TEMPERATURE VARIATION OF THE RAMAN SPECTRUM OF TOPAZ

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1. Introduction

The temperature variation of Raman spectra of solids is of great interest because of its direct bearing on the theory of the solid state. The Raman spectrum of a solid yields directly its characteristic vibrations and any theory of the solid state can be valid only if it conforms to the observed vibration spectrum of the solid. The study of the temperature variation of Raman spectrum in such substances as diamond and quartz has clearly indicated that the failure of the Gruneisen's Law of thermal expansion lies in assuming a constant value of γ for all frequencies. But such data on the temperature variation of Raman spectra are available only for relatively a few simple crystals. It was therefore considered desirable to investigate the temperature variation of the Raman spectrum of topaz in some detail.

The Raman spectrum of topaz was recorded by R. S. Krishnan (1947) at room temperature using the powerful ultraviolet technique and he reported the appearance of 32 sharp Raman lines. The Raman spectrum of topaz was photographed by T. Kopcewicz (1937) at two temperatures, namely, 20° and 500° C. using λ 4358 ÅU as the exciting radiation. He found that the low frequency lines shifted proportionately more than the high frequency lines. He could, however, claim an accuracy of 5 wave numbers only for his measurements.

2. Details of Experiment

Only colourless crystals of topaz are transparent to the λ 2537 radiation. One such piece having dimensions $6\times6\times5$ mm. was used in the present investigation. To record the spectrum at higher temperatures, the crystal was kept inside a heater provided with suitable windows. The heating current was taken from the D.C. mains through a series of adjustable resistances. The temperature was controlled by periodic adjustment of the resistance so as to keep the current flowing through the heater constant. Such adjustment was not found to be frequently necessary. The temperature

remained constant and very steady [illegible] as much as 24 hours. The steady state [illegible] on the heating current. The [illegible] iron-constantan thermocouple [illegible] To measure the thermo E.M.F. [illegible] the range from room temperature to [illegible] above 250° C.

The λ 2537 radiation from a [illegible] was used for exciting the Raman spectrum and a Hilger [illegible] graph for recording it. With a slit width of [illegible] hours was sufficient to get a fairly [illegible] iron arc spectrum was superposed [illegible] were made using a Hilger [illegible] Spectrograms were taken at [illegible] and 450° C.

The spectrograms were microphotometered with the aid of a M. [illegible] photometer.

3. RESULTS

The results of the experiment are given in the following tables. Table I contains the frequency shifts in [illegible] Raman lines of topaz at various temperatures. It should be mentioned that on certain negatives the frequency shifts of some of the lines could not be measured. They are therefore not entered in Table I.

TABLE I

Frequency Shifts of Some of the Prominent Raman Lines of Topaz at Various Temperatures

Temp. °C.	269·6 cm.⁻¹	458 cm.⁻¹	[illegible]	[illegible]	[illegible]	[illegible]
30	269·6	457·8	[illegible]	[illegible]	[illegible]	[illegible]
110	269·1	457·4	[illegible]	[illegible]	[illegible]	[illegible]
150	268·3	456·1	[illegible]	[illegible]	[illegible]	[illegible]
200	267·6	456·5	[illegible]	[illegible]	[illegible]	[illegible]
250	266·7	455·4	[illegible]	[illegible]	[illegible]	[illegible]
300	265·9	454·5			[illegible]	[illegible]
350	264·8		[illegible]	[illegible]	[illegible]	[illegible]
400	264·5	452·6		[illegible]		[illegible]
450	263·0	451·1		[illegible]	[illegible]	[illegible]

The intense Raman lines of topaz form close doublets and as such their widths at different temperatures could not be measured accurately. The Raman line at 458 cm.$^{-1}$ was free from this trouble. Its width at half intensity was therefore estimated from the microphotometer records and the values for different temperatures are entered in Table II.

