International Journal of Scientific Research in Modern Science and Technology
© IJSRMST \ Vol. 1 \ Issue 4 \ 2022
ISSN: 2583-7605 (Online)
www.ijsrmst.com

Study of Theoretical Derivative of Temperature Variation of Refractive Indices

D.N. Pandey

Department of Physics, Shri L.B.S. Degree College, Gonda, Uttar Pradesh, India

ABSTRACT:

In this paper we have studied the theoretical derivation of the temperature variation of the refractive indices. The temperature derivatives of the refractive indices of ionic crystals are useful to estimate the quantum dependence of some useful parameters such as the electronegative parameter etc.

Keywords: Theoretical derivative, temperature, refractive indices, electronegative parameter, ionic crystal.

Introduction:

The temperature dependence of optical refractive index (n) and average energy gap (E_g) separately at constant pressure and constant volume of ionic solids, covalent semiconductors and complex binary crystal have been of great interest industrially due to wide ranging properties of optical, semiconducting, photo elastic, photoconductivity and solar applications. The temperature application causes a family of crystals to significantly alter their optical refractive index and average energy gap, which is advantageous in the aforementioned applied fields. The temperature derivatives of the refractive indices of ionic crystals are useful to estimate the quantum dependence of some useful parameters such as the electronegative parameter etc. Studies of dn/dT for diamond and III–V zineblende type crystals are in good agreement with the limit of 40%. Further attempts were made to relate the values of dn/dT to thermal expansion effects in crystals, but did not account for the effect of variations in the system energy levels and the strength of the associated oscillators. Both lattice and electronic contributions were calculated for the dn/dT of alkali halides as well as the temperature derivatives of E_g. But for impure materials the free carrier effect can have major influence on the dispersion theory for temperature variation of refractive indices and dielectric constants in the whole transparent region. This theory of lattice spacing and broadening of the energy band with temperature suggests that a small change in the optical refractive index is expected due to a change in the energy gap of the solid. Calculated temperature derivatives of the dielectric constant and mean energy difference using the macroscopic Clausius Mosoty relation as a basis.

Theoretical Derivative of Temperature Variation:

To study the temperature dependent behavior of electronic dielectric constant ($\in_\propto$) and average energy gaps (E_g), In 1968 Samara extended the microscopic Clausius Mosotti relation in a much broader way, arguing that Frölich (1949) and Hinga and Bosman (1963) proved the Clausius Mosotti relation to be quite valid for cubic or isotropic materials. He calculated the logarithmic derivative of the Clausius Mosotti relation with respect to temperature as follows:

$$\frac{3\in_{\propto}}{(\in_{\propto}-1)(\in_{\propto}+2)}\left(\frac{dlog\in_{\propto}}{dT}\right)_P = -\gamma + \gamma\left(\frac{d\,log\,\alpha}{d\,log\,V}\right)_T + \left(\frac{d\,log\,\alpha}{dT}\right)_V \qquad .....(1)$$

In the equation (1), the first term of RHS ($-\gamma$) represnts the change in $\in_{\propto}$ due to change in density and the second term of RHS $\gamma\left(\frac{d\,log\,\alpha}{d\,log\,V}\right)_T$ is for the change in $\in_{\propto}$ due to change in polarisability of a fixed number of particle with changing volume.

In this equation, the factor $\left(\frac{d\,log\alpha}{d\,log\,V}\right)_T$ can be calculated from the pressure dependence of $\in_{\propto}$ as

$$\frac{3\in_{\propto}}{(\in_{\propto}-1)(\in_{\propto}+2)}\left(\frac{dlog\in_{\propto}}{dP}\right)_T = -\beta\left(\frac{d\,log\,\alpha}{d\,log\,V}\right) + \beta \quad ....(1.2)$$

Where, $-\beta = -\left(\frac{d\,logV}{dP}\right)_T$ is the volume compressibility. Thus, equations (1.2) and (1.1) will provide the values of $\left(\frac{d\,log\alpha}{dT}\right)_V$.

Simultaneously samara (1968) also predicted a direct temperature derivatives of optical dielectric constant ($\in_{\propto}$) at constant volume in terms of total polarisability as

$$\left(\frac{d\in_{\propto}}{dT}\right)_V = \frac{1}{3}[(\in_{\propto}-1)(\in_{\propto}+2)]\left(\frac{d\,log\alpha}{dT}\right)_V .... (1.3)$$

Later on 1973, samara explained that the temperature dependence of electronic dielectric constant ($\in_{\propto}$) at constant pressure arises from the following contributions:

(i) The changes obtained are due to changes in lattice spacing or density only

(ii) The apparent temperature dependence that will occur even when the volume of the sample remains constant as $\in_{\propto} = \in(v,t)$ which provide

$$\left(\frac{dlog\ \in_{\propto}}{dT}\right)_P = \left(\frac{d\ log\ V}{dT}\right)_P\left(\frac{d\ log\ \in_{\propto}}{d\ log\ V}\right)_T + \left(\frac{dlog\ \in_{\propto}}{dT}\right)_V$$

