

## ROTATORY DISPERSION OF HEXAGONAL CRYSTALS OF $\text{Al}(\text{IO}_3)_3 \cdot 2\text{HIO}_3 \cdot 6\text{H}_2\text{O}$ AND ITS TEMPERATURE VARIATION

M. S. MADHAVA AND R. SOMASHEKAR

*Department of Physics, University of Mysore, Mysore, 570 006, India*

### INTRODUCTION

THE crystalline phase of  $\text{Al}(\text{IO}_3)_3 \cdot 2\text{HIO}_3 \cdot 6\text{H}_2\text{O}$  of the  $\text{Al}(\text{OH})_3\text{-HIO}_3\text{-H}_2\text{O}$  system crystallizes in the space group  $\text{P6}_3$  exhibiting strong piezoelectric, electro-optic and other polar properties<sup>1,2</sup>. Preliminary measurements of the optical rotatory power show the effect which is quite comparable to that exhibited by quartz, although less compared to that of  $\text{LiIO}_3$ . Hence a detailed and systematic investigation of the optical rotatory dispersion and its temperature variation was undertaken and is reported in this communication.

### EXPERIMENTAL

The spectropolarimetric arrangement used to measure the rotatory dispersion was essentially the same as used in the earlier investigations<sup>3-5</sup>. A series of spectrograms were recorded with and without the crystal for different positions of the nicol, and thus the entire region of the spectrum in the range  $0.6234 \mu$  to  $0.3125 \mu$  was scanned. Measurement below  $0.3125 \mu$  was not possible as the crystal is strongly absorbing. The exact orientation of the optic axis perpendicular to faces was confirmed by observing the uniaxial conoscopic interference figures under a polarizing microscope. A stainless steel electric oven was constructed to measure the rotation at different temperatures. The temperature was measured using a calibrated thermocouple to an accuracy of  $\pm 0.5^\circ\text{C}$ . Measurements of the optical rotatory power were made at the room temperature ( $25^\circ\text{C}$ ),  $46^\circ\text{C}$  and at  $72^\circ\text{C}$  on four different specimens of thicknesses 4.65, 2.03, 1.28 and 0.6 mm respectively and the values in the four cases agreed to within  $\pm 1\%$ . The average values of the rotatory power at different temperatures are given in table 1. The temperature variation of the rotatory power ( $d\rho/dt$ ) is shown in figure 1.

Refractive indices for both ordinary and extraordinary rays were measured using a goniometer spectrometer by normal incidence method, in conjunction with a hot stage. The refractive dispersions for different temperatures are given in table 2.

### RESULTS AND DISCUSSION

The rotatory power can be expressed by a two-term Chandrasekhar<sup>6</sup> formula

$$\rho = \frac{K_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{K_2 \lambda^2}{\lambda^2 - \lambda_2^2} + 0.49 \quad (1)$$

TABLE I

*Rotatory power of hexagonal  $\text{Al}(\text{IO}_3)_3 \cdot 2\text{HIO}_3 \cdot 6\text{H}_2\text{O}$*

$\lambda$ in $\mu$	$\rho$ exp 25° C in deg/ mm	$\rho$ cal 25° C in deg/ mm	$\rho$ at 45° C in deg/ mm	$\rho$ at 72° C in deg/ mm
0.623437	29.20	29.30	—	—
0.5780	34.70	34.80	34.61	34.51
0.546074	39.60	40.00	39.41	39.21
0.491604	52.60	51.80	—	—
0.435835	71.80	71.40	71.30	71.20
0.407783	86.30	86.60	85.89	85.78
0.404656	88.80	88.60	88.38	87.76
0.39064	98.60	98.70	—	—
0.386108	101.50	102.40	—	—
0.382013	105.60	106.00	—	—
0.378982	108.90	108.80	—	—
0.366239	122.10	122.30	121.48	119.83
0.365015	123.40	123.70	122.67	120.91
0.334148	172.40	174.00	171.13	168.50
0.313155	237.50	235.60	—	—
0.312566	239.20	238.00	—	—