TABLE II

Width of the 458 cm.$^{-1}$ *line at Various Temperatures*

Temp. T °K	Width (W) cm.$^{-1}$	W/ $\sqrt{T}$
303	12	0·69
423	12·6	0·61
523	13·9	0·61
623	15·5	0·62
723	16·9	0·63

From the measured frequency shifts, the values of $\chi \left(= -\frac{1}{\tilde{\nu}} \frac{d\tilde{\nu}}{dT}\right)$ for eight Raman lines have been calculated for 3 different ranges—and are entered in Table III.

TABLE III

χ *for Various Raman Frequencies*

$\tilde{\nu}$ value in cm.$^{-1}$ at 30° C.	$\tilde{\nu}$ value in cm.$^{-1}$ at 450° C.	$\chi = -\frac{1}{\tilde{\nu}} \frac{d\tilde{\nu}}{dT} \times 10^6$		
		30–150° C.	150–300° C.	300–450° C.
240·9	236·5	21	46	65
269·6	263·0	42	57	71
289·5	283·2	46	55	59
457·8	451·1	15	36	51
521·8	..	55	97	..
926·9	915·1	45	34	18
985·0	967·5	56	41	30
3643·2	3628·1	20	6	6

remained constant and very steady over long intervals of time—as much as 24 hours. The steady state was reached within 30 minutes after switching on the heating current. The temperature was measured by means of an iron-constantan thermocouple whose junction was kept close to the crystal. To measure the thermo E.M.F. a calibrated microammeter was used for the range from room temperature to 250° C. and a standard millivoltmeter above 250° C.

The λ 2537 radiation from a specially designed quartz mercury arc was used for exciting the Raman spectrum and a Hilger medium quartz spectrograph for recording it. With a slit width of 0·04 mm. an exposure of twenty hours was sufficient to get a fairly intense spectrogram. A comparison iron arc spectrum was superposed on each spectrogram. The measurements were made using a Hilger cross-slide micrometer reading upto 1/1000 mm. Spectrograms were taken at 30°, 110°, 150°, 200°, 250°, 300°, 350°, 400° and 450° C.

The spectrograms were microphotometered with the aid of a Moll microphotometer.

3. RESULTS

The results of the experiment are given in the following tables. Table I contains the frequency shifts in wave numbers of the prominent Raman lines of topaz at various temperatures. It should be mentioned that on certain negatives the frequency shifts of some of the lines could not be measured. They are therefore not entered in Table I.

TABLE I

Frequency Shifts of Some of the Prominent Raman Lines of Topaz at Various Temperatures

Temp. °C.	269·6 cm.$^{-1}$	458 cm.$^{-1}$	520 cm.$^{-1}$	927 cm.$^{-1}$	985 cm.$^{-1}$	3643 cm.$^{-1}$
30	269·6	457·8	521·8	926·9	985·0	3643·2
110	269·1	457·4	521·1	925·4	979·9	3636·2
150	268·3	456·1	518·5	922·2	980·0	3634·7
200	267·6	456·3	515·3	920·6	975·6	3633·6
250	266·7	455·4	511·1	918·6	973·6	3632·1
300	265·9	454·5	..	..	971·7	3631·6
350	264·8	..	508·8	916·6	969·4	3630
400	264·5	452·6	..	915·5	..	3629·2
450	263·0	451·1	..	915·1	967·5	3628·1

The intense Raman lines of topaz form close doublets and as such their widths at different temperatures could not be measured accurately. The Raman line at 458 cm.$^{-1}$ was free from this trouble. Its width at half intensity was therefore estimated from the microphotometer records and the values for different temperatures are entered in Table II.

TABLE II

Width of the 458 cm.$^{-1}$ *line at Various Temperatures*

Temp. T °K	Width (W) cm.$^{-1}$	W/ $\sqrt{T}$
303	12	0·69
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From the measured frequency shifts, the values of $\chi \left(= -\frac{1}{\tilde{\nu}} \frac{d\tilde{\nu}}{dT}\right)$ for eight Raman lines have been calculated for 3 different ranges—and are entered in Table III.

