PHYSICAL REVIEW B VOLUME 8, NUMBER 6 15 SEPTEMBER 1973

Theory of the Temperature Derivative of the Refractive Index in Transparent Crystals

Yet-ful Tsay*

Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

Bernard Bendow

Solid State Sciences Laboratory, Air Force Cambridge Research Laboratories, Bedford, Massachusetts 01730

Shashanka S. Mitra*†

Laboratoire des Hautes Pressions, CNRS, 1 Place A. Briand, 92-Bellevue, France

A simplified model is introduced to study the temperature dependence of the index of refraction n in the transparent regime of crystals. The dielectric susceptibility is written as a sum of an electronic contribution due to band-to-band transitions and a lattice contribution, viewed as due to a single mode ω_0. Each of the latter undergoes a temperature variation consisting of contributions due to thermal expansion, as well as contributions due to the explicit temperature dependence at constant volume. The temperature derivative dn/dT is investigated for various materials. It is found that for zinc-blende- and diamond-type semiconductors, electronic effects, in particular the temperature variation of the band gap at constant volume, yield the dominant contribution. Theoretical calculations of the latter are carried out employing a temperature-dependent-pseudopotential band-structure model; the resulting values for dn/dT are in good agreement with experiment. For ionic materials, it is found that both lattice and electronic contributions may be important, as are both explicit temperature variation and thermal-expansion effects. Experimental data on the temperature dependence of ω_0 and the band gap are employed to obtain good agreement with the frequency variation of dn/dT for a variety of ionic crystals. The results demonstrate that the major physical mechanisms responsible for dn/dT can be understood within the present simplified model, and that the model is useful in predicting the magnitude and frequency dependence of dn/dT for a wide variety of crystals of interest.

I. INTRODUCTION

The temperature dependence of the refractive index n of crystals is of considerable interest, especially in connection with a wide variety of optics applications. This is the case, for example, with optical instrumentation,[1] such as high-resolution photographic lenses, which are required to operate under a wide variety of temperature conditions. Another area in which dn/dT, the temperature derivative of n, has come to play an important role, is the thermal distortion of high-power laser beams traversing various optical elements and/or windows.[2] The associated aberration, under most conditions, is approximately proportional to[3] dn/dT. Both the absolute magnitude of dn/dT, as well as its frequency dependence, are of considerable interest in conjunction with applications such as the latter.

Although a wide body of experimental data[4] exists on dn/dT, much of it is concentrated in specific limited spectral regions, usually in the visible. Useful data outside these regimes, especially at longer wavelengths than the visible, are very often unavailable. For this reason, it is highly desirable to obtain theoretical prescriptions which allow prediction of dn/dT over a wide range of frequencies based on, at most, a small number of known values at a few frequencies.

Ramachandran[5] presented a semiempirical theory of thermo-optical effects in crystals, in which the dispersion was fitted to experimental data, employing a series of oscillator frequencies and strengths as adjustable parameters. A close correlation was found between temperature shifts of various parameters and those of the fundamental oscillator frequencies. Unfortunately, the parameters chosen were rather numerous, and often physically obscure or not unique; no general prescription was presented for determining their temperature variations, which are necessary for calculating dn/dT. Moss[6] and Antoncik[7] in studying dn/dT near the fundamental gap of Si and Ge, successfully correlated the temperature shift of the absorption edge with measured variations in dn/dT. A somewhat similar approach was taken by Yu and Cardona,[8] who calculate the variation of the gap energy E_g in an approximate fashion utilizing the Yu-Brooks theory.[9] These authors find that the agreement in the visible between calculated and experimental values of dn/dT for diamond and III-V zinc-blende- (ZB-) type crystals is within ~40%. A variety of papers[10] exist in the literature which attempt to relate the value of dn/dT in crystals to thermal-expansion effects, but do not properly account for the effects of the shifts of the system energy levels and the corresponding oscillator strengths.

The purpose of this work is to present a simplified two-oscillator model of dn/dT applicable to a fairly wide variety of crystals, from which dn/dT may be calculated at frequencies throughout the transparent regime ($\omega_0 < \omega < \omega_g$), once the temperature dependences of just a small number of physically meaningful parameters are determined. The theory is designed primarily for cubic diatomic crystals, although various aspects are applicable for other crystals, when appropriate generalizations are carried out. The two fundamental oscillators are the TO phonon ω_0 for the lattice response, and E_g, an appropriately-weighted average band gap for the electronic response. In the present paper we calculate only the electronic contributions for diamond, and III-V and II-VI ZB-type crystals, where the lattice contributions may be shown to be negligible. Both the lattice and electronic contributions to dn/dT of alkali halides are calculated.

It will be found that certain of the parameters arising in the theory are more readily amenable to first-principles calculation, while others are not. We therefore consider the necessary parameters as being available either from theory or experiment. For example, we calculate $d\omega_g/dT$ for semiconductors from first principles employing a temperature-dependent-pseudopotential energy-band approach.[9] The corresponding information for ionic crystals, where the first-principles calculation meets with special difficulties, is obtained from experiment.

One finds that a wide range of measured values of dn/dT characterize crystals in the transparent regime.[4] At wavelength $\lambda = 10.6$ μm, for example, typical values range from -25 to $+25\times10^{-5}/°\text{K}$; it is therefore important to identify the principal physical mechanisms responsible for this large variation in dn/dT. We note that dn/dT is found[10] to be relatively independent of temperature over a fairly wide range of temperatures, and assume this to be generally the case here.

