

THE THERMO-OPTIC BEHAVIOUR OF QUARTZ

BY A. K. RAMDAS

(From the Raman Research Institute, Bangalore)

Received January 18, 1952

(Communicated by Sir C. V. Raman)

1. INTRODUCTION

THE refraction, dispersion and birefringence of quartz and their temperature variations have been the subject of numerous investigations. The literature on this subject prior to 1927 has been elaborately reviewed by Sosman¹ in his book on the properties of silica. Amongst the most significant of the earlier investigations was the work of Micheli² who showed that the temperature coefficients of the refractive indices which are negative in the visible region of the spectrum diminish in absolute magnitude with decreasing wave-length and after passing through a zero value actually change sign and become positive for the shortest ultra-violet wave-lengths. The work of Rinne and Kolb³ is also of interest as they determined both the ordinary and extraordinary indices over a wide range of temperatures covering that at which the trigonal α -form undergoes a reversible transformation to the hexagonal β -form. More recently also, Radhakrishnan⁴ has determined by an interferometric method the temperature coefficients of the ordinary and the extraordinary indices of α -quartz for temperatures between 0° C. and 400° C. Mention may also be made of the recent determinations by M. Barbaron⁵ of the ordinary and the extraordinary indices of α -quartz from -200° C. to 50° C. for the wave-length 5460 Å.

The temperature variation of the refractive indices of quartz was explained in a general way by Pockels⁶ and by Sosman.⁷ As the volume of quartz increases with temperature, the refractive indices should decrease correspondingly. The actual changes are negative, as predicted, but numerically less. The true temperature effect, independent of the dilatation, must therefore be positive. This positive true temperature effect may be ascribed to the drift of the electronic dispersion wave-lengths towards longer wave-lengths. Using the Ketteler-Helmholtz formula and estimating the effect of temperature on the constants of the formula, Sosman has shown that the change in λ , the absorption wave-length comes out the same for

quartz and vitreous silica, the difference in the course of the indices in the two cases being entirely due to the difference in thermal expansions.

Radhakrishnan⁸ has dealt with the thermo-optic behaviour of α -quartz on the basis of the general theory for crystals developed by Dr. G. N. Ramachandran. It is proposed in the present paper to discuss the thermo-optic behaviour of quartz over the entire range from -200°C . to 765°C . adopting a procedure different from that followed by Radhakrishnan.

2. GENERAL DISCUSSION OF THE DATA

As noted before, the course of the refractive indices with temperature depends upon the density changes and a positive part attributed to the drift of the spectral position of the dispersion frequencies. For a qualitative analysis of the data, we may base our discussion on the Gladstone-Dale formula connecting the indices with the density. S. Chandrasekhar⁹ has shown that, when the close similarity in the spectroscopic behaviour of quartz and vitreous silica is considered and if one attempts to calculate the refraction of vitreous silica, the Gladstone-Dale formula gives the best results for refraction. Hence we may write

$$\left. \begin{aligned} n_{\omega 0} - 1 &= c_{\omega} \rho_0 \\ n_{\epsilon 0} - 1 &= c_{\epsilon} \rho_0 \end{aligned} \right\}, \quad (1)$$

at any initial temperature. Thus at any temperature t ,

$$\begin{aligned} n_{\omega t} - 1 &= [n_{\omega 0} + \Delta n_{\omega}] - 1 \\ &= c_{\omega} \rho_0 + c_{\omega} \Delta \rho + \rho \Delta c_{\omega} \\ &= c_{\omega} \rho_t + F_{\omega}(t) \end{aligned}$$

