THE THERMO-OPTIC BEHAVIOUR OF CALCIUM FLUORIDE, AMMONIUM CHLORIDE AND ZINC-BLENDE AT LOW TEMPERATURES

By C. P. Gopalakrishnan

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

Received November 8, 1956

Abstract

Using the data on the refraction at low temperatures given by Barbaron, the values of the proportionate shift with temperature of the ultraviolet dispersion frequencies ($\chi = -1/\nu\, d\nu/dt$) of CaF_2, NH_4Cl and ZnS have been calculated and it has been found that the values of χ tend to very low values near the absolute zero. In the case of ammonium chloride, a new dispersion formula has been proposed. In NH_4Cl and CaF_2, the values of χ for the dispersion frequencies obtained from thermo-optic data are compared with the values of χ of the lattice lines obtained from the temperature variation of the Raman spectra.

1. Introduction

Very scanty data are available on the thermo-optic behaviour of cubic crystals at low temperatures. Recently Barbaron (1951) has determined the refractive indices at low temperatures of calcium fluoride, zinc-blende, ammonium chloride, ammonium bromide and sodium chloride down to $-200°$ C. for λ 5461 of mercury. As the measurements are only for one wavelength, those crystals whose dispersion of refractive index could be expressed by one-term formulæ could be studied. Applying the phenomenological theory for the variation of refractive index with temperature put forward by Ramachandran (1947), the values of the proportionate shift with temperature of the ultraviolet dispersion frequencies ($\chi = -1/\nu\, d\nu/dt$) in the case of calcium fluoride, zinc-blende and ammonium chloride have been evaluated and reported in this paper.

2. Calculation and Results

A dispersion formula of the following type employed by Ramachandrar (1947) and Radhakrishnan (1950, 1951) for similar studies, has been used for the calculations.

$$n^2 - 1 = \sum_r \frac{a_r \lambda^2}{(\lambda^2 - \lambda_r^2)} \qquad (1)$$

Differentiating the above equation and applying Ramachandran's theory, we get

$$2n\frac{dn}{dt} = -\gamma(n^2-1) + \sum_r \frac{2a_r\lambda^4}{(\lambda^2-\lambda_r^2)^2}\chi_r \qquad (2)$$

where γ = coefficient of cubical expansion,

$$\chi_r = -\frac{1}{v_r}\frac{dv_r}{dt}$$

1. *Calcium Fluoride.*—The ultraviolet absorption spectrum of this substance was investigated experimentally by Tousey (1936) who found the absorption wavelengths to be at 900 and 1115 Å.U. For investigating the thermo-optic behaviour of calcium fluoride above room temperature, Radhakrishnan (1951) used a value of 943 Å.U. for the one-term formula, being the weighted mean of the two absorption wavelengths observed by Tousey. The one-term formula [equation (3)] used by Radhakrishnan has been employed by the author for the present calculations.

$$n^2-1 = 0{\cdot}3502 + \frac{0{\cdot}68898\,\lambda^2}{\lambda^2-(0{\cdot}0943)^2} + \frac{4{\cdot}01586\,\lambda^2}{\lambda^2-(35{\cdot}5)^2} \qquad (3)$$

In the region under study, the infrared contribution to dn/dt is negligible. Using the necessary constants, from equation (2) we get

$$\chi_t = 1{\cdot}961\left(\frac{dn}{dt}\right)_t + 3{\cdot}504\,\alpha_t \qquad (4)$$

where

$$\chi_t = -\left(\frac{1}{v}\frac{dv}{dt}\right)_t$$

α_t = coefficient of linear expansion at temperature t. The values of dn/dt, α and χ at various temperatures obtained by using the data of Barbaron are given in Table I.

TABLE I

Ten perature °C.	$(dn/dt)\times10^6$	$\alpha\times10^6$	$\chi\times10^6$
−171	− 7·14	7·9	13·7
−125	−10·00	11·9	22·1
− 75	−12·00	15·2	29 7
− 50	−13·00	16·4	30·8
− 25	−14·00	17·5	31·8

The values of α in Table I are from Valentiner and Wallot (1915).

2. *Zinc-Blende.*—The following dispersion formula given by Mell (1923) has been used for zinc-blende.

$$n^2 - 1 = 2{\cdot}0221 + \frac{2{\cdot}0998\,\lambda^2}{\lambda^2 - (0{\cdot}2532)^2} \tag{5}$$

Using the data of Barbaron which are available up to — 200° C., the values of χ at low temperatures have been computed. For evaluating χ. substituting necessary constants from (5) in equation (2),

$$\chi_t = 0{\cdot}701 \left(\frac{dn}{dt}\right)_t + 2{\cdot}068\,\alpha_t \tag{6}$$

The values of dn/dt, α and χ are entered in Table II.

TABLE II

Temperature °C.	$(dn/dt)\times 10^6$	$\alpha\times 10^6$	$\chi\times 10^6$
— 177·5	14·3	1·38	12·9
— 140·0	27·5	3·25	26·0
— 100·0	45·0	4·50	40·8
— 60·0	62·5	5·40	55·0
— 20·0	67·5	6·05	59·8

The thermal expansion values are from Adenstedt (1936).