In the following development, we point out the relative contributions of electronic and lattice effects to dn/dT. It is also useful to distinguish between two sorts of physical effects which influence dn/dT. One is the thermal expansion; when T increases, the material expands, becoming less dense. Were this the only mechanism operative, it would tend to make dn/dT negative. The other effect is the change in the thermal occupancies and spectra of the energy levels of the material as a function of temperature. For most materials, ω_0 decreases with temperature; so does E_g. For transparent materials, where ω's of interest lie inbetween these two energies, both of these changes tend to increase n. In the extreme limits where ω is such that either $\omega \to \omega_g$ or $\omega \to \omega_0$, dn/dT becomes very large and positive.

In the above discussion we have ignored contributions to dn/dT from free carriers.[11] These are generally negligible for pure materials, except for those with very narrow gaps, and will therefore be omitted henceforth. It should be noted, on the other hand, that for impure materials,[12] free-carrier effects may become a dominant influence on the dispersion of dn/dT throughout much of the transparent regime.

II. TWO-OSCILLATOR MODEL FOR *dn/dT*

As discussed above, we seek a formulation of dn/dT based on variation with temperature of the fundamental optical transitions in crystals, which for our purposes are the energy gap E_g ($\equiv \hbar\omega_g$) and fundamental phonon frequency ω_0, and their corresponding optical oscillator strengths.[11] In the simplest view, one obtains[11] the electronic susceptibility at frequency ω, neglecting damping effects, as

$$4\pi\chi_e(\omega) = \omega_{pe}^2(\omega_g^2 - \omega^2)^{-1} \quad (\omega < \omega_g) \ , \tag{1}$$

where ω_{pe} is the electronic plasma frequency. A more detailed account of optical transitions, such as given by Wemple and DiDomenico,[13] for example, leads to χ_e of a very similar form, except that $\omega_g^2 - \omega^2$ is replaced by $\omega_g^2 - c^2\omega^2$, where c is approximately unity and is nearly independent of temperature and frequency under the conditions of interest here; ω_g is an average optical band gap, defined in the Van Vechten sense[14] (see, also, Ref. 15). Similarly, the lattice susceptibility of a diatomic material may be taken as

$$4\pi\chi_l(\omega) = \omega_{pl}^2(\omega_0^2 - \omega^2)^{-1} \ , \tag{2}$$

where[16] $\omega_{pl}^2 = 4\pi N e^{*2}\mu^{-1} = (\epsilon_0 - \epsilon_\infty)\omega_0^2$, where e^* is the transverse effective charge, and the other symbols have their usual meanings. For crystals with more than one infrared-active phonon, one of course requires a sum of susceptibilities of the above form.

In the transparent region we need just the real part of the dielectric function, $\epsilon = n^2 = 1 + 4\pi(\chi_e + \chi_l)$. Employing the fact that ω_{pe}^2 is inversely proportional to the volume,[11] one obtains (for $\omega < \omega_g$)

$$\frac{dn}{dT} = \left(\frac{dn}{dT}\right)_e + \left(\frac{dn}{dT}\right)_l \ ,$$

where

$$\left(\frac{dn}{dT}\right)_e = \frac{1}{2n}\left[4\pi\chi_e\left(-3\alpha - \frac{2}{\omega_g}\frac{d\omega_g}{dT}\frac{1}{1-\omega^2/\omega_g^2}\right)\right] \tag{3a}$$

and

$$\left(\frac{dn}{dT}\right)_l = \frac{1}{2n}\left[4\pi\chi_l\left(-3\alpha + \frac{2}{e^*}\frac{de^*}{dT} - \frac{2}{\omega_0}\frac{d\omega_0}{dT}\frac{1}{1-\omega^2/\omega_0^2}\right)\right], \tag{3b}$$

where $(dn/dT)_e$ and $(dn/dT)_l$ are the electronic and lattice contributions to dn/dT, and α is the linear-thermal-expansion coefficient. The above formula will serve as a starting point for the calculations of this paper.

It is useful to further reexpress $d\omega_g/dT$ itself in terms of thermal expansion and explicit temperature variation terms:

$$\frac{1}{\omega_g}\frac{d\omega_g}{dT} = 3\alpha\,\frac{V}{\omega_g}\left(\frac{\partial\omega_g}{\partial V}\right)_T + \frac{1}{\omega_g}\left(\frac{\partial\omega_g}{dT}\right)_V \quad . \tag{4}$$

Following Yu and Cardona[8] one may employ the Van Vechten theory[14] to express $(\partial\omega_g/\partial V)_T$ in terms of the ionicity f in Phillip's scale[17]; the result is

$$\frac{V}{\omega_g}\left(\frac{\partial\omega_g}{\partial V}\right)_T \cong -0.8(1-f) \quad . \tag{5}$$

It should be noted, however, that the derivation of Eq. (5) involves approximations which are appropriate only for covalent materials.[8] We also note that in semiconductors the $(\partial\omega_g/\sigma V)_T$ term contributes[8] only a small fraction to the total change of the band gap with temperature, $d\omega_g/dT$; the dominant term is $(\partial\omega_g/\partial T)_V$.

III. ELECTRONIC CONTRIBUTION TO *dn/dT*

Inspection of Eq. (3) reveals that $(dn/dT)_e$ requires knowledge of the thermal-expansion coefficient α and the proportional change in band gap with temperature, $\omega_g^{-1}\,d\omega_g/dT$. The coefficient α is rather accurately known for most crystals, so that just the evaluation of $(\partial\omega_g/\partial T)_V$ becomes the central problem in evaluating $(dn/dT)_e$. Yu and Cardona[8] evaluated this quantity employing an approximate relation following from the Yu-Brooks formalism[9]; ω_g was assumed[18] to correspond to the gap at the X point of the Brillouin zone, which can be expressed, approximately, in closed form in terms of pseudopotential form factors. By screening the latter with appropriate Debye-Waller factors, they obtained

$$\frac{1}{\omega_g}\left(\frac{\partial\omega_g}{\partial T}\right)_V \simeq 2\,|\vec{G}(111)|^2\,\frac{\partial\bar{B}}{\partial T} \quad , \tag{6}$$

where $\vec{G}(111)$ is the reciprocal-lattice vector $2\pi a^{-1}(1,1,1)$, and $\partial\bar{B}/\partial T$ is related[8] to temperature derivatives of the Debye-Waller factor. In deriving the above expression, they assumed, among other things, that the mean-square displacements of the cation and anion were equal. One feature of Eq. (6) is that $\omega_g^{-1}(\partial\omega_g/\partial T)_V$ is determined entirely by thermal vibrations, while being independent of the specific nature of the electronic structure of the crystal. The justification and/or validity of this conclusion is not apparent. As mentioned previously, discrepancies to within 40% of experimental values were found.

