature coefficient of the long-wavelength refractive index of several group IV and III-V semiconductors using the Penn model for the electronic contribution to the dielectric constant. The isotropic band gap of this model is identified with the band gap at the X point of the Brillouin zone, which can be simply expressed in terms of pseudopotential coefficients. The explicit temperature dependence of this gap is calculated by applying to these pseudopotential coefficients the appropriate Debye-Waller factors. The thermal expansion effect is obtained in the manner suggested recently by Van Vechten. Good agreement between the calculated and the observed temperature dependence of the long-wavelength refractive index is found.

1. Introduction

Recently Phillips' theory of ionicity[1] has been applied successfully
to calculate various properties, namely ionization potential[2],
cohesive energy[3], non-linear optical susceptibilities[4,5,6] etc.,
of a large number of covalent and ionic compounds. At the heart of
this theory is a very simple isotropic one-gap model of the band
structure due to Penn[7]. Heine and Jones[8] pointed out that one reason
why such a simple model works for the diamond-type semiconductors is
that the gap on the surface of the Jones-zone is nearly constant over
a large area. By identifying the "Penn gap" with the band gap at the
center of the (110) Jones-zone face, they calculated the hydrostatic
pressure coefficient of the dielectric constant of Si and Ge. In this
paper we generalise Heine and Jones' calculation to the III-V semi-
conductors and obtain the "Penn gap" as a function of the pseudo-
potential coefficients. We then calculate with this model the tempe-
rature coefficient of the refractive index of several group IV and
group III-V semiconductors.

2. Penn Model

The electronic centribution to the long-wavelength dielectric constant
of a solid in the Penn model is given by:[7,9]

$$\varepsilon(o) \simeq 1 + D \frac{\omega_p^2}{\omega_g^2} \qquad (1)$$

where ω_p is the plasma frequency of the valence electrons, ω_g the
"Penn gap", and D is a parameter introduced by Van Vechten[9] to take
into account the effect of d-like core electrons. It is difficult to
speculate on how D will vary with temperature and volume. Since D is

of the order of unity and its variations are not expected to be large we shall neglect this factor in our calculation..

By differentiation of Eq. (1) with respect to temperature (throughout this paper pressure is assumed to be constant when the d-sign of differentiation is used) we obtain:

$$\frac{1}{\varepsilon} \frac{d\varepsilon}{dT} = \frac{\varepsilon-1}{\varepsilon} \left[\frac{1}{\omega_p^2} \frac{d\omega_p^2}{dT} - 2 \left(\frac{1}{\omega_g} \frac{d\omega_g}{dT} \right) \right]$$
$$= \frac{\varepsilon-1}{\varepsilon} \left[-3\alpha - 2 \left(\frac{1}{\omega_g} \frac{d\omega_g}{dT} \right) \right] \tag{2}$$

where α = coefficient of linear expansion. In Eq. (2) we have made use of the known proportionality of ω_p^2 to the valence electron concentration. We decompose the temperature coefficient of ω_g which appears in Eq. (2) into its "explicit" temperature dependence at constant volume and its volume expansion effect:

$$\frac{1}{\omega_g} \frac{d\omega_g}{dT} = \frac{1}{\omega_g} \left(\frac{\partial \omega_g}{\partial T} \right)_V + 3\alpha \frac{V}{\omega_g} \left(\frac{\partial \omega_g}{\partial V} \right)_T \tag{3}$$

3. Explicit Temperature Dependence of the Penn Gap

Following Heine and Jones[8] we identify the "Penn gap" ω_g with the gap at the X point of the Brillouin zone. As is well known, its energy is close to that of the strongest peak in the oscillator strength and the reflectivity of the group IV and group III-V semiconductors[10]. An expression for this gap as a function of the pseudopotential form factors v(111), and v(220) has been calculated by Heine and Jones[8] for germanium-type materials using perturbation theory. This expression can be easily generalized to zincblende-type compounds. We find, in Rydbergs[11]

$$\omega_g^{\pm} = 2v_s(220) \pm 2v_a(200) + \frac{2 \left(v_s(111) \pm v_a(111) \right)^2}{\left(\frac{2\pi}{a} \right)^2} \tag{4}$$

where a is the lattice constant in Bohr radii. The subscript s and a
of the pseudopotential coefficients v (220), v (200) and v(111) denotes
their symmetric and antisymmetric components respectively. The anti-
symmetric coefficients $v_a(200)$ and $v_a(111)$ are responsible for the
splitting of the X_1 conduction bands $\left(\pm \text{ sign in Eq. (4)}\right)$ but does not
change, to first order, the average value of ω_g. Since the splitting
is known to be small for III-V compounds, it can be neglected for the
purpose of calculating dielectric properties.
We thus obtain

$$\omega_g = 2 \left(v_s(220) + \frac{\left(v_s(111)\right)^2 + \left(v_a(111)\right)^2}{\left(\frac{2\pi}{a}\right)^2} \right) \tag{5}$$

