09

# The analytical description of the refractive index temperature coefficient in III–V semiconductors within the normal dispersion theory approach

© I.I. Vrubel[1], E.D. Cherotchenko[1], D.A. Mikhailov[1], R.G. Polozkov[2], V.V. Dyudelev[1], G.S. Sokolovsky[1]

[1] Ioffe Institute, St. Petersburg, Russia
[2] Alferov Federal State Budgetary Institution of Higher Education and Science Saint Petersburg National Research Academic University of the Russian Academy of Sciences, St. Petersburg, Russia
E-mail: echerotchenko@gmail.com

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In the framework of the normal dispersion theory we obtain the energy dependence of the refractive index temperature coefficient in the transparency window of the III–V family typical compounds. Additionally, we show that the main results are also applicable to compounds of other classes: monomolecular compounds of group IV, as well as zinc-based chalcogenide semiconductors. It is shown that the growth of the refractive index is caused by a simultaneous decrease in the probability of interband transitions and the width of the band gap of these semiconductors upon heating. The fundamental relationship of the obtained results with the Varshni formula is considered. The applicability of the obtained results to the problem of dual-comb spectrometry is discussed.

**Keywords:** QCL, refractive index, dual-comb spectroscopy.

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Semiconductor quantum cascade lasers have found many technical applications. The most promising engineering applications are gas analysis and sampling, where lasers with their comb emission spectrum are used as sources of probing signals in a two-beam heterodyne-like arrangement (dual-comb-spectroscopy [1]). The energy dependence of the macroscopic absorption cross section in the infrared range, which is unique to different materials, is measured in such devices to determine the chemical composition of samples. The macroscopic IR cross section of the sample is estimated by analyzing the attenuation of a superposition of beams from two independent lasers that have passed through a cell containing this sample. Since the typical spectrum of IR laser radiation includes tens of modes in a comb spectrum, energy selection (selection of a pair of attenuated interfering longtitudinal modes) may be performed by measuring the amplitude of beats of the lowest frequency within the range from several tens to a hundred megahertz.

One of the challenges in such a device is to ensure controllable variability of two comb spectra relative to each other. The authors of the original study [1] proposed to use heating [2] as the primary method of adjusting the spectral characteristics of a laser by altering the refractive index of the active region ($dn/dT$). Since most infrared solid-state lasers are based on III–V compounds, we consider the coefficient of temperature dependence of the refractive index for this group of materials, propose a model for predicting its dispersion, and examine its applicability. In addition, we extrapolate the proposed model to II–VI compounds and monomolecular group IV semiconductors.

The starting point for determining the temperature coefficient of the refractive index is the basic approximation aimed at characterizing the refractive index of a material: the normal dispersion theor. In the present study, we use the basic equation formulated in the energy representation in [3] for a single effective oscillator:

$$n(\hbar\omega) = \sqrt{1 + \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2}}. \quad (1)$$

Here, $n(\hbar\omega)$ is the refractive index of a medium, which depends on photon energy, and $E_0$ and $E_d$ are problem parameters. A comparative analysis of the first parameter for typical III–V compounds, which are listed in the Table, reveals that, as a first approximation, the $E_0$ parameter may be taken equal to twice the value of the band gap of the material ($E_g$). In turn, the parameter $E_d$ has the meaning of effective oscillator strength and a more complex origin, and its value obeys the following empirical rule [7]:

$$E_d = \gamma N_c Z_a N_e, \quad (2)$$

where $\gamma$ is a parameter with the dimension of energy, which characterizes the measure of covalence/ionicity of a material and assumes the values from 0.26 (for truly ionic compounds) to 0.39 (for truly covalent compounds); and parameters $N_c$, $Z_a$, $N_e$ denote the cation coordination number, the anion formal valence, and the effective number of electrons per anion in a given crystal respectively. The temperature dependence of a dielectric permittivity $\varepsilon_\infty$ (where $\varepsilon_\infty = n_\infty^2$) the long wavelength limit ($\hbar\omega \to 0$, but $\hbar\omega > E_{phonon}$ to exclude non-optical polarization) in the presented approximation has been extensively studied in literature. Let us consider its analytical expression based