Semiconductors

In the present work, we carry out computations of $d\omega_g/dT$ for various semiconductors, employing a full pseudopotential calculation, and utilizing Debye-Waller (D-W) factors obtained recently[19] from a rigid-ion lattice-dynamical calculation.[20] The latter D-W factors are believed to be more systematic and reliable than those available from fragmentary experimental data. In our computation, we identify the average gap as that at $\vec{k} = 2\pi a^{-1}\left(\frac{1}{2}, \frac{1}{2}, 0\right)$, as suggested by recent theoretical and experimental works.[21] The pseudopotential method of calculating $d\omega_g/dT$ has been described previously by Tsay *et al.*[22] and Mitra *et al.*,[23] to which the interested reader is referred. Our calculated values of $d\omega_g/dT$, and the corresponding predicted values of dn/dT, are listed in Table I, as are those obtained by Yu and Cardona.[8] The over-all agreement between theory and experiment is reasonably good, considering the simplicity of the theoretical model and the uncertainty in the experimentally measured values. This uncertainty stems in part from the lack of careful characterization of many of the measured samples. As an example of the scatter in the data, $n^{-1}\,dn/dT$ for Ge was reported as $6.9\times10^{-5}/°\mathrm{K}$ by Cardona *et al.*,[24] but as $1.0\times10^{-4}/°\mathrm{K}$ by Lukes.[25] Sufficient reliable data does not exist to decide on the merits of the present calculations, as opposed to the approximate version of Ref. 8; however, we believe our method to be more accurate for the reasons pointed out above.

Ionic Crystals

We have explored the possibility of a Yu-Brooks calculation of $d\omega_g/dT$ for alkali halides, in a manner similar to that described above for semiconductors. However, the results we have obtained appear to predict values about an order of magnitude greater than those implied by available experimental data of dn/dT at $\omega \gg \omega_0$ for these crystals, implying that Yu-Brooks theory may not be adequate for these crystals. For example, we carried out for NaCl and MgO the identical calculation as described above for semiconductors, except that an average of the four principal optical transitions identified in Ref. 26 were employed ($\Gamma_{15}\rightarrow\Gamma_1$, $\Sigma_4\rightarrow\Sigma_1$, $L_3\rightarrow L_2'$, $X_5'\rightarrow X_3$); values of the pseudopotential form factors were taken from Ref. 26, and D-W factors as computed by Namjoshi.[27] The results for $\omega_g^{-1}\,d\omega_g/dT$ were -3.1 and $-6.3\times10^{-4}/°\mathrm{K}$ for NaCl and MgO, respectively, about a factor of 10 and 2 too large. Actually, Radkowsky[28] also obtained values of the explicit temperature term $(\partial\omega_g/\partial T)_V$ an order of magnitude too large. His method involved calculations of electronic and hole energy level broadenings due to virtual phonon absorption and emission.

We here discuss a variety of alternative ways by which $d\omega_g/dT$ may be obtained for ionic crystals. It turns out that the term $(\partial\omega_g/\partial V)_T$ in ionic crystals tends to dominate the contribution to $d\omega_g/dT$. In fact it appears that one might obtain a qualita-

TABLE I. $n^{-1}\, dn/dT$ of crystals with diamond and ZB structures.

Crystal	ϵ_∞	α[a] (10^{-6}/°K)	ω_g[b] (eV)	$\frac{-dE_g}{dT}$ (10^{-4} eV/°K)	$\frac{1}{n}\frac{dn}{dT}$ (10^{-5}/°K)		
					Calc. (This work)	Calc. (Ref. 8)	Expt.[c]
GaAs	10.9	5.7	5.2	3.76	5.8	5.4	5.72[d] (5 ~ 20 μm)
GaSb	14.4	6.3	4.1	3.8	7.7	9.3	8.20[d] (5 ~ 20 μm)
InAs	12.3	5.4	4.6	3.55	6.3	6.7	...
InSb	15.7	5.1	3.7	3.46	8.0	15.0	11.9[d] (~ 3 μm)
InP	9.6	4.9	5.2	4	6.2	3.6	2.7[d] (5 ~ 20 μm)
GaP	9.1	5.7	5.8	3.25	4.2	2.2	3.7[e]
ZnS	5.2	6.7	7.9	5	4.3	...	3.3[f]
ZnSe	5.9	7.7	7.4	5.4	5.1	...	2.0[g]
ZnTe	7.3	8.4	5.8	6.3	8.3	...	...
CdTe	7.2	4.5	5.4	4.2	6.1	...	4.4[h] (10.6 μm)
C	5.7	1.1	13.6	...	...	1.1	0.5[i]
Si	12.0	4.2	4.8	3.0	5.1	3.7	3.9[j]
							4.7[k] (~ 5 μm)
Ge	16.0	6.0	4.3	3.5	6.8	6.1	6.9[j]
							10.0[l] (~ 5 μm)

[a] ZnTe from S. I. Novikova and K. Kh. Abrikosov, Sov. Phys. Solid State 5, 1558 (1964); others from *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963).