The values of the pseudopotential coefficients $v_s(220)$, $v_s(111)$ and
$v_a(111)$ for several group IV and group III-V semiconductors are listed
in Table I together with other parameters relevant for our calculations.
The values of ω_g obtained from these parameters with Eq. (5) are listed
in Table II, together with the values obtained from the dielectric
constant $\left(\text{see Eq. (1)}\right)$ by Van Vechten[9] and the energy E_2 of the corresponding
reflectivity peak. The good agreement between these three sets of values
confirms the validity of Eq. (5).

Equation (5) can be used to calculate the temperature dependence of ω_g
by multiplying the Fourier component of the pseudopotential $v(g)$ by the
appropriate Debye-Waller factor[12,13]:

$$e^{-B(T)\,|\underline{g}|^2} = e^{-\frac{|\underline{g}|^2}{6}\,\langle u^2 \rangle} \quad \text{(for cubic crystals)} \tag{6}$$

For a crystal with r atoms per unit cell the average square displacement of atom K is[14]:

$$\langle u^2{}_K \rangle = \frac{1}{2NM_K} \sum_{q,j} |e(K,j,q)|^2 \quad \frac{\coth \frac{1}{2} \beta \omega_j(q)}{\omega_j(q)} \tag{7}$$

where $\beta = kT$. M_K is the mass of the K-th atom, N the number of unit cells per unit volume, $\omega_j(q)$ is the frequency of the normal mode with wavevector q in the j th-branch and e (K, j, q) the polarization vector of the corresponding displacement of atom K.

In group IV semiconductors the two atoms of the unit cell are identical and Eq. (7) simplifies to:

$$\langle u^2 \rangle = \frac{1}{2NM} \sum_{q,j} \frac{\coth \frac{1}{2} \beta \omega_j(q)}{2 \omega_j(q)} \tag{8}$$

we calculate $\frac{\partial B(T)}{\partial T}$ with the Debye model for the phonon spectrum and obtain with Eq. (8):

$$\frac{\partial B(T)}{\partial T} = \frac{3}{2} \frac{1}{MkT^2} \quad F \left(\frac{\Theta_D}{T} \right) \ , \tag{9}$$

with

$$F(x) = \frac{1}{x^2} \left[\frac{2}{x} \int_0^x \frac{y \, dy}{e^y - 1} - \frac{x}{e^x - 1} \right] \tag{10}$$

We shall use in our calculation values of the Debye temperature Θ_D at room temperature, since most experimental data are obtained around room temperature. The function F(x) has been evaluated by Benson and Gill[15].

For the III-V compounds it is no longer possible to relate $\langle u^2 \rangle$ directly to the phonon spectrum with Eq. (7) since the masses of the two constituent

atoms are not equal. However for those of the III-V compounds we are considering we find that the ratio of the heavier mass to the lighter is smaller than two. In the case of the alkali halides it was found that at room temperature the average square displacements for the anion and cation differ by less than 10 % even for masses which differ by a factor of 3.[16] Hence we assume for the sake of simplicity that $\langle u^2_{III} \rangle = \langle u^2_V \rangle$. The validity of this assumption cannot be checked until the Debye-Waller factors for the III-V compounds have been determined. However the results of our calculation seem to support this assumption. Thus for the III-V compounds we use the formula:

$$\frac{\partial B_{III}}{\partial T} = \frac{\partial B_V}{\partial T} \simeq \frac{\partial \bar{B}}{\partial T} = \frac{3}{kT^2 (M_{III} + M_V)} \ F \ \left(\frac{\Theta_D}{T}\right) \tag{11}$$

combining Eqs. (5) and (6) we obtain:

$$\left(\frac{\partial \omega_g}{\partial T}\right)_V \cong 2 \left[v_s(220)\left(- \mid g(220) \mid^2 \frac{\partial \bar{B}}{\partial T}\right) + \right.$$
$$\left. + \frac{\left(v_s(111)\right)^2 + \left(v_a(111)\right)^2}{\left(\frac{2\pi}{a}\right)^2} \ \left(- 2 \mid g(111) \mid^2 \frac{\partial \bar{B}}{\partial T}\right) \right] \tag{12}$$