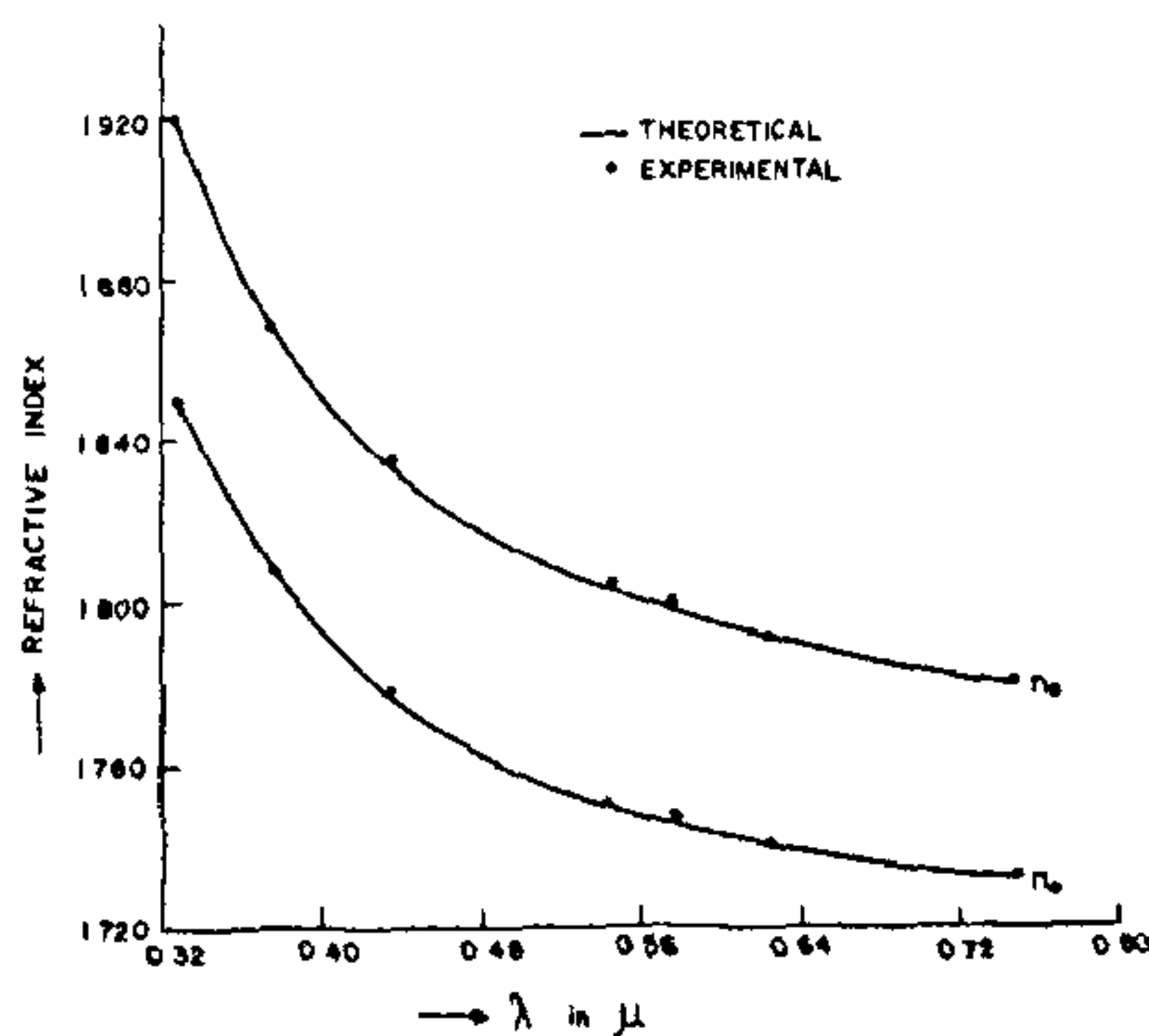


Figure 1. Variation of refractive index with wavelength.