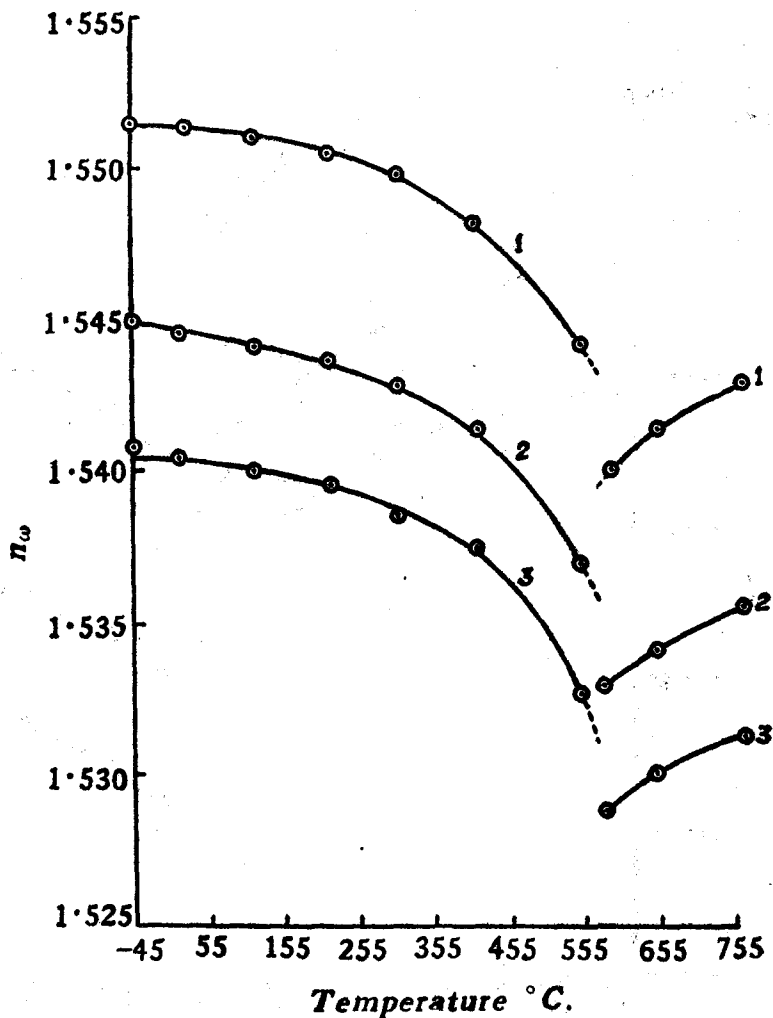
where ρ_t is the density at t , and $F_{\omega}(t)$ is the positive contribution due to this temperature change, c_{ω} being considered approximately a constant. Thus we have at any temperature

$$\left. \begin{aligned} n_{\omega} - 1 &= c_{\omega} \rho + F_{\omega}(t) \\ n_{\epsilon} - 1 &= c_{\epsilon} \rho + F_{\epsilon}(t) \end{aligned} \right\} \quad (2)$$

where c_{ω} and c_{ϵ} are evaluated at any initial temperature.

Figs. 1 and 2 showing the refractive indices at different temperatures for three typical wave-lengths have been plotted from Rinne and Kolb's data. As the temperature increases, the refractive indices fall off more and more rapidly as 573°C . is approached. At 573°C . the indices show a sudden drop. On further heating the refractive indices increase with temperature. This increase of the refractive indices beyond 573°C ., *i.e.*, in β -quartz cannot