[b] Reference 14.

[c] The wavelengths to which the experimental data correspond are indicated in the parentheses.

[d] Reference 12.

[e] A. N. Piphtin and D. A. Yaskov, Sov. Phys. Solid State 9, 107 (1967).

[f] Reference 5.

[g] *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963).

[h] J. E. Keifer and A. Yariv, Appl. Phys. Letters 15, 21 (1969).

[i] P. T. Narasimham, Proc. Roy. Soc. (London) B 68, 315 (1955).

[j] Reference 24.

[k] F. Lukes, Czech. J. Phys. B10, 317 (1960).

[l] Reference 25.

tive estimate of $d\omega_g/dT$ to begin with, generally to within 30%, by neglecting the explicit temperature term $(\partial\omega_g/\partial T)_V$ entirely. Unfortunately, as indicated previously, the expression in terms of ionicity [Eq. (5)] is not adequate for quantitative prediction of the $(\partial\omega_g/\partial V_T)$ term in ionic crystals.

One body of data which supplies information about $d\omega_g/dT$ is the temperature dependence of the reflectance peaks in the spectra of alkali halides, as measured recently by Rubloff,[29] for example. $d\omega_g/dT$ deduced in this fashion is of the same order of magnitude as that deduced from experimental values of dn/dT but may differ by about 20% or more, as indicated in Table II. This is not unexpected, as an appropriate weighting of all transitions needs to be performed to accurately obtain $d\omega_g/dT$; the exciton structure[30] in the spectra of alkali halides further complicates such a procedure.

An alternative method of calculating $(dn/dT)_e$ in alkali halides abandons the formulation in terms of $d\omega_g/dT$, but relates dn/dT instead directly to dn/dp, where p is the pressure. What we have meant so far by dn/dT is the temperature derivative of n at constant pressure (more exactly atmospheric pressure), which should more appropriately be written $(\partial n/\partial T)_p$. In the regime $\omega_0 \ll \omega \ll \omega_g$, one obtains

$$\left(\frac{\partial\epsilon}{\partial T}\right)_p = (\epsilon - 1)\left[-3\alpha - \frac{6\alpha V}{\omega_g}\left(\frac{\partial\omega_g}{\partial V}\right)_T - \frac{2}{\omega_g}\left(\frac{\partial\omega_g}{\partial T}\right)_V\right]. \tag{7}$$

On the other hand, by assuming the existence of an equation of state, one has

$$\left(\frac{\partial\epsilon}{\partial p}\right)_T = \left(\frac{\partial\epsilon}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T$$

$$= (\epsilon - 1)\left[-3\alpha - \frac{6\alpha V}{\omega_g}\left(\frac{\partial\omega_g}{\partial V}\right)_T\right]\left(-\frac{K}{3\alpha}\right), \tag{8}$$

where K is the isothermal compressibility. If one assumes for the moment that $(\partial\omega_g/\partial T)_V$ is negligible compared with the other terms above, then

$$\left(\frac{\partial n}{\partial T}\right)_p = -3B\alpha\left(\frac{\partial n}{\partial p}\right)_T, \tag{9}$$

where $B = K^{-1}$ is the bulk modulus.

Data on $(\partial n/\partial p)_T$ are available for some alkali halides. Table III lists experimental values of

TABLE II. Temperature coefficients of ω_g of some ionic crystals.

Crystal	n	$-\frac{dn}{dT}$ $(10^{-5}/°\mathrm{K})$	3α $(10^{-5}/°\mathrm{K})$	$-\frac{1}{\omega_g}\frac{d\omega_g}{dT}$ $(10^{-5}/°\mathrm{K})$ Average of proportional shift of strong peaks	$-\frac{1}{\omega_g}\frac{d\omega_g}{dT}$ $(10^{-5}/°\mathrm{K})$ From fitting Expt. data of dn/dT
LiF	1.38	1.27	11.7	···	3.6
NaCl	1.5	3.65	13.2	···	2.3
NaF	1.3	1.6	10.8	···	2.4
KCl	1.45	3.6	11.8	1.9	1.5
KBr	1.52	4.0	12.9	1.3	1.8
KI	1.64	5.0	12.8	···	1.6
AgCl	2.0	6.1	9.0	···	0.43
CsI	1.74	10.0	14.7	···	-1.5
CsBr	1.66	6.3	14.7	2.1	1.2
CsCl	1.61	···	···	2.5	···
RbCl	1.47	···	10.5	0.6	···

$(\partial n/\partial T)_p$ and values of $(\partial n/\partial T)_p$ calculated from Eq. (9), using experimental values of B, α, and $(\partial n/\partial p)_T$. The agreement is seen to be excellent in the case of LiF, NaF, NaCl, and KCl and probably within experimental error for KBr and KI. The experimental value listed for MgO has been obtained by extrapolating data given in Ref. 31 for $\lambda = 0.405$ to 0.59 μm, where the pressure data was taken.

IV. LATTICE CONTRIBUTION TO *dn*/*dT*

The lattice contribution $(dn/dT)_l$ involves the temperature derivatives of the two fundamental lattice parameters, ω_0 and e^*. A variety of theoretical and experimental results exist which enable one to determine these quantities for a number of crystals.

TABLE III. dn/dT of ionic crystals calculated from experimental values of $(\partial n/\partial p)_T$.