TABLE III

χ *for Various Raman Frequencies*

$\tilde{\nu}$ value in cm.$^{-1}$ at 30° C.	$\tilde{\nu}$ value in cm.$^{-1}$ at 450° C.	$\chi = -\frac{1}{\tilde{\nu}} \frac{d\tilde{\nu}}{dT} \times 10^6$		
		30–150° C.	150–300° C.	300–450° C.
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3643·2	3628·1	20	6	6

The variation of $\Delta\tilde{\nu}$ with temperature for 6 Raman lines is illustrated in Figs. 1 to 4. In Fig. 2 is also included the curve showing the variation of width with temperature for 458 cm.$^{-1}$

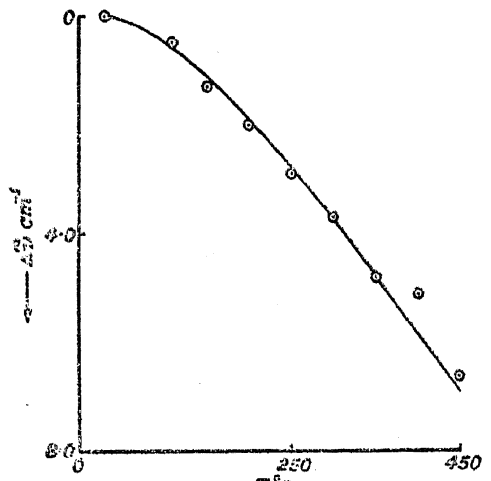

Fig. 1 $\Delta\tilde{\nu}$-T curve for 270 cm^{-1}

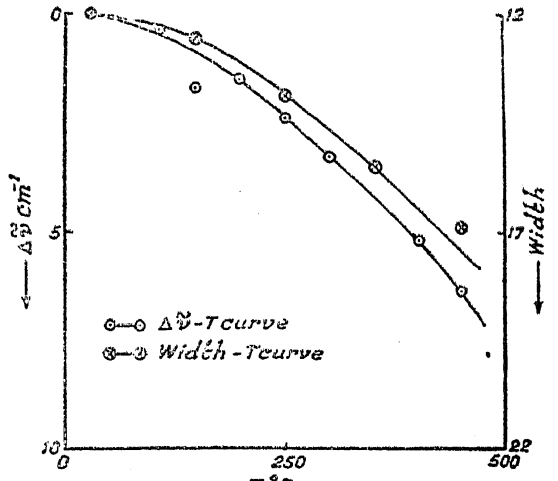

Fig. 2 $\Delta\tilde{\nu}$-T curve for 458 cm^{-1}

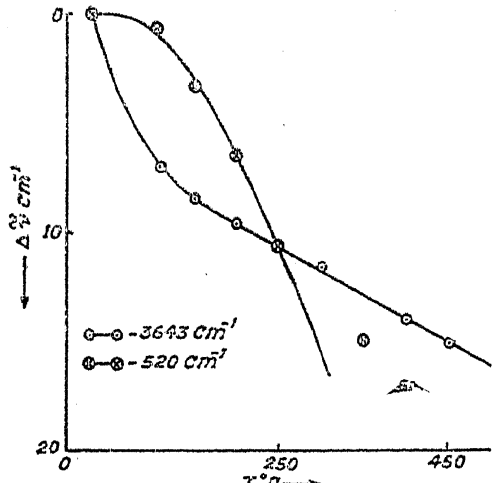

Fig. 3 $\Delta\tilde{\nu}$-T curves for 3643 & 520 cm^{-1} Lines

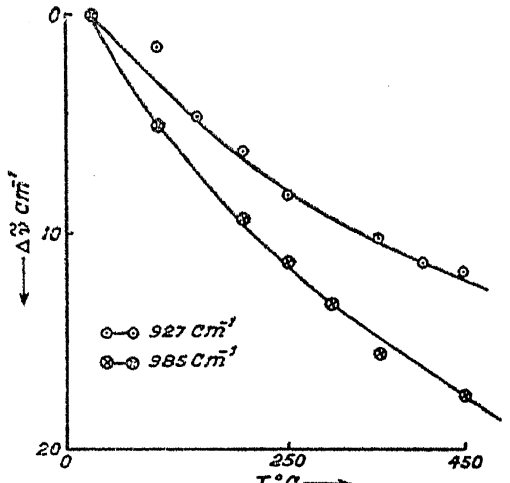

Fig. 4 $\Delta\tilde{\nu}$-T curves for 927 & 985 cm^{-1} Lines

FIGS. 1–4

The specimen of topaz used in the present investigation was rather small and in order to get the photographs in a resonable time it became necessary to use a small dispersion instrument and a reasonably wide slit. In view of this, the doublets 920–934 and 3636–3649 reported by R. S. Krishnan could be recorded by the author only as 2 lines having frequency shifts 926·9 and 3643·2 cm.$^{-1}$ respectively.

4. Discussion

From a perusal of the χ values given in Table III and the curves exhibited in Figs. 1 to 4, it is apparent that the Raman lines in topaz can be classified into two groups, namely:—

(1) those whose χ values increase with temperature and

(2) those whose χ values decrease with temperature.

Under the first category come the lines with low frequency shifts, namely, 241, 270, 290, 458 and 522 cm.$^{-1}$ The lines 927, 985 and 3643 cm.$^{-1}$ fall under the second category. It should be mentioned, that in all the crystals investigated so far by the earlier workers the values of χ progressively increase with temperature irrespective of the nature of the Raman lines.

The second important result that emerges from the present investigation is the fact that the Raman lines of topaz do not exhibit wide variations in their χ values. For example, in the range from 30°–150° C., the χ values for the different lines vary from 15×10^{-6} to about 56×10^{-6}, *i.e.*, by a factor of 4. In the case of quartz and calcite, on the other hand (Narayanaswami, 1947), χ values vary by a factor of 45 and 20 respectively. Moreover, unlike in the case of quartz and calcite, the Raman lines of topaz do not exhibit any grouping based on the absolute values of χ.