where  $K_1 = 6.82$ ,  $K_2 = 3.18$  and  $\lambda_1 = 0.09 \mu$  and  $\lambda_2 = 0.23 \mu$  and the third term represents the total contribution of the infrared bands. The calculated values of rotatory power using equation (1) are

TABLE 2  
Refractive index data of hexagonal  $Al(PO_3)_2 \cdot 2H_2O$ .

Temp.	$\lambda$ in $\mu$	0.4358	0.5461	0.5780	0.6230
25° C	$n_e$	1.8281	1.7954	1.7897	1.7857
	$n_o$	1.7710	1.7442	1.7395	1.7355
48° C	$n_e$	1.8263	1.7938	1.7882	1.7842
	$n_o$	1.7692	1.7420	1.7380	1.7350
67° C	$n_e$	1.8237	1.7915	1.7858	1.7820
	$n_o$	1.7667	1.7407	1.7364	1.7324

tabulated in table 1, and the agreement is within 1%. The refractive indices of the ordinary and extraordinary rays can be represented by two-term Sellimier-Drude type formula (see. ref. 3) with the following constants.

	$C_1$	$C_2$	$B_1$
Ordinary (o)	1.5770	0.3698	0.0376
Extraordinary(e)	1.6683	0.4524	0.1130

The calculated values of refractive indices using two-term Sellimier-Drude type formula are in reasonably good agreement as shown in figure 2. It is observed that the same characteristic wavelengths explain rotatory and refractive dispersions fairly accurately.