Crystal	B[a] $(10^{12}$ dyn/cm$^2)$	$\left(\frac{\partial n}{\partial p}\right)_T$ $(10^{-12}$ cm^2/dyn$)$	$\frac{dn}{dT}$ $(10^{-5}/°\mathrm{K})$ Calc.	Expt.[b]
LiF	0.67	−0.198[c]	-1.5	-1.27
NaF	0.465	0.272[c]	-1.36	-1.6
NaCl	0.24	1.17[c]	-3.7	-3.65
NaBr	0.2	1.57[c]	-3.96	···
KCl	0.174	1.82[c]	-3.42	-3.6
KBr	0.148	2.44[c]	-4.66	-4.0
KI	0.117	3.85[c]	-5.75	-5.0
MgO	1.693	-0.158[d]	0.86	1.51
RbCl	0.156	2.24[e]	-3.78	···
RbBr	0.130	3.0[c]	-4.2	···

[a] C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971).

[b] For sources of experimental data of dn/dT, see Table IV.

[c] Appeared in J. Fontanella, C. Andeen, and D. Schuele, Phys. Rev. B 6, 582 (1972), as private communication from K. Vedam to the authors.

[d] K. Vedam and E. D. D. Schmidt, Phys. Rev. 146, 548 (1966).

[e] K. Vedam and E. D. D. Schmidt, J. Mater. Sci. 1, 310 (1966).

Semiconductors

For most semiconductors, the lattice terms are negligible except in a very narrow frequency region near ω_0. This situation is a consequence of small values of e^* [or, equivalently, $(\epsilon_0 - \epsilon_\infty)$], and relatively small values of $d\omega_0/dT$ and α. Indeed, measurements[32] of dn/dT in InP, GaAs, and GaSb demonstrate that dn/dT is nearly independent of frequency from 5 to 20 μm. A spectral dependence observed in InSb was attributed to free carriers. We therefore present only a brief discussion of the lattice terms in semiconductors.

Experimental data on $\omega_0^{-1} d\omega_0/dT$ is available for some semiconductors. Typical values are $-1.0 \times 10^{-4}/°\mathrm{K}$ for[33] ZnTe, $-2.3\times 10^{-5}/°\mathrm{K}$ for[34] GaP, and $-2.7\times 10^{-6}/°\mathrm{K}$ for[35] diamond. It does not appear that an adequate theoretical treatment of $d\omega_0/dT$ for semiconductors has yet been given.

The value of de^*/dT can be estimated from Szigeti's theory for the effective charge, as has been done by Jones *et al.*[36] It is found that $(e^*)^{-1} de^*/dT$ is of the same order of magnitude as $\omega_0^{-1} d\omega_0/dT$, although it is not certain how accurate this prescription is for diamond and ZB crystals. Independent experimental evidence for de^*/dT does not appear to be available.

Ionic Crystals

In ionic crystals, α and $\omega_0^{-1} d\omega_0/dT$ are typically about an order of magnitude larger than the corresponding values in semiconductors; also, $\epsilon_0 - \epsilon_\infty$ is relatively large in these crystals. Consequently, the dispersion of dn/dT owing to the lattice terms turns out to be important over a fairly large frequency range for most ionic crystals.

TABLE IV. Observed and calculated values of dn/dT for ionic crystals.

Crystal	α[a] (10^{-5}/°K)	$-\frac{1}{\omega_0}\frac{d\omega_0}{dT}$[b] ($10^{-4}$/°K)	$\frac{dn}{dT}$ (10^{-5}/°K)		$\frac{dn^c}{dT}$ (10^{-5}/°K) λ = 3.9 μm		λ = 5.3 μm		λ = 10.6 μm		l[d]
			Calc.[e]	Expt.[f]	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	
LiF	3.7	1.3	⋯	−1.27	−0.37	⋯	0.48	⋯	9.3	⋯	⋯
LiCl	4.3	~2.1	−3.1	⋯	−2.6	⋯	−2.1	⋯	1.3	⋯	⋯
LiBr	4.9	~2.5	−4.8	⋯	−4.4	⋯	−4.0	⋯	−1.5	⋯	⋯
NaF	3.6	1.25	⋯	−1.6	−1.5	−1.6	−1.3	⋯	−0.2	⋯	0.4
NaCl	4.4	~2.8	⋯	−3.65	−3.5	−3.3	−3.3	−3.2	−1.98	−2.0	1.4
NaBr	4.2	~3.2	−4.8	⋯	−4.7	⋯	−4.5	⋯	−3.8	⋯	⋯
NaI	4.5	~2.9	−5.9	⋯	−5.8	⋯	−5.7	⋯	−5.2	⋯	⋯
KF	3.5	~2.3	−1.2	⋯	−0.93	⋯	−0.63	⋯	1.4	⋯	⋯
KCl	3.6	~2.7	⋯	−3.6	−3.5	−3.6	−3.3	−3.6	−2.75	−2.8	⋯
KI	4.26	3.4	⋯	−5.0	−5.0	⋯	−4.9	⋯	−4.6	⋯	⋯
KBr	4.3	3.6	⋯	−4.0	−3.9	⋯	−3.8	⋯	−3.4	⋯	⋯
RbCl	3.5	3.4	−3.0	⋯	−2.9	⋯	−2.8	⋯	−2.4	⋯	⋯
RbBr	3.6	3.8	−3.4	⋯	−3.35	⋯	−3.3	⋯	−3.0	⋯	⋯
CsCl	~4.7	3.2	−6.1	⋯	−6.0	⋯	−5.9	⋯	−5.4	⋯	⋯
CsI	4.7	3.4	⋯	−10.0	−10.0	−9.9	−10.0	−9.9	−9.8	−9.5	⋯
CsBr	4.7	4	⋯	−6.3	−6.26	⋯	−6.2	⋯	−5.98	⋯	⋯
AgCl	3.0	9.3	⋯	−6.1	−5.8	⋯	−5.5	⋯	−3.5	⋯	⋯
AgBr	3.5	7.3	−6.3	⋯	−6.1	⋯	−6.0	⋯	−5.0	⋯	⋯
MgO	1.1	0.54	⋯	1.51	2.0	⋯	2.5	⋯	8.7	⋯	⋯

[a] Thermal-expansion data are taken from A. J. Moses, *Handbook of Electronic Materials* 1 (Plenum, New York, 1971), and *American Institute Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963).