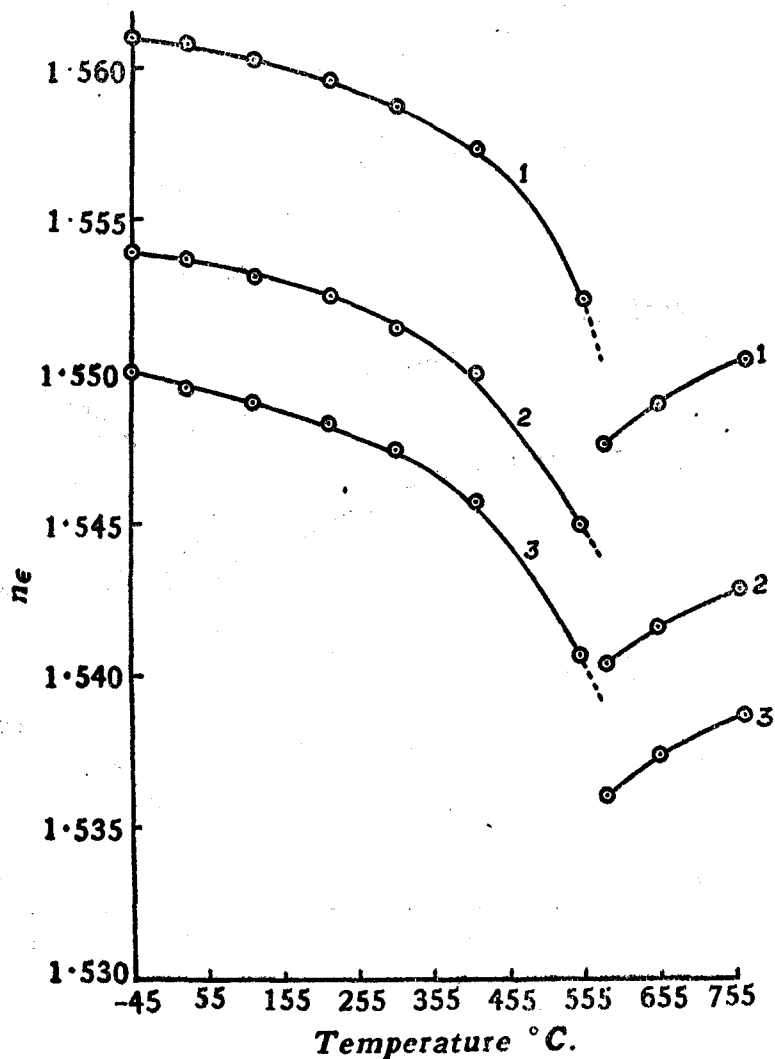
The Thermo-optic Behaviour of Quartz



- 1 → 466.8 $m\mu$.
- 2 → 588.99 „
- 3 → 718.9 „

FIG. 1. Variation of ordinary refractive index with temperature

be fully explained by the small or negligible negative coefficient of thermal expansion, thus clearly showing that there is a positive part in the temperature variation of the refractive indices. In the region preceding 573°C., i.e., in α -quartz, the refractive indices drop very much because of the enormous thermal expansion which is increasingly accelerated as the transition point is approached.



1 \rightarrow 466.8 $m\mu$

2 \rightarrow 588.99 ,,

3 \rightarrow 718.9 ,,

FIG. 2. Variation of extraordinary refractive index with temperature

Figs. 3 and 4 show $F_{\omega}(t)$ and $F_e(t)$ at various temperatures. The c_{ω} 's and c_e 's are calculated from the data for -45°C . We see from Figs. 3 and 4 that both in α -quartz and β -quartz, there is a positive part in the temperature variation of the refractive indices and this shows a steady increase. This part is completely submerged by the predominant negative effect in

the range preceding 573° as can be seen on comparing Figs. 1 and 3. We also see in Figs. 3 and 4 that there is a sudden increase in $F(t)$ at the transition temperature, while in Figs. 1 and 2 there is a sudden drop in the refractive indices. This means that the abrupt diminution in the refractive indices at the transition temperature is not wholly explicable in terms of the abrupt change of density. The structural changes represented by the α - β transformation cause a change in the opposite direction, *i.e.*, an increase in the refractive indices.