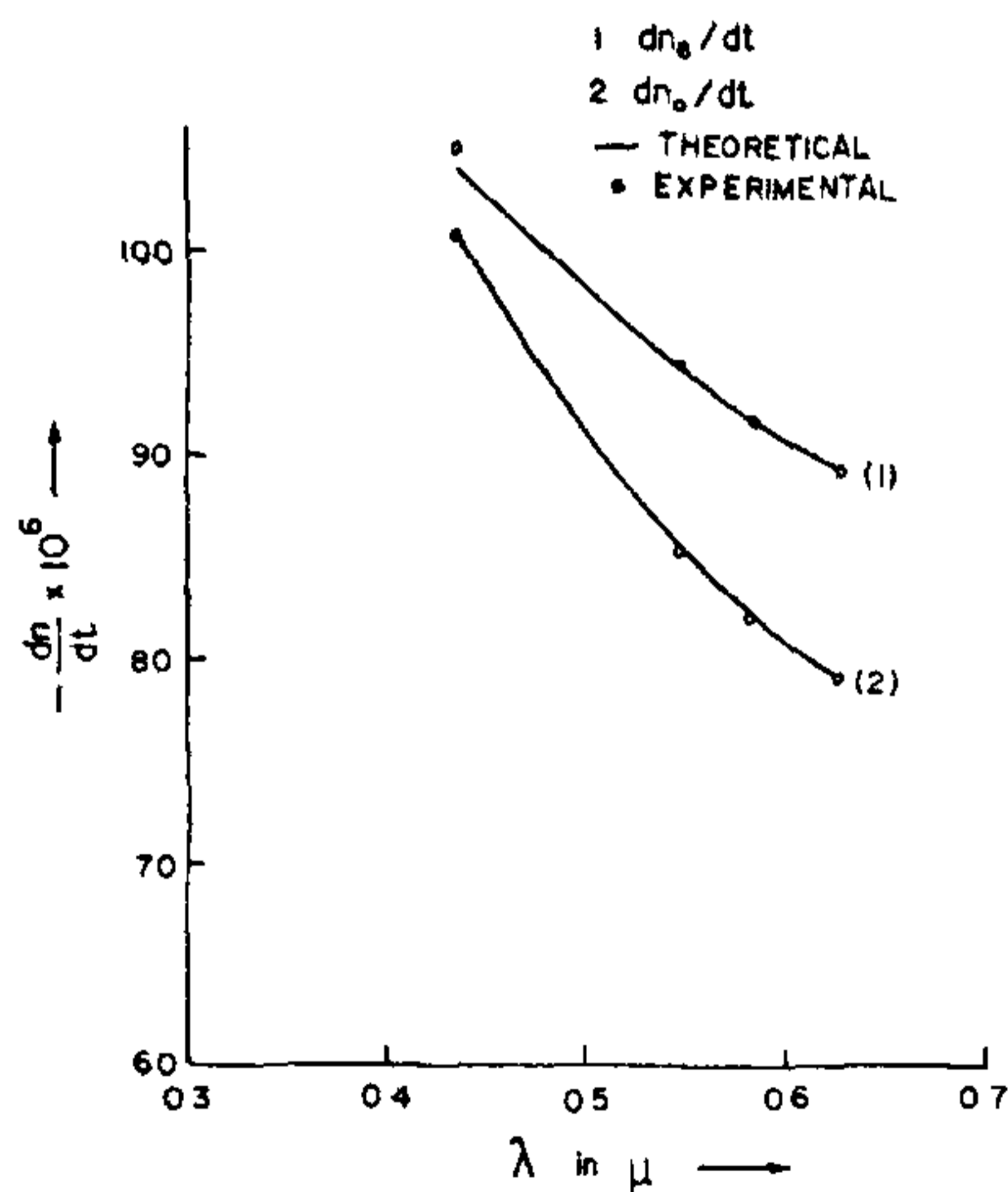


Figure 2. Variation of  $dn/dt$  for ordinary and extraordinary rays with wavelength.

The thermal variation of refractive index of crystals has been explained<sup>7</sup> and has been used by one of us in the case of  $NaClO_3$  and  $NaBrO_3$ .<sup>5</sup> Using the Ramachandran<sup>7</sup> theory, the variation of refractive

index with temperature of the above crystal, can be adequately explained with the values of  $\chi_1 = -1.1873 \times 10^{-4}$  and  $\chi_2 = 1.5033 \times 10^{-4}$  where  $\chi_1$  and  $\chi_2$  represent the effect of temperature on the absorption bands.

The variation of rotatory power with temperature is given by

$$\frac{d\rho}{dt} = \sum_r \frac{K_r \lambda^2}{(\lambda^2 - \lambda_r^2)^2} \Gamma_r + \sum_r \frac{4 K_r \lambda^4}{(\lambda^2 - \lambda_r^2)^3} \chi_r \quad (2)$$

where  $\Gamma_r = \frac{1}{K_r} \frac{dk_r}{dt}$  and again  $\chi_r = -\frac{1}{\lambda_r} \frac{d\lambda_r}{dt} \cdot \Gamma_r$

represents the total effect of temperature on the number of oscillators per unit volume, the oscillatory strength of the band and the coupling constant.

The  $\chi_r$ s in equation(2) which determine the effect of temperature on the absorption bands, by definition are the same. From the values of  $\chi_1$  and  $\chi_2$  calculated using the data of the thermal variation of the refractive indices, it is found that equation (2) fits the experimental data well when

$$\Gamma_1 = 1.669 \times 10^{-4} \quad \Gamma_2 = 1.991 \times 10^{-4}$$

which is shown in figure 3.