Or

$$\left(\frac{dlog\in_{\propto}}{dT}\right)_P = \frac{-\gamma}{k}\left(\frac{d\ log\in_{\propto}}{dP}\right)_T + \left(\frac{dlog\in_{\propto}}{dT}\right)_V ....(1.4)$$

Here γ is the same $\left(\frac{d\ log\ V}{dT}\right)_P$ (volume thermal expansion coefficient) and $k = \left(\frac{-d\ log\ V}{dP}\right)_T$ is the isothermal compressibility. The equation enables to compute constant volume contribution.

In 1969 Van Vechten suggested a linear relation for electronic contribution to the low frequency dielectric constant of solids as

$$\in(0) = 1 + D\left(\frac{\omega_P}{\omega_g}\right)^2 \quad ....(1.5)$$

Where ω_P is the plasma frequency of valence electrons while ω_g is the frequency corresponding to the Penn gap (Penn,1962) and D is core-d effect parameter. Using the fact that D is of the order of unity and its variations are not expected to be large, Yu and Cardona (1970) neglected this factor and differentiated equation (1.5) to predict

$$\frac{1}{\in_{\propto}}\left(\frac{d\in_{\propto}}{dT}\right)_V=\left(\frac{\in_{\propto}-1}{\in_{\propto}}\right).\left[\frac{1}{\omega^2{}_P}\frac{\omega^2{}_P}{dT}-2\left(\frac{1}{\omega_g}\right)\left(\frac{d\omega_g}{dT}\right)\right]$$

Or

$$\frac{1}{\in_{\propto}}\left(\frac{d\in_{\propto}}{dT}\right)=\left(\frac{\in_{\propto}-1}{\in_{\propto}}\right)\left[-3\eta-2\left(\frac{1}{\omega_g}\right)\left(\frac{d\omega_g}{dT}\right)\right]\text{........}(1.6)$$

Here η is the coefficient of linear expansion. Yu and Cardona Further decomposed the temperature coefficient of ω_g in to its explicit temperature dependence at constant volume and its volume expansion effect comes out as

$$\frac{1}{\omega_g}\left(\frac{d\omega_g}{dT}\right)=\frac{1}{\omega_g}\left(\frac{d\omega_g}{dT}\right)_V+3\eta\left(\frac{V}{\omega_g}\right)\left(\frac{d\omega_g}{dV}\right)_T\text{......}(1.7)$$

Later in 1973 Tsay et al. suggested a temperature derivative of refractive index as

$$\frac{dn}{dT}=\left(\frac{dn}{dT}\right)_e+\left(\frac{dn}{dT}\right)_1\text{............................}(1.8)$$

Where $\left(\frac{dn}{dT}\right)_e$ is electronic contribution and $\left(\frac{dn}{dT}\right)_1$ is the lattice contribution to $\left(\frac{dn}{dT}\right)$, which are represented as

$$\left(\frac{dn}{dT}\right)_e=\frac{2}{2\pi}\left[4\pi\chi_e\left(-3\alpha\frac{2}{\omega_g}.\frac{d\omega_g}{dT}.\frac{1}{1-\left(\frac{\omega^2}{\omega^2{}_g}\right)}\right)\right]\text{........}(1.9)$$

$$\left(\frac{dn}{dT}\right)_1=\frac{1}{2\pi}\left[4\pi\chi_e\left(-3\alpha\frac{2}{e^*}.\frac{de^*}{dT}-\frac{2}{\omega_0}\left(\frac{d\omega_0}{dT}\right)\frac{1}{1-\left(\frac{\omega^2}{\omega^2{}_0}\right)}\right)\right]\text{........}(1.10)$$

In equation (1.6) and (1.7) $\left(\frac{d\omega_g}{dT}\right)$ is expressed in terms of thermal expansion and explicit temperature variation is given by

$$\frac{1}{\omega_g}\left(\frac{d\omega_g}{dT}\right)=3\alpha\frac{V}{\omega_g}\left(\frac{d\omega_g}{dV}\right)_T+\frac{1}{\omega_g}\left(\frac{d\omega_g}{dT}\right)_V\text{........}(1.11)$$

Here Van Vevhten's theory (1969) can be employed to express $\left(\frac{d\omega_g}{dV}\right)$ in terms of ionicity f in Phillip's scale (Phillips 1970) which provide the conclusion as

$$\frac{V}{\omega_g}\left(\frac{d\omega_g}{dV}\right)_T\approx-0.8(1-f)\text{......................}(1.12)$$

Moss finally reviewed this topic in 1985 and noted that, in general, the energy gap of semiconductors decreases with increasing temperature (Phillips 1973), neglecting the effect of thermal expansion. They explained the variation of the energy gap with respect to temperature on the basis of two factors (i) lattice dispersion and (ii) broadening of the energy band by lattice vibrations. This change in energy gap is expected to give a small effect on the refractive index and in absence of thermal broadening, the value of $\frac{dn}{dT}$ should be positive and net shift of absorption edge will be significant.