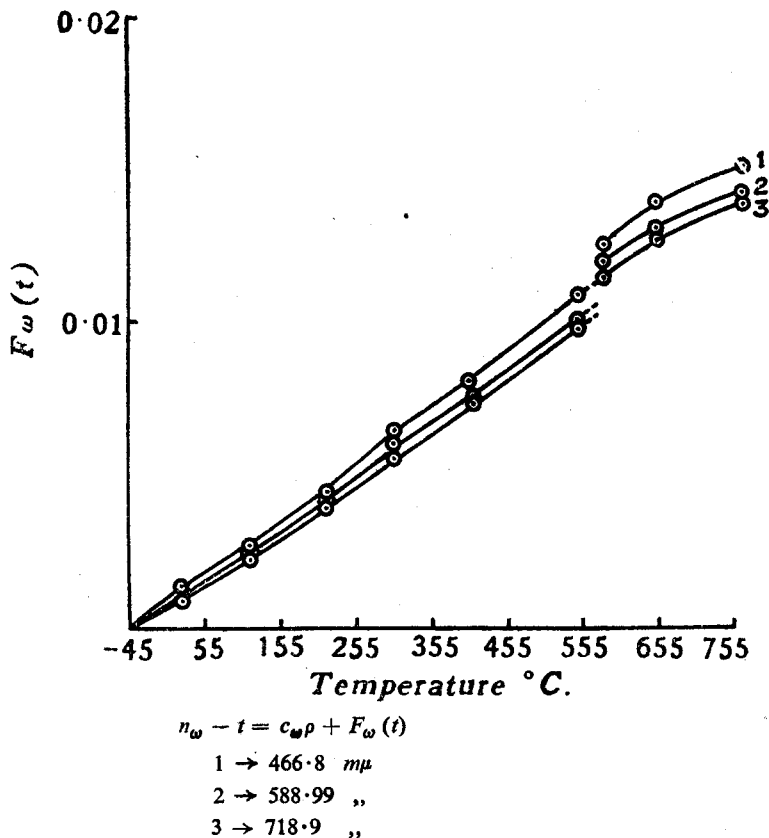
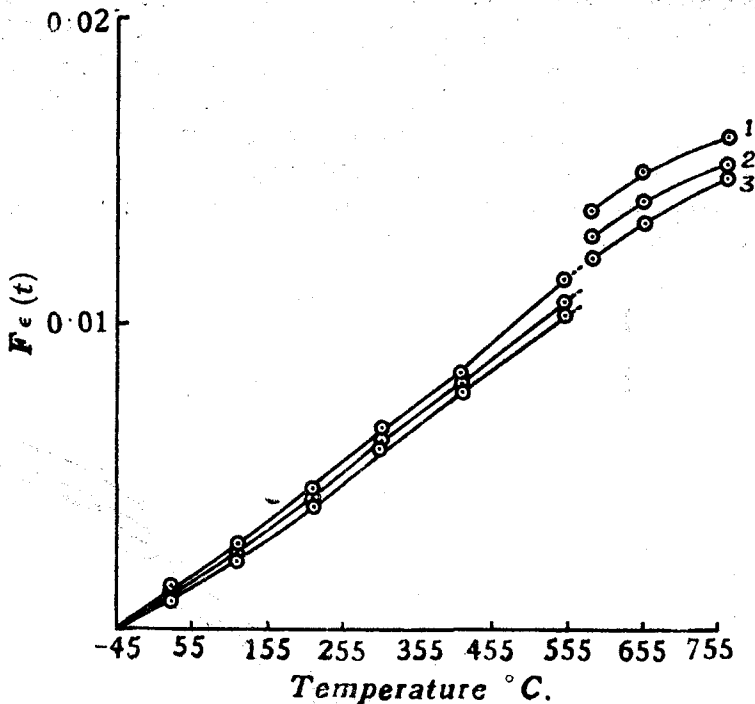


FIG. 3. Positive part in the temperature variation of ordinary index

3. DISPERSION FREQUENCIES OF QUARTZ

A variety of dispersion formulæ have been proposed for quartz. Our knowledge of the ultra-violet absorption spectrum of quartz is very meagre. Quartz even in the thinnest layers, is opaque to ultra-violet beyond about 1,400 Å. Tousey has observed two reflection maxima at 1,060 Å and 1,190 Å. If a dispersion formula using 1,060 Å and 1,190 Å is devised, a



$$n_e - t = c_e \rho + F_e(t)$$

$$1 \rightarrow 466.8 \text{ m}\mu$$

$$2 \rightarrow 588.99 \text{ ,,}$$

$$3 \rightarrow 718.9 \text{ ,,}$$

FIG. 4. Positive part in the temperature variation of extraordinary index

very substantial part of the refraction has to be attributed to a hypothetical absorption wave-length below 1,000 Å. Indeed it is quite possible to devise a number of different formulæ, using different absorption wave-lengths with suitable weights, all of which represent the refractive indices within known limits of accuracy. Thus it is not possible to fix uniquely the ultra-violet absorption wave-lengths from the refractive index data, and an element of arbitrariness therefore arises in devising such formulæ. However, if we limit ourselves to a particular part of the spectrum, say the visible spectrum, it is found in the case of quartz that a single term formula of the Drude type represents the refractive indices in that region reasonably well and also uniquely. This absorption term represents the weighted mean of the dispersion frequencies in respect of the particular region of the spectrum covered by the data. Naturally the weighted mean of the dispersion frequencies would not be the same for a different part of the spectrum, say the near

ultra-violet or the remote ultra-violet. In the latter cases, the longer absorption wave-lengths would play a more important part and the mean dispersion frequency would therefore appear to shift towards the visible spectrum.

Table I shows that the following formulæ fit the refractive index data of Rinne and Kolb at 23° C.

$$\left. \begin{aligned} n_{\omega}^2 &= 1 + \frac{1.35159 \lambda^2}{\lambda^2 - 92.5^2} \\ n_e^2 &= 1 + \frac{1.37863 \lambda^2}{\lambda^2 - 92.5^2} \end{aligned} \right\} \quad (3)$$

(λ in $m\mu$)

The same dispersion wave-length fits the ordinary and the extraordinary indices and the birefringence appears as a consequence of different oscillator strengths in the two directions.