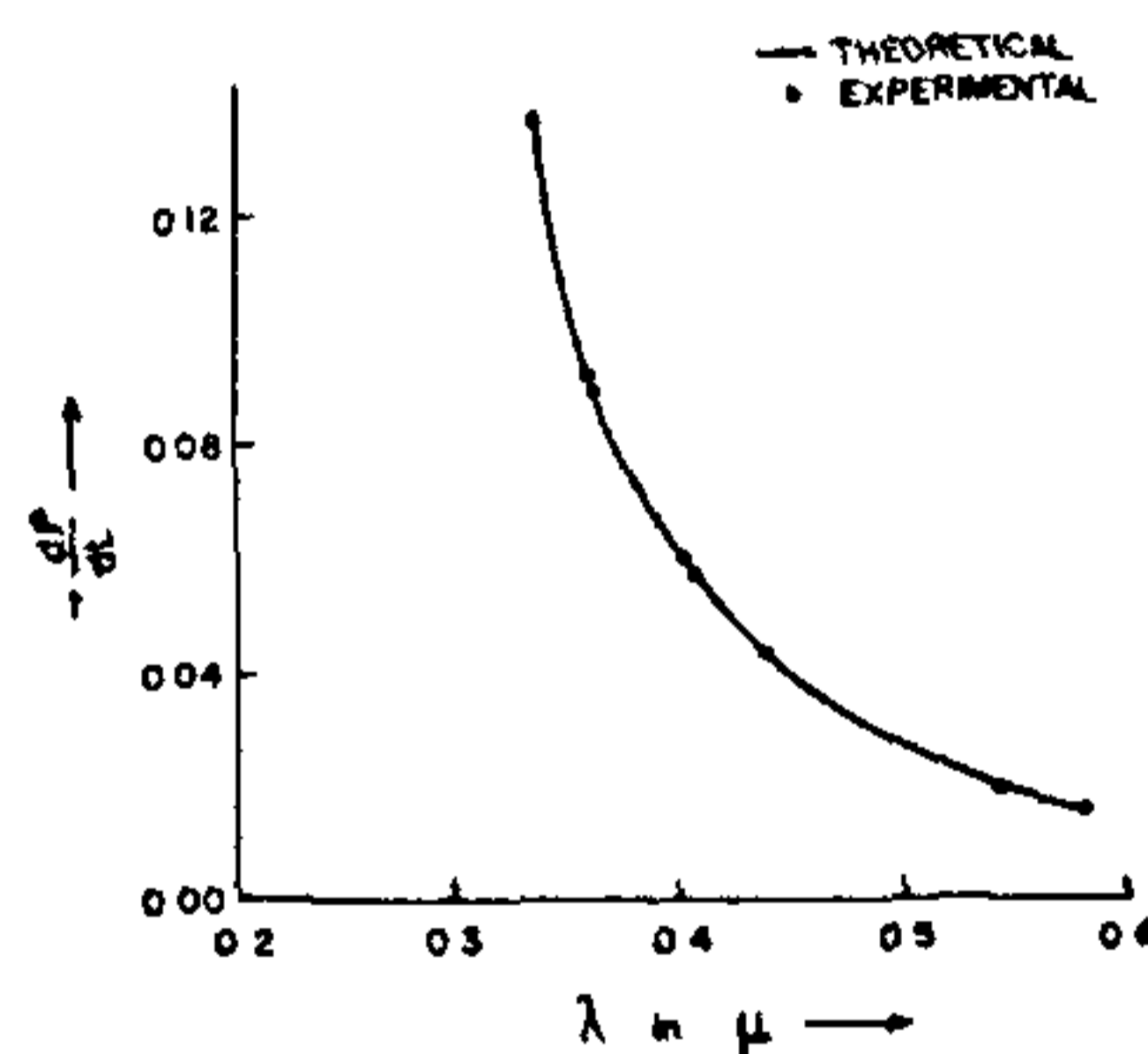


Figure 3. Variation of  $d\rho/dt$  with wavelength.

It is observed that the rotatory dispersion and its temperature variation can be well explained using the quadratic formula of Chandrasekhar. The temperature variation of rotatory dispersion can be interpreted as arising due to (i) a pure temperature effect on the absorption wavelength and (ii) the change in volume.