3. *Ammonium Chloride.*— Only very recently the dispersion of the refractive index of this substance has been determined accurately (Poinsot and Mathieu, 1955). Using their data, a new formula in the required type has been proposed using two absorption wavelengths in the ultraviolet 1200 and 1600 Å.U., the infra-red absorption wavelength being 69 μ [from Rubens and Wartenberg (1914) after Fosterling's correction]. The formula is

$$n^2 - 1 = 0{\cdot}295904 + \frac{0{\cdot}944147\,\lambda^2}{\lambda^2 - (0{\cdot}1200)^2} + \frac{0\ 376091\,\lambda^2}{\lambda^2 - (0{\cdot}1600)^2} + \frac{4{\cdot}3044\,\lambda^2}{\lambda^2 - (69{\cdot}0)^2} \tag{7}$$

The refractive indices determined using this formula agree very well with the observed data for the spectral range from 3130 Å.U. to 7682 Å.U. The dielectric constant for static fields calculated using the above formula comes out to be 6·92 which agrees quite well with the experimental value of 6·90. As the data of dn/dt

are available for one wavelength, for evaluating the value of χ, it has been assumed that $\chi_{1200} = \chi_{1600}$. Combining equations (2) and (7) we get

$$\chi_t = 1 \cdot 101 \left(\frac{dn}{dt}\right)_t + 1 \cdot 708\, \alpha_t \tag{8}$$

The results are given in Table III.

TABLE III

Ten perature °C.	$(dn/dt) \times 10^6$	$\alpha \times 10^6$	$\chi \times 10^6$
— 172	— 40·0	7·51	31·2
— 150	— 54·5	8·48	45·5
— 130	— 66·7	9·90	55·5
— 110	— 70·0	12·35	56·0
— 85	— 78·6	18·64	54·7
— 65	—100·0	28·65	61·2
— 50	—125·0	49·52	63·1
— 30	—550·0	166·47	321·2
— 10	—100·0	26·90	64·2

The values of α are from Adenstedt (1936).

4. DISCUSSION

It is seen from Tables I, II and III that the values of χ in all the cases tend to very low values as we approach the absolute zero. Radhakrishnan (1951) from his measurements on dn/dt of CaF_2, finds that the value of $\chi_{0\cdot0943}$ decreases from 39×10^{-6} at 400° C. to 30×10^{-6} at 50° C. The present calculations reveal that the value of χ decreases still further to $13 \cdot 7 \times 10^{-6}$ at — 171° C. In zinc-blende, Ramachandran (1947) finds from his calculations the value of $\chi_{0\cdot2532}$ at — 40° C. comes out as 56×10^{-6} which agrees well with the present values of $55 \cdot 0 \times 10^{-6}$ at — 60° C. and $59 \cdot 8 \times 10^{-6}$ at — 20° C. The case of ammonium chloride is particularly interesting as it has a transition point at — 30° C. Near this temperature its various physical properties exhibit anomalous behaviour. For instance Simon and Bergmann (1930) from thermal expansion studies find a catastrophic change of length at this temperature. Naturally such a behaviour is reflected in its thermo-optic properties as well. At — 30° C. the numerical value of χ increases to a

phenomenally high value of 320×10^{-6} and as the temperature is lowered below the λ-point it progressively decreases.

As we have data of the temperature variation of Raman spectra of NH_4Cl and CaF_2, we can compare the values of χ of the lattice frequencies with those of the dispersion frequencies for these two substances. In the case of NH_4Cl, Krishnan (1947) has made a detailed investigation from liquid-air temperature to 120° C. and according to him, the χ of the principal lattice line has a value of 575×10^{-6} at $-50°$ C. and 186×10^{-6} at $-150°$ C. The corresponding values of χ obtained from dn/dt measurements are 63×10^{-6} and 46×10^{-6} at the same two temperatures.

In the case of CaF_2, the value of χ of the lattice line is equal to 162×10^{-6} at 165° C. (Press, 1950) while the value of χ of the dispersion frequency comes out to be 32×10^{-6} at $-20°$ C. It is seen that the values of χ for the electronic frequencies are not in agreement with the values of χ for the lattice frequencies. Similar results have been obtained by the author in the case of sodium chlorate [(Gopalakrishnan (to be published)].

5. ACKNOWLEDGEMENT

I am very grateful to Professor R. S. Krishnan for guidance and encouragement. My sincere thanks are due to Dr. K. Vedam and Dr. S. Ramaseshan for the discussions I had with them.

6. REFERENCES

1. Adenstedt .. *Ann. der Phy.*, 1936, **26**, 69.
2. Barbaron .. *Ann. des Phy.*, 1951, **6**, 889.
3. Krishnan .. *Proc. Ind. Acad. Sci.*, 1947, **26**, 432.
4. Mell .. *Zeit. f. Phys.*, 1923, **16**, 244.
5. Poinsot and Mathieu .. *Ann des Phy.*, 1955, **10**, 483.
6. Press .. *Proc. Ind. Acad. Sci.*, 1950, **31**, 56.
7. Radhakrishnan .. *Ibid.*, 1948, **27**, 44; 1950, **31**, 224, 229; 1951, **33**, 44
8. Ramachandran .. *Ibid.*, 1947, **25**, 266, 286, 375, 481.
9. Rubens and Wartenberg .. *Ber. des. Chem. Ges.*, 1914, p. 69.
10. Simon and Bergmann .. *Zeit. f. Phys. Chem.*, 1930, **8 B**, 255.
11. Tousey .. *Phys. Rev.*, 1936, **50**, 1037.
12. Valentiner and Wallot .. *Ann. d. Phy.*, 1915, **46**, 837.