In order to simplify the evaluation of Eq. (12) we note that for the semiconductors we are considering $v(220)$ is small and $\mid g(220) \mid^2 \sim 2 \mid g(111) \mid^2$. Equation (12) can thus be approximated by the expression:

$$\frac{1}{\omega_g} \left(\frac{\partial \omega_g}{\partial T}\right)_V \simeq - 2 \mid g(111) \mid^2 \ \frac{\partial \bar{B}}{\partial T} \tag{13}$$

with an error smaller than 10 %.

4. Volume Dependence of the "Penn gap"

The volume coefficient of ω_g can be calculated with Eq. (5) and the known derivatives of $v(q)$ with respect to $|q|$.[8] Since this volume dependence is only responsible for less than 20 % of the total calculated temperature dependence of ω_g, we choose for its evaluation the simpler, although possibly less accurate procedure given by Van Vechten[9].

We start with the equation:

$$\omega_g = (\omega_h^2 + C^2)^{1/2} \tag{14}$$

where ω_h is the homopolar energy gap of the material, and C the hetero-polar energy gap. In order to calculate the volume dependence of ω_g it is necessary to know the corresponding dependence of $\omega_h \left(\omega_h \propto a^{-2.48} \right)$[9] and C. As suggested by the value of $(\frac{\partial C}{\partial V})_T$ for the alkali halides[9], we take $(\frac{\partial C}{\partial V})_T \simeq 0$. Our result does not depend critically on this assumption since C only accounts for a small fraction of ω_g, whose volume dependence, in turn, only accounts for a small fraction of the total temperature dependence of ω_g. We thus find:

$$\frac{V}{\omega_g} \left(\frac{\partial \omega_g}{\partial V} \right)_T \cong - 0.8 \times \frac{\omega_h^2}{\omega_g^2} \tag{15}$$

5. Temperature Dependence of the long-wavelength Refractive Index

We have listed in Table I the parameters used for our calculation of $\frac{1}{n}(\frac{\partial n}{\partial T})_P$ based on Eqs. (2), (3), (13), and (15). We have used for the Debye temperature the values obtained from specific heat measurements. Batterman and Chipman[17] found that the Debye temperatures obtained for Ge and Si

from x-ray intensity measurements were about 20 % lower than those from specific heat. This fact introduces an uncertainty of about 40 % in our calculation of $\frac{1}{\omega_g} (\frac{\partial \omega_g}{\partial T})_V$. We believe this uncertainty is our main source of error.

In Table II we show the temperature coefficient $\frac{d\omega_g}{dT}$ calculated with Eqs. (13) and (15) and those determined experimentally for E_2. The agreement is satisfactory.

In Table III we show the calculated value of $\frac{1}{n} \frac{dn}{dT}$ at 300° K compared with experimental results. Theoretical I are the values obtained by using in Eq. (2) the calculated coefficients $\frac{1}{\omega_g} \frac{d\omega_g}{dT}$ while Theoretical II are the values obtained by using the experimental $\frac{1}{E_2} \frac{dE_2}{dT}$ and assuming $\frac{1}{\omega_g} \frac{d\omega_g}{dT} = \frac{1}{E_2} \frac{dE_2}{dT}$. We note that the trend in the experimental values in going from one material to another is better represented by Theoretical I than by Theoretical II. A possible explanation is that the values of $\frac{dE_2}{dT}$ determined by the wavelength modulation technique are sensitive to the detailed critical point structures while ω_g represents the somewhat different average gap. The agreement between the calcualted values of $\frac{1}{n} \frac{dn}{dT}$ and the experimental values is always better than 40 %, which is the error of our calculation due to uncertainties in the Debye temperature.

Acknowledgments

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Table I

The various parameters used in this article for calculating the temperature dependence of the long wavelength refractive index of group IV and III-V semiconductors.