The behaviour of the 458 cm.$^{-1}$ line of topaz may be compared with that of the 466 cm.$^{-1}$ line of crystal quartz. Over the same range of temperature, the χ's for these two Raman lines have nearly the same value.

The temperature-width curve for the 458 cm.$^{-1}$ line of topaz shows a close parallelism to the $\Delta\tilde{\nu} - T$ curve (curve II). Such a correlation between the width-temperature curves and the frequency-temperature curves was suggested by Raman (1947) and experimentally verified by Narayanaswami (1947) in calcite and quartz. The width of the 458 cm.$^{-1}$ line of topaz is also found to be proportional to the square root of the absolute temperature (see Table II). It may be recalled that such a relation was reported for the Raman lines of calcite and quartz by Ornstein and Went (1935) and for diamond by R. S. Krishnan (1946).

In conclusion, the author wishes to express his gratitude to Prof. R. S. Krishnan for having suggested this problem and for his kind interest throughout the course of the investigation. He also expresses his sincere thanks to Dr. P. S. Narayanan for his unstinting help and co-operation.

Summary

The temperature variation of the frequency shifts of the intense Raman lines of topaz has been investigated over the range of temperature from 30° C.

to 450° C., using the λ 2536 AU radiation of the mercury arc as the exciter. From the observed variation, values of X $\left(= \frac{1}{I} \frac{dI}{dT} \right)$ have been calculated for the lines 241, 270, 289, 458, 522, 927, 985 and [illegible] cm.$^{-1}$ In the case of the first five lines, X increases with temperature, while for the rest, X decreases with temperature. Unlike the case of calcite and quartz the absolute values of X for the different Raman lines of topaz do not show wide variations.

The temperature variation of the width of the 458 cm.$^{-1}$ line has also been measured. The width of this line is found to increase proportional to the square root of the absolute temperature.

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