Optical characteristics and parameters of the electronic structure of typical semiconductors

| Material | $E_0$, eV [4] | $E_g$, eV [5] | $n_\infty(\sqrt{\varepsilon_\infty})$ [5] | $\frac{dE_g}{dT}$, $10^{-4}$ eV · K$^{-1}$ [5] | $\frac{d\varepsilon_\infty}{dT}$, $10^{-4}$K$^{-1}$ [6] |
|---|---|---|---|---|---|
| Ge | 2.7 | 0.7 | 4.0 | −4 | 22 |
| Si | 4 | 1.1 | 3.4 | −3 | 9.3 |
| C | 11 | 5.5 | 2.4 | −0.5 | 0.6 |
| GaAs | 3.6 | 1.4 | 3.3 | −5 | 12 |
| GaP | 4.5 | 2.3 | 2.9 | −4 | 6.7 |
| ZnSe | 5.5 | 2.7 | 2.4 | −6 | 3.0 |
| ZnS | 6.4 | 3.5 | 2.2 | −5 | 3.4 |

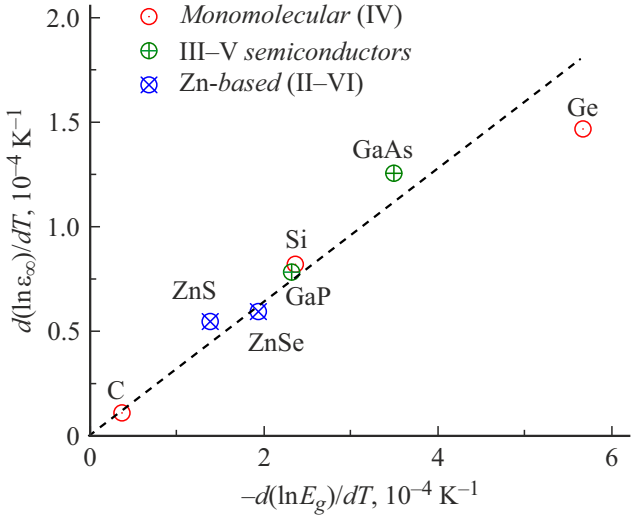


**Figure 1.** The diagram plotted based on the experimental data (see the Table) and illustrating the linear relation between the logarithmic derivative of the band gap width and the left-hand side of expression (5) with proportionality coefficient $\chi$. Red, green, and blue colors correspond to monomolecular Ge, Si, and C (diamond) compounds; III−V semiconductors (GaAs, GaP); and zinc-based II−VI compounds (ZnSe, ZnS), respectively. A color version of the figure is provided in the online version of the paper.

on the presented parameters:

$$n_\infty^2 = \varepsilon_\infty = 1 + \frac{E_d}{E_0}. \tag{3}$$

The temperature dependence of permittivity may then be written in a trivial form

$$\frac{d\varepsilon_\infty}{dT} = (\varepsilon_\infty - 1)\left(\frac{1}{E_d}\frac{dE_d}{dT} - \frac{1}{E_0}\frac{dE_0}{dT}\right). \tag{4}$$

This expression may be calibrated against the available experimental data (see the Table) by applying the following ansatz: let us assume that the relation between parameter $E_0$ and band gap width $E_g$, which has been identified earlier in the description of parameters of the normal dispersion theory, is valid for their increments induced by an increase in temperature (i. e., $dE_0 = 2dE_g$). The previous expression is then simplified to the form

$$\frac{1}{\varepsilon_\infty - 1}\frac{d\varepsilon_\infty}{dT} = \frac{2n_\infty}{n_\infty^2 - 1}\frac{dn_\infty}{dT} \approx \frac{1}{E_d}\frac{dE_d}{dT} - \frac{1}{E_g}\frac{dE_g}{dT}, \tag{5}$$