[a]	Pseudopotential Coeff.(Ryd)			$\epsilon(o)$ (b)	Coeff. of linear Expansion at room temperature	Debye Temp. θ_D at 300°K	Lattice Constant (in Bohr radii) (b)
	$v_s(220)$	$v_s(111)$	$v_a(111)$				
C	−0.022 +0.337	−0.514 −0.811	−	5.7	[c] 1.1×10^{-6} /°K	[g] 1880 °K	6.74
Si	+0.04	−0.21	−	12.0	[c] 2.5×10^{-6}	[h] 647	10.26
Ge	+0.01	−0.23	−	16.0	[d] 5.7×10^{-6}	[h] 354	10.69
GaAs	+0.01	−0.23	+0.07	10.9	[d] 5.7×10^{-6}	[d] 360	10.68
GaSb	0.0	−0.22	+0.06	14.4	[d] 6.3×10^{-6}	[d] 230	11.56
InAs	0.0	−0.22	+0.08	12.3	[e] 5.4×10^{-6}	[d] 270	11.41
InSb	0.0	−0.20	+0.06	15.7	[d] 5.1×10^{-6}	[d] 150	12.24
InP	+0.01	−0.23	+0.07	9.6	[e] 4.9×10^{-6}	[d] 420	11.09
GaP	+0.03	−0.22	+0.12	9.1	[f] 5.81×10^{-6} [e] 5.3×10^{-6}	[i] 470	11.03

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i   The Debye temperature of GaP at room temperature is not avail-
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Debye temperature (446° K) calculated from the elastic
constants (E.F. Steigmeier, Appl.Phys. Letters <u>3</u>, 6 (1963))

Table II

Calculated and experimental values of the "Penn gap" ω_g, energy E_2 of the highest peak in the reflection spectrum, and temperature coefficient of ω_g (theoretical) and E_2 (experimental).

	ω_g(theoretical) from Eq. (5) in eV	ω_g(experimental) from Eq. (1) in eV	Highest Peak in Reflection Spectrum (E_2) in eV	$\frac{d\omega_g}{dT}$(calc.) in eV/°K	$\frac{dE_2}{dT}$ (exp.) in eV/°K
C	7.8 29.6	13.6	[a] 12.6	-1.17×10^{-4} -4.6×10^{-4}	--
Si	4.2	4.8	[b] 4.44	-1.9×10^{-4}	[b] -2.2×10^{-4} [d] $+0.5 \times 10^{-4}$
Ge	4.4	4.3	[b] 4.49	-3.3×10^{-4}	[b] -2.4×10^{-4} [d] -2×10^{-4}
GaAs	4.9	5.2	[b] 5.11	-3.5×10^{-4}	[b] -3.6×10^{-4} [f] -3.3×10^{-4}
GaSb	4.8	4.1	[b] 4.35	-4.7×10^{-4}	[b] -4.1×10^{-4} [e] -6.2×10^{-4}
InAs	4.9	4.58	[b] 4.74	-3.8×10^{-4}	[b] -5.6×10^{-4}
InSb	4.5	3.74	[b] 4.23	-6.9×10^{-4}	[b] -3.6×10^{-4} [e] -5.2×10^{-4}
InP	5.2	5.2	[c] 5.0	-2.3×10^{-4}	--
GaP	5.85	5.75	[c] 5.3	-1.9×10^{-4}	[f] -4.5×10^{-4}

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Table III

Temperature coefficient of long wavelength refractive index of group IV and III-V semiconductors.

	$\frac{1}{n}\frac{dn}{dT}$ (Theoretical I)	$\frac{1}{n}\frac{dn}{dT}$ (Theoretical II)	$\frac{1}{n}\frac{dn}{dT}$ (Experimental)
C	1.1×10^{-5} /° K	--	[a] 0.5×10^{-5} /° K
Si	3.7×10^{-5}	4.2×10^{-5} /° K	[b] 3.9×10^{-5} /° K
Ge	6.1×10^{-5}	4.2×10^{-5}	[b] 6.9×10^{-5}
GaAs	5.4×10^{-5}	5.7×10^{-5} 5.1×10^{-5}	[c] 4.5×10^{-5}
GaSb	9.3×10^{-5}	8.0×10^{-5} 12.4×10^{-5}	[c] 8.2×10^{-5}
InAs	6.7×10^{-5}	10.3×10^{-5}	--
InSb	15.0×10^{-5}	7.4×10^{-5} 11.9×10^{-5}	[c] 11.9×10^{-5}
InP	3.6×10^{-5}	--	[c] 2.7×10^{-5}
GaP	2.2×10^{-5}	6.8×10^{-5}	[d] 3.7×10^{-5}

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