[b] The experimental data of $\omega_0^{-1}\, d\omega_0/dT$ are from the following sources: LiF and MgO, J. R. Jasperse, A. Kahan, J. N. Plendl, and S. S. Mitra, Phys. Rev. 146, 526 (1966); NaF, T. F. Chang and S. S. Mitra, Phys. Rev. B 5, 4994 (1972); those having a "~" sign in the front are estimated from the Grüneisen approximation (see text); all others are from Ref. 31.

[c] Experimental data of dn/dT at $\lambda = 3.9$, 5.3, and 10.6 μm are obtained by interpolation and extrapolation from the following sources: NaF, H. W. Hohls, Ann. Physik 29, 433 (1937); NaCl, *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963); KCl, Ref. 7; CsI, W. S. Rodney, J. Opt. Soc. Am. 45, 987 (1955).

[d] $l = 1$ unless specified.

[e] Corresponds to dn/dT at frequencies in the "intermediate" region where both electronic and lattice dispersions have negligible effect. For most ionic crystals, this corresponds to $3 \gtrsim \lambda \gtrsim 0.5$ μm.

[f] All expt. values of dn/dT in the intermediate frequency region are from *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963) and references therein, except CsBr and LiF, which are from M. Brodsky and E. Burstein, Bull. Am. Phys. Soc. 7, 214 (1962).

A reasonable amount of experimental data on $d\omega_0/dT$ is available for ionic crystals.[36, 37] Alternatively, $d\omega_0/dT$ may be deduced from the Grüneisen expression[37]

$$\omega_0(T) = \omega_0(0)\exp\left(-3\gamma \int_0^T \alpha\, dT\right) , \qquad (10)$$

where γ is the mode Grüneisen parameter for ω_0. The above expression accounts only for volume-induced changes, in the quasiharmonic approximation. Strictly speaking, Eq. (10) is applicable only when the anharmonic self-energy is negligible; however, a propitious cancellation of anharmonic contributions in $\omega_0(T)$ enables reasonably good predictions of $d\omega_0/dT$ to be made for many ionic crystals. For example, experimental values[36] of $\omega_0^{-1}\, d\omega_0/dT$ for KBr and KI are -3.6 and -3.4×10^{-4}/°K, respectively, while the corresponding theoretical values computed from Eq. (10) are -3.4 and -3.0×10^{-4}/°K. When the cancellations do not occur, or if more accurate values are required, one also needs to calculate self-energy shifts due to anharmonicity.[37] Such calculations require detailed knowledge of the phonon spectrum.[38]

Theoretical treatments of de^*/dT do not appear to exist. Scant experimental data,[36] employed in conjunction with the Szigeti theory, yields values of $-(e^*)^{-1} de^*/dT$ of 2.4, 2.4, 1.9, and 5.7×10^{-4}/°K for KI, RbCl, CsCl, and AgBr, respectively. The corresponding values of $-\omega_0^{-1} d\omega_0/dT$ are 3.4, 3.4, 3.2, and 7.3×10^{-4}/°K. This suggests that a useful parametrization is $e^*(T)^2 \propto \omega_0^l(T)$, where $l \approx 1.5$. Actually, the reliability of the experimentally deduced values of de^*/dT is rather questionable, and it is probably preferable for the time being to fit l from the spectral dependence of dn/dT, whenever possible. It turns out that values of