where the only unknown is the logarithmic derivative of the effective strength of a single oscillator. The results of a systematic comparative analysis of the left-hand side of the approximate equality and the logarithmic derivative of the band gap width for typical semiconductor materials (see Fig. 1) revealed that their magnitudes are related by a proportionality coefficient $\chi$. Thus, expression (5) may be rewritten as

$$\frac{1}{E_d}\frac{dE_d}{dT} - \frac{1}{E_g}\frac{dE_g}{dT} \approx -\chi\left(\frac{1}{E_g}\frac{dE_g}{dT}\right), \tag{6}$$

where $0 < \chi < 1$. Alternatively,

$$\frac{1}{E_d}\frac{dE_d}{dT} = (1-\chi)\frac{1}{E_g}\frac{dE_g}{dT}. \tag{7}$$

Let us now consider the complete expression for the temperature coefficient of the refractive index derived from expression (1):

$$\frac{dn}{dT}(\hbar\omega) = \frac{1}{2n(\hbar\omega)}\frac{E_d E_0}{E_0^2 - (\hbar\omega)^2}\left(\frac{1}{E_d}\frac{dE_d}{dT} + \frac{1}{E_0}\frac{dE_0}{dT} - \frac{2E_0^2}{E_0^2 - (\hbar\omega)^2}\frac{1}{E_0}\frac{dE_0}{dT}\right), \tag{8}$$

which assumes the following form after the substitution of expressions including $E_0$ and $E_d$ with the equivalent ones containing $E_g$:

$$\frac{dn}{dT}(\hbar\omega) = \frac{(n(\hbar\omega)^2 - 1)}{2n(\hbar\omega)}\frac{1}{E_g}\frac{dE_g}{dT} \times \left((2-\chi) - \frac{2}{1 - \left(\frac{\hbar\omega}{2E_g}\right)^2}\right). \tag{9}$$

Having optimized this expression by estimating the proportionality coefficient as $\chi = 1/3$ based on the data from Fig. 1 and omitting the refractive index dispersion, we obtain the final form of the dependence of the temperature coefficient of the refractive index:

$$\left(\frac{1}{E_g}\frac{dE_g}{dT}\right)^{-1}\frac{dn}{dT}(\hbar\omega) = \frac{n_\infty^2-1}{2n_\infty}\left(\frac{5}{3}-\frac{2}{1-\left(\frac{\hbar\omega}{2E_g}\right)^2}\right). \quad (10)$$

This final formula may be verified directly with a high reliability for key III–V compounds, since the values on the left-hand side of the expression are determined solely by the experimental data, while the right-hand side may be calculated theoretically under the assumption that $n_\infty \approx 3$ for a typical III–V compound. The result is presented in Fig. 2, which shows that the energy dependence of the temperature coefficient fits various compounds and is approximated closely by theoretical functional dependence (10). It is evident that the temperature coefficient normalized to the temperature logarithmic derivative of the band gap width undergoes a twofold change in the transparency window: this quantity tends to 0.5 in absolute value in the long wavelength limit and approaches unity near the fundamental absorption edge ($\hbar\omega \to E_g$).

In the long-wave limit ($\hbar\omega \ll E_g$), which corresponds to the infrared range, expression (9) is simplified significantly in the III–V semiconductor family, where inequality $n_\infty^2 \gg 1$ is valid:

$$\frac{dn_\infty}{dT} = \frac{n_\infty}{2}\left(-\chi\frac{1}{E_g}\frac{dE_g}{dT}\right). \quad (11)$$