TABLE I

λ in $m\mu$	n_{ω} (cal.)	n_{ω} (obs.)	n_e (calc.)	n_e (obs.)
434.047	1.5543	1.5540	1.5634	1.5634
466.8	1.5514	1.5514	1.5605	1.5608
486.133	1.5500	1.5500	1.5590	1.5593
495.75	1.5493	1.5494	1.5584	1.5587
517.27	1.5480	1.5481	1.5570	1.5574
588.997	1.5446	1.5446	1.5536	1.5537
627.8	1.5432	1.5431	1.5522	1.5522
656.278	1.5424	1.5423	1.5513	1.5513
687.2	1.5416	1.5414	1.5505	1.5504
718.9	1.5409	1.5405	1.5495	1.5498

Sosman has given the most probable values of the refractive indices at 18° C. Table II shows the fit of these refractive indices for wave-lengths between 250.329 $m\mu$ and 410.174 $m\mu$ according to the formulæ

$$\left. \begin{aligned} n_{\omega}^2 &= 1 + \frac{1.3500 \lambda^2}{\lambda^2 - 92.5^2} \\ n_e^2 &= 1 + \frac{1.3786 \lambda^2}{\lambda^2 - 92.5^2} \end{aligned} \right\} \quad (4)$$

It is seen that the same dispersion frequency as in (3) holds good in this region also. The strength of the extraordinary is very nearly the same in (3) and (4) but the strength of the ordinary shows a slight difference in (3) and (4).

TABLE II

λ in $m\mu$	n_{ω} (calc.)	n_{ω} (obs.)	n_{ϵ} (cal.)	n_{ϵ} (obs.)
250.329	1.6003	1.6003	1.6114	1.6114
303.412	1.5775	1.5770	1.5874	1.5872
325.253	1.5712	1.5709	1.5808	1.58005
358.68	1.5640	1.5639	1.5738	1.5737
396.848	1.5581	1.5581	1.5677	1.5677
410.174	1.5564	1.5565	1.5660	1.5661

Differentiating the dispersion formulæ with respect to the temperature t we get

$$\frac{dn_{\omega}}{dt} = -\frac{\gamma(n_{\omega}^2 - 1)}{2n_{\omega}} + \frac{1}{n_{\omega}} \frac{k_{\omega} \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \chi_r$$

$$\frac{dn_{\epsilon}}{dt} = -\frac{\gamma(n_{\epsilon}^2 - 1)}{2n_{\epsilon}} + \frac{1}{n_{\epsilon}} \frac{k_{\epsilon} \lambda^4}{(\lambda^2 - \lambda_r^2)^2} \chi_r,$$

where γ = coefficient of cubical expansion and $\chi_r = \frac{1}{\lambda_r} \frac{d\lambda_r}{dt}$.

Using these formulæ and the data of Radhakrishnan and Barbaron, χ 's for different temperatures and wave-lengths have been calculated and tabulated in Table III.

TABLE III

 $\chi \times 10^5$

Temp. Range °C.	$\lambda = 253.7 m\mu$		$\lambda = 365 m\mu$		$\lambda = 546 m\mu$		$\lambda = 589 m\mu$		Author
	Ord.	Extra.	Ord.	Extra.	Ord.	Extra.	Ord.	Extra.	
- 200 to - 150					0.2	0.1			Barbaron
- 150 to - 100					0.5	0.45			do
- 100 to - 50					0.7	0.60			do
- 50 to + 0					0.82	0.76			do
0 to + 50					1.0	0.96			do
	1.25	1.14	1.1	1.0	1.1	0.96	1.00	0.91	Radhakrishnan
50 to 100	1.4	1.31	1.3	1.15	1.2	1.1	1.14	1.07	do
100 to 150	1.5	1.39	1.34	1.27	1.3	1.2	1.23	1.10	do
150 to 200	1.6	1.47	1.4	1.33	1.4	1.29	1.33	1.16	do
200 to 250	1.68	1.59	1.55	1.4	1.45	1.35	1.44	1.2	do
250 to 300	1.77	1.69	1.63	1.44	1.53	1.5	1.53	1.3	do
300 to 350	1.86	1.8	1.7	1.51	1.64	1.56	1.58	1.42	do
350 to 400	1.98	1.87	1.8	1.62	1.72	1.63	1.69	1.5	do

From Table III we see that χ increases steadily with temperature. It is also noticed that χ approaches zero at very low temperatures. Ramachandran¹⁰ has shown in the case of diamond and Radhakrishnan¹¹ in the case of quartz and vitreous silica that the value of χ tends to zero for very low temperatures.