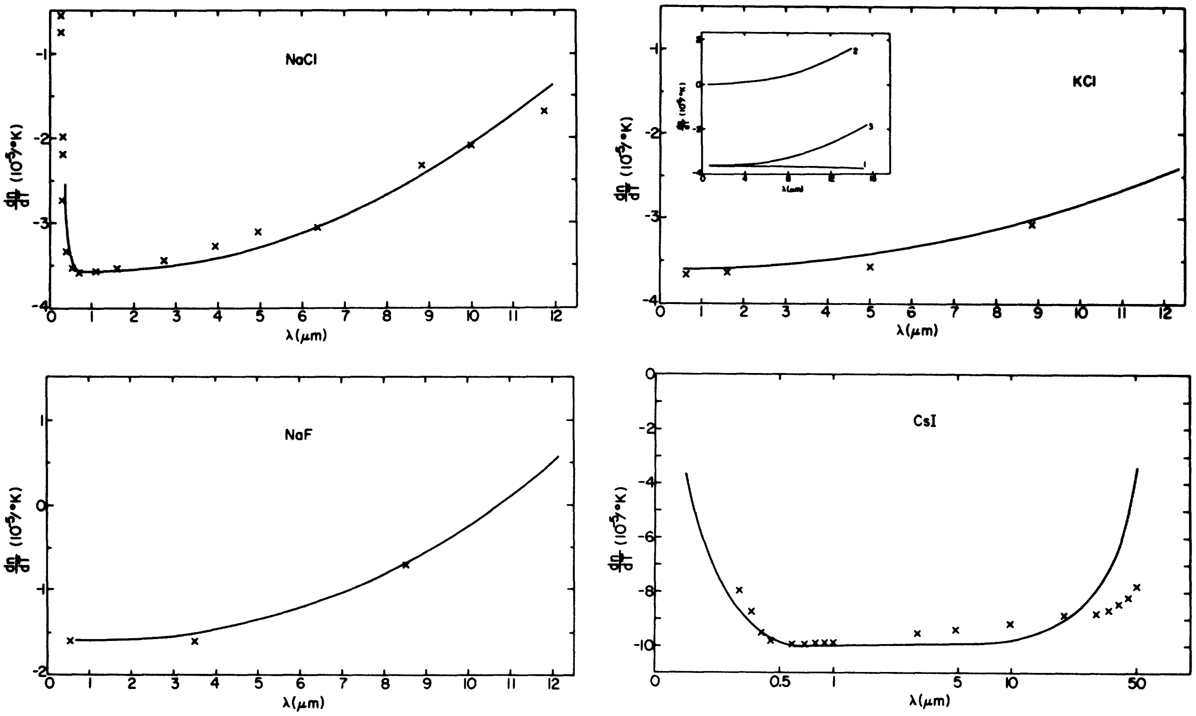

FIG. 1. dn/dT of various ionic crystals as a function of wavelength; solid line is the calculated result and crosses indicate experimental data. For NaCl, experimental data is from *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963); for KCl, from Ref. 5; for NaF, from H. W. Hohls, Ann. Physik 29, 433 (1937); and for CsI, from W. S. Rodney, J. Opt. Soc. 45, 987 (1955). Calculated curves employ values indicated in text and Table IV. Insert for KCl shows separate contributions: curve 1, electronic; curve 2, phonon; and curve 3, their total.

$l \approx 0.5-1.5$ are appropriate for those ionic crystals where such a fit is possible. It is reasonable to assume that other ionic crystals fall within the same range, so that the above prescription allows for, at the very least, an estimate of the contribution of the de^*/dT terms.

In Table IV, we present a comparison of available experimental data and calculated results for dn/dT. Values in the dispersionless regime, and at the wavelengths of spectral interest for laser applications, $\lambda = 3.9$, 5.3, and 10.6 μm, are listed. $-\omega_g^{-1} d\omega_g/dT$ was chosen as 1.5, 2.4, and 3.5 $\times 10^{-5}$/°K for potassium, sodium, and lithium salts, respectively, as deduced from the patterns evidenced in Table II; when no data was available, this value was approximated as 1.0×10^{-5}/°K. The exponent l was fitted from the dispersion of $(dn/dT)_l$ when such was possible, and chosen as unity otherwise. For the most part, the agreement between theory and experiment is encouraging. A more detailed comparison is presented in Fig. 1, which illustrates the dispersion of dn/dT for NaCl, KCl, NaF, and CsI; the insert indicates the electronic and phonon contribution to dn/dT for KCl. In this case, it is observed that phonon dispersion is instrumental in determining dn/dT even for wavelengths as small as 5 μm.

V. DISCUSSION

We have presented a simplified two-oscillator model of dn/dT in the transparent regime of diatomic cubic crystals. In addition to the usual parameters appearing in the expression for the refractive index, the only parameters required to evaluate dn/dT as a function of frequency are the thermal-expansion coefficient α and the temperature derivatives of the lattice mode ω_0, the effective band gap ω_g, and the effective transverse charge e^*. Values of α are readily available for almost all crystals of interest. Theoretical and/or experimental values of $d\omega_g/dT$ and $d\omega_0/dT$ are available for many crystals; de^*/dT is less well known, but may be estimated from the limited available data. In our presentation we have distinguished between electronic and lattice contributions, and between thermal-expansion and explicit temperature contributions to dn/dT.

For the case of semiconductors the electronic contribution $(dn/dT)_e$ dominates throughout the transparent regime, except for a narrow region of frequencies near ω_0. The electronic contribution, in turn, is dominated by the $(\partial\omega_g/\partial T)_V$ term, as opposed to those resulting from thermal-expansion effects. Our calculation of $d\omega_g/dT$ for various ZB-and diamond-type semiconductors, employing a temperature-dependent-pseudopotential formalism, is found to yield values in good agreement with experiment.

In the case of ionic crystals both $(dn/dT)_l$ as well as $(dn/dT)_e$ are important in the transparent regime, although $(dn/dT)_e$ is generally much larger throughout this regime. The electronic contribution stems primarily from the thermal-expansion terms. Theoretical attempts to calculate $d\omega_g/dT$ appear inadequate for these crystals; however, experimental data on temperature dependence of reflectivity peaks, and relations between dn/dp and dn/dT provide alternative methods of obtaining information on the electronic contribution. As for $(dn/dT)_l$, the terms involving α, $d\omega_0/dT$ and de^*/dT may all be important, depending on the particular crystal and the frequency of interest. $d\omega_0/dT$ values are available experimentally, as well as from a quasiharmonic theoretical treatment; de^*/dT determined from experiment, as well as from fitting the spectral dependence of dn/dT, indicates that $e^*(T)^2 \propto \omega_0^l(T)$, where $l \approx 0.5-1.5$. Although a reliable comparison is hindered by the sparsity and uncertainty of available data, the present model does appear to predict results in reasonable agreement with experiment.

The typical magnitude and sign of dn/dT of crystals in the visible region may easily be understood on the basis of the above results. For semiconductors, where the $d\omega_g/dT$ term is much larger than the thermal-expansion term, dn/dT is positive, and of the order of $\omega_g^{-1} d\omega_g/dT \sim 10^{-4}$. For highly ionic crystals, thermal-expansion terms dominate the electronic contribution, and dn/dT takes on large negative values of the order of $\sim 3\times10^{-5}$. The value of dn/dT increases towards positive values as $\omega \to \omega_0$, were lattice dispersion effects become large.

The present simplified model does not account for higher-order phonon terms, which make a small, but highly temperature-dependent contribution to dn/dT. In crystals that are not infrared active these are the only lattice contributions, and may become important at very high temperatures. In addition, free-carrier effects may become important, even in relatively pure materials, at sufficiently high temperatures. All such effects are outside the purview of the present approach.