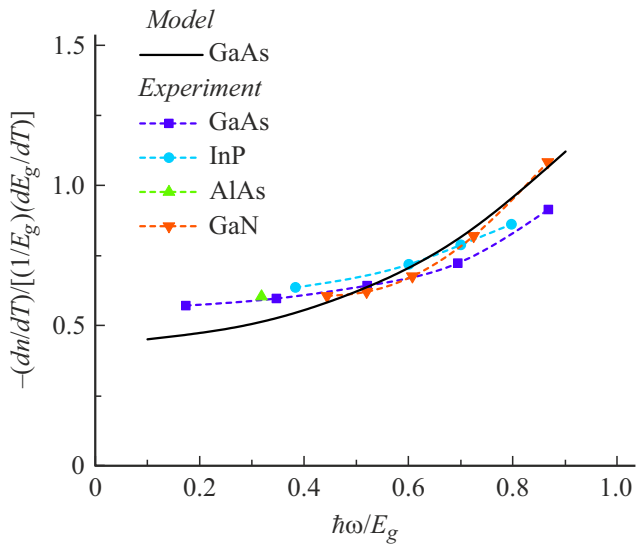


**Figure 2.** The comparison of the theoretical formula (expression (10)) for the energy dependence of the temperature coefficient of the refractive index (solid curve) with the experimental data for typical III–V compounds: GaAs [8], InP [9], AlAs [10], GaN [11].

The part of this expression in brackets, which is present in explicit form in formula (6), implies that the thermally stimulated refractive index variation in the long wavelength limit is actually determined by the direct difference between relative temperature changes in the an oscillator strength and its effective resonant energy.

The relative temperature coefficient of the band gap width present in formula (11) incorporates its fundamental relation to optical characteristics. Indeed, this value decreases monotonously in accordance with the empirical Varshni law [12]:

$$E_g(T) = E_g^0 - \frac{\alpha T^2}{T+\beta}, \quad (12)$$

where $E_g^0$ is the band gap width at absolute zero and $\alpha$ and $\beta$ are coefficients. The latter parameter specifies the characteristic temperature above which the dependence of the band gap width changes from a parabolic to an almost linear one. Its correlation with the Debye temperature [13] illustrates the fact that the electronic structure (and, consequently, the refractive index) are perturbed only when high-energy lattice phonon modes are activated. Since the functional dependence changes at a certain point, the temperature coefficient of the refractive index in a very wide range (on the order of several hundred degrees) should be considered as a function $\frac{dn_\infty}{dT}(T)$. The obtained results specify the key requirements for the design of a dual-comb spectrometer. The constant temperature coefficient of the refractive index and its robustness against the specifics of manufacture and usage lead to the fact that its value is an external boundary parameter of the system being designed. Let us assume that the lowest energy modes (to be specific, $i$ and $j$) form the lowest frequency beats at a stabilized temperature of both lasers and estimate the change in refractive index at which the modes of scanning and reference lasers pass through all possible mutual positions; i. e., $\lambda_i = \lambda_j = \lambda_{j-1}^*$, where $i$ — the reference laser mode number and $j$ — starting mode number of the scanning laser. This is equivalent to the condition that the wavelength of mode $j$ of the scanning laser changes by a value equal to the intermode distance upon heating; i. e.,

$$\lambda_j^* - \lambda_j = \frac{\lambda_j \Delta n}{n} = \frac{\lambda_j^2}{2nL}. \quad (13)$$

The relative refractive index change for wavelengths within the range of 8 $\mu$m and a resonator length of 1.5 mm may then be expressed as $\Delta n/n \approx 0.001$. Taking into account the typical values of refractive index (approximately 3) and its long-wave temperature coefficient (about 0.0002 $\mathrm{K}^{-1}$), one finds that the entire energy range is scanned when the second laser is heated by 15 K. An estimate of the dual-comb spectrometer energy scale length, i. e., the region of overlap of laser emission spectra, gives a value of the order of 500 GHz [1], while the order of magnitude of the intermode gap of the comb spectra is 10 GHz [1]. This provides 50 discrete intervals over the entire heating scale. Thus, if a single-band low-frequency beat detector

is used, one should be able to set the temperature of the active region of the heated laser with an accuracy no worse than 0.15 K. This condition is crucially important, as it sets the overall resolution of the system as a whole, and constitutes one point in the list of technical requirements for the design of a device intended for application outside of a laboratory.

Finally, we calculated the universal energy dependence of the refractive index temperature coefficient for III−V semiconductors in the transparency window. We established the fundamental reasons for the increase in refractive index of these materials upon heating due to thermally stimulated changes in the parameters of their electronic structure. Technical and methodological guidelines for application of the studied effect in laser technology were formulated.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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