Theoretically, the χ calculated for different wave-lengths should be the same. Actually, we notice that it shows a systematic, though slight increase with decreasing wave-length. This apparent increase with decreasing wave-lengths can be explained as follows. The dispersion formula which is used in these calculations assumes a single absorption wave-length with an appropriate weight to represent the indices in the particular region. But when we move from one part of the spectrum, say from the visible to the near ultra-violet, the absorption wave-lengths having longer wave-lengths would become more effective than the rest, and the weighted mean of the absorption wave-lengths would therefore register an increase. The χ 's of all the absorption wave-lengths would also be generally not the same. Normally, it might be expected that the longer absorption wave-lengths would have a greater χ . Hence, the effective χ should show an apparent increase.

We also notice that the value of χ evaluated for the ordinary ray comes out slightly higher than that for the extraordinary. This may be explained as follows. The birefringence is a consequence of the same absorption wave-lengths having different oscillator strengths in the two principal directions. If the strengths of the deeper terms are larger for extra-ordinary than for the ordinary, the effective χ will be smaller for the former. The value of χ as calculated above using a single term dispersion formula would then come out as larger for the ordinary ray than for the extraordinary one.

The comparison of the thermo-optic behaviour of quartz and vitreous silica is very interesting. Vitreous silica has a negligible coefficient of thermal expansion and hence the refractive index shows a continuous increase with temperature quite similar to the positive part of the temperature variation of the refractive indices of quartz. A single term dispersion formula with the same dispersion wave-length as in quartz fits the refractive indices of vitreous silica in the same region of the spectrum. The formula at 18° C. is

$$n^2 = 1 + \frac{1.0994 \lambda^2}{\lambda^2 - 92.5^2}$$

The χ can be calculated as above, and we again find a close parallelism between the behaviour of quartz and vitreous silica.

TABLE IV

$$\chi \times 10^5$$

Temp. Range °C.	Vitreous silica	Quartz (approx.)
-160 to 18	0.8	0.7
- 64 to 130	1.1	1.1
18 to 235	1.3	1.25
130 to 365	1.5	1.5
235 to 475	1.63	1.7

My sincere thanks are due to Prof. Sir C. V. Raman, F.R.S., N.L., for the suggestion of the problem and for his kind and encouraging interest.

4. SUMMARY

The temperature variation of the refractive indices of α -quartz contains a positive part, though it is completely submerged by the predominant negative part due to the thermal expansion. At the α - β transition temperature of 573°C., the structural changes represented by the α - β transformation cause a change in a direction opposite to that of the density change, *i.e.*, an increase in the refractive indices. The rate of change of the electronic dispersion wave-lengths decreases with decreasing temperatures tending to zero at very low temperatures. The thermo-optic behaviour of quartz and vitreous silica bear a close resemblance, the difference in the two cases being due to the difference in the thermal expansions.

REFERENCES

1. Sosman .. *The Properties of Silica*, 1927.
2. Micheli .. *Ann. d. Phys.*, 1902, 7.
3. Rinne and Kolb .. *Neues. Jahrb. Min.*, 1910, 2, 138-58.
4. Radhakrishnan .. *Proc. Ind. Acad. Sci.*, 1951, 33 A, 22.
5. Barbaron .. *Compt. Rendus*, 1948, 226, 1443.
6. Pockels .. *Ann. d. Physik. u. Chem. (Wiedemann)*, 1889, 37, 269-305.
7. Sosman .. *The Properties of Silica*, 1927, 748.
8. Radhakrishnan .. *Proc. Ind. Acad. Sci.*, 1951, 33 A, 22 ; 1948, 27 A, 44; 1947, 25 A, 382.
9. Chandrasekhar .. *Ibid.*, 1951, 34 A, 275.
10. Ramachandran .. *Ibid.*, 1947, 25 A, 266.
11. Radhakrishnan .. *Ibid.*, 1948, 27 A, 44.