In conclusion, we believe the present approach has successfully identified the major physical mechanisms affecting dn/dT, and provides a theoretical prescription for predicting dn/dT over a wide range of frequencies, for many semiconductors and ionic crystals. Only a small number of physically meaningful parameters are employed. More detailed measurements in the future on well-characterized samples will enable a more meaningful comparison between theory and experiments.

---

*Supported by U.S. Air Force under Contract No. F19628-72-C-0286.

†Permanent address: Department of Electrical Engineering, University of Rhode Island, Kingston, R.I. 02881.

[1] See, for example, A. Smakula, Opt. Acta **9**, 205 (1962).

[2] Conference on High Power Laser Window Materials, edited by C. Sahagian and C. Pitha, Technical Report No. AFCRL-71-0592, AFCRL, Bedford, Mass., 1971 (unpublished), (available from Natl. Tech. Info. Center, Def. Doc. Center, AFCRL, or the authors). M. Sparks, J. Appl. Phys. **42**, 5029 (1971); J. R. Jasperse and P. D. Gianino, J. Appl. Phys. **43**, 1686 (1972).

[3] B. Bendow and P. D. Gianino, Theory of On-Axis Intensity Distribution in Thermal Lensing, Technical Report No. AFCRL-72-0322, AFCRL, Bedford, Mass., 1972 (unpublished), (available from Natl. Tech. Info. Center, Def. Doc. Center, AFCRL, or the authors).

[4] See, for example, *Progress in Crystals*, edited by K. S. Krishnan (Vaswanathan, Madras, India, 1958), Vol. I; Compendium on High Power Laser Window Materials, edited by C. Sahagian and C. Pitha, Technical Report No. AFCRL-72-0170, AFCRL, Bedford, Mass., 1972 (unpublished) (available from Natl. Tech. Info. Center, Def. Doc. Center, AFCRL, or the authors).

[5] G. N. Ramachandran, Proc. Indian Acad. Sci. A **25**, 266 (1947); Proc. Indian Acad. Sci. A **25**, 280 (1947); Proc. Indian Acad. Sci. A **25**, 286 (1947).

[6] T. S. Moss, *Photoconductivity* (Butterworth, London, 1952).

[7] E. Antoncik, Czech. J. Phys. **6**, 209 (1956).

[8] P. Y. Yu and M. Cardona, Phys. Rev. B **2**, 3193 (1970).

[9] S. C. Yu, Ph.D. thesis (Harvard University, 1964) (unpublished); S. C. Yu and H. Brooks (unpublished).

[10] See, for example, R. A. Hilton and C. E. Jones, Appl. Opt. **6**, 1513 (1967); T. Baak, J. Opt. Soc. Am. **59**, 851 (1969); M. Sparks, J. Appl. Phys. **42**, 5029 (1971).

[11] See, for example, J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U. P., Cambridge, England, 1964).

[12] This appears to be the case for the InSb sample measured by M. Cardona, in *Proceedings of the International Conference on the Physics of Semiconductors, Prague* (Academic, New York, 1961), p. 388.

[13] S. H. Wample and J. DiDomenico, Phys. Rev. B **3**, 1338 (1971).

[14] J. VanVechten, Phys. Rev. **182**, 891 (1969).

[15] D. Penn, Phys. Rev. **128**, 2093 (1962).

[16] E. Burstein, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, England, 1965).

[17] J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970).

[18] V. Heine and R. O. Jones, J. Phys. C **2**, 719 (1969).

[19] J. F. Vetelino, S. P. Gaur, and S. S. Mitra, Phys. Rev. B **5**, 2360 (1972).

[20] J. F. Vetelino and S. S. Mitra, Phys. Rev. **178**, 1349 (1969).

[21] See, for example, M. L. Cohen and V. Heine, in *Solid State Physics* (Academic, New York, 1970) Vol. 24; M. Welkowsky and R. Braustein, Phys. Rev. B **5**, 497 (1971).

[22] Y. F. Tsay, G. Gong, S. S. Mitra, and J. F. Vetelino, Phys. Rev. B **6**, 2330 (1972).

[23] S. S. Mitra, Y. F. Tsay, and J. F. Vetelino, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors* (Polish Science Publishers, Warsaw, 1972).

[24] M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

[25] F. Lukes, Czech. J. Phys. **B10**, 742 (1960).

[26] C. Y. Fong and M. L. Cohen, Phys. Rev. Lett. **21**, 22 (1968) (NaCl) and M. L. Cohen, P. J. Lin, D. M. Roessler, and W. C. Walker, Phys. Rev. **155**, 992 (1967) (MgO).

[27] K. V. Namjoshi (private communication).

[28] A. Radkowsky, Phys. Rev. **73**, 749 (1948).

[29] G. W. Rubloff, Phys. Rev. B **5**, 622 (1972).

[30] R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

[31] R. E. Stephens and I. H. Malitson, J. Res. Natl. Bur. Stand. (U.S.) **49**, 249 (1952).

[32] M. Cardona, Ref. 12.

[33] J. L. LaCombe and J. C. Irwin, Solid State Commun. **8**, 1427 (1970).

[34] A. S. Barker, Phys. Rev. **165**, 917 (1968).

[35] S. Solin and A. Ramdas, Phys. Rev. B **1**, 1687 (1970).

[36] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. R. Soc. A **261**, 10 (1961).

[37] S. S. Mitra, *Optical Properties of Solids*, edited by S. Nudelman and S. S. Mitra (Plenum, New York, 1969).

[38] R. A. Cowley, Adv. Phys. **12**, 421 (1963); I. P. Ipatova, A. A. Maradudin, and R. F. Wallis Fiz. Tverd. Tela **8**, 1064 (1966) [Sov. Phys.-Solid State **8**, 850 (1966)]; Phys. Rev. **155**, 882 (1967); A. S. Pine and P. E. Tannenwald, Phys. Rev. **178**, 1424 (1969).