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## MICROPLANKTONS FROM THE LATE PRECAMBRIAN SIMLA GROUP, HIMACHAL PRADESH

AVINASH CH. NAUTIYAL

*Department of Geology, University of Lucknow, Lucknow 226007, India*

### ABSTRACT

The "unfossiliferous" Precambrian Simla Group sediments (silty shale, siltstone, sandstone) in parts of Himachal Pradesh, revealed microplanktons, common to profuse, comprising acritarchs: *Granomarginta primitiva*, *G. simlaensis* sp. nov., *G. dhalii* sp. nov., *Vavososphaeridium* sp. A, and cyanophytes: *Satpulispora psilata*, *S. microreticulata* and *S. major*. They suggest a shallow marine condition of some units of the Simla Group and age as late as Precambrian.

### INTRODUCTION

THE Precambrian argillaceous "unfossiliferous" sediments of the Lesser Himalayan region of Himachal Pradesh (HP) commonly referred to as the Simla Slates (Simla Group about 4,400 metres thick) are problematic regarding the environment of deposition and age<sup>1-12</sup>. The sequence, however, in HP and Garhwal regions has been suggested as turbidite flysch on the basis of graywacke and sedimentary structures<sup>3-5</sup>. The present author, on the contrary reported the part of the same sequence in the Garhwal (at Satpuli) region as partly restricted, near shore (or protected tidal mud flat) environment on the basis of high concentration of microplanktons, filamentous algal and fungal (?) remains and oxidising nature of sediments<sup>8,10</sup>. The study of the rocks of Simla Group of HP was therefore undertaken (Valdiya's collection lodged in Lucknow University Museum).

The Simla Group in HP has been divided into four units viz. Basantpur, Kunihar, Chhaosa and Sanjauli Formations, unconformably overlying the Shali Formation<sup>4,5</sup>. Rocks from Chhaosa and Sanjauli (Lower Member) Formations were selected for the present study. In addition, some rocks of the Simla Group, which could not be placed in proper position were also examined for microorganisms. In general they yielded microplanktons and fungal remains, common to profuse, in quantitative composition (figures 1-14). Although the mode of preservation of fossils is poor (dark brown to black in colour) they can

be conveniently identified, as their morphological characters are apparently visible. Table 1 includes stratigraphy of Simla Group of HP<sup>1-5</sup>.

### MICROFLORAL (MICROFAUNAL) DISTRIBUTION

Olive gray sinus groove-casted and prod-casted siltstone (M.N. 1533) of the Sanjauli Formation (Lower member) (= Dhali Formation of Valdiya<sup>3</sup>), at Bhaili Ridge, NW of Simla, displayed common distribution of acritarchs, *Granomarginata simlaensis* sp. nov. and *Vavososphaeridium* sp. A (figures 2, 3, 6). Further, medium gray flute-casted sandstone (M.N. 1524) of the same formation and locality exhibited *G. simlaensis* sp. nov. and *G. dhalii* sp. nov. (figures 4, 5) in common. However, greenish gray flute-casted siltstone<sup>3</sup> (M.N. 1523) of the Chhaosa Formation<sup>3-5</sup> (at 2 km of Kandaghat) revealed sporadic distribution of filamentous fungal remains (figure 14).

In addition, medium dark gray, flute-casted silty shale (M.N. 1067) of the Sanjauli Formation (Lower Member) at Simla comprises profuse concentration of microplanktons: *Granomarginata primitiva*, *G. dhalii* sp. nov., ? *Micrhystridium* sp. A, *Micrhystridium* sp. B, *Satpulispora major*, *S. psilata*; and filamentous fungal remains (figures 1, 4, 5, 7, 8, 10, 14). Whereas, greenish gray laminated siltstone (M.N. 1071) of the above-mentioned formation, at Simla-Phagu road, displayed very high concentration of *Satpulispora psilata* and *S. microreticulata* (figure 9). Medium dark gray sandstone with pseudo-coprolite structure