In 1981 Ravindra compared the measured values of $\frac{dn}{dT}$ with prediction from his relation and with moss relation for Si, Ge and 3rd-v solids. Much earlier, using the existing data on $\frac{dn}{dT}$, Burstein et al. (1948) had already predicted that for simple solids which does not contain any radicals and has a small value of λ_0, The change of the refractive index with temperature is strongly determined by the density contribution $\left(\frac{dn}{dP}\right)_T \cdot \left(\frac{dP}{dT}\right)$. The temperature contribution is small and $\left(\frac{dn}{dT}\right)$ is negative. But crystals with large values of λ_0, Similar in magnitude to the positive density contribution, the temperature contribution is positive. These aspects suggest that $\left(\frac{dn}{dT}\right)$ value for MgO is positive. Similar reason have also been given for the positive value of $\left(\frac{dn}{dP}\right)$ (i.e. λ_0 >1) in case of ZnS.

In crystals containing radicals and in certain glasses, positive $\frac{dn}{dT}$ values are frequently obtained even when their $\left(\frac{dn}{dP}\right)$ values are negative. In such materials, there are effects within the radical which contribute mainly to $\left(\frac{dn}{dT}\right)$ and only slightly to $\left(\frac{dn}{dP}\right)$. Positive $\left(\frac{dn}{dP}\right)$ values are frequently obtained in glasses and crystals containing radicals, even when their $\left(\frac{dn}{dP}\right)$ values are negative. In such materials, there are radical-level effects that primarily affect $\left(\frac{dn}{dP}\right)$ and minimally affect $\left(\frac{dn}{dP}\right)$.

However, all these proposed formulations are found to be sufficient if they are to be applied in general to simple and complex binary families simultaneously. We will critically analyze these theories to show the necessity of deriving proper formulations for temperature derivatives of refractive indices.

Conclusion:

We have accounted for the temperature derivatives of the refractive index and the mean energy gap under constant volume or constant pressure conditions using the ion dependent quantum dielectric theory, and we have obtained satisfactory and useful results for both simple and complex binary families. In view of the available experimental values, our computed values of $(1/n)(dn/dT)_{P,V}$ and $(1/E_g)(dE_g/dT)_{P,V}$ are in very close agreement, which confirm that the developed relation are quit valid? The strain and temperature derivatives in our proposed correlation can be applied in various technological and industrial fields. Further, the effective variation in energy gap contributes to the change in optical refractive index as well as electronic dielectric constant.

References:

1. Reddy, R.R.; Anjaneyula, S. and sarma, C.I.N., j. Phys, chem, solids 54, 635(1993).
2. https://archive.org/details/samara1968elmw/page/18/mode/2up
3. Sarkar, K.K and Goyal, S.C.Phys. Rev.,B-21,879(1980).
4. Phillips, J.C., Bonds and Bands in semiconductor (Academic Press, new York,1973).
5. Penn, D.R., Phys.rev.128,2093(1962).
6. Phillips, J.C.Rev.Mod.Phys.42,317(1970)
7. Van Vechten, J.A., Phys.Rev.182,891(1969)
8. Lawaetz, p., Phys. Rev. B-4, 3460(1971)

9. Weast,R.C (Ed), Handbook of chemistry and physics (The chemical rubber co., clereland, 46th ed.,1965)
10. Burstein, E,; Brodsky, m., and lucousky,G, Int.Jour. Quant. Chem..15,759(1967).
11. Tsay, Y.F.; Corey, A.J and Mitra,S.S., Phys.Rev., B-12,1354(1975)
12. Hass, M and Henvis,B.W., jour.Phys.Chem.Sol.,23,1099 (1962).
13. H. Fröhlich. (1949) Theory of dielectrics; dielectric constant and dielectric loss.
14. Eby, J.E; Teegarden, K.J. and Dulton, D.B., Phys.Rev., 116,1099 (1959).
15. Phillip, H.R. and Ehrenreich, H., Phys.Rev.,131,02016 (1963).
16. Temperature Dependence of Dielectric Constants of Cubic Ionic Compounds. A. J. Bosman and E. E. Havinga Phys. Rev. **129**, 1593 (1963)
17. N.M. Ravindra *et al.* Phys. Stat. Sol (b) (1979)
18. Salater, J.C., Quantum theory of molecules and solids (vol.2,McGraw Hill, new York,1965)
19. Goryyunova.N.A.,Chemistry of diamonds like semiconductor (Chapman and Hall, London,1965)