

# TEMPERATURE VARIATIONS OF THE RAMAN FREQUENCIES IN DIAMOND

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## 1. INTRODUCTION

WHEN the temperature of a crystal is raised the atoms get less tightly packed resulting in an increase in the inter-atomic distances and a corresponding diminution of the forces acting on them. The frequencies of atomic vibrations which are determined by the inter-atomic forces will therefore be decreased. These frequency changes should in turn be related to the expansion of the crystal. The actual form of the relationship will necessarily depend on the law of force between the atoms. For constructing a simple theory of thermal expansion, Grüneisen (1908) assumed that the relative change of any vibration frequency was directly proportional to the relative change in the volume. In other words,

$$-\frac{\Delta \nu_i}{\nu_i} \times \frac{V}{\Delta V} = -\frac{d(\log \nu_i)}{d(\log V)} = \gamma_i, \quad (1)$$

where  $\gamma_i$  is a constant. If we assume with Grüneisen (1912) that  $\gamma_i$  is the same for all the frequencies in the vibration spectrum of a crystal which is justified on the Debye theory, we then get from strictly thermodynamical considerations

$$-\frac{d(\log \nu)}{d(\log V)} = \gamma = \frac{\alpha V_0}{\chi_0 C_v}, \quad (2)$$

where  $\gamma$  is the well-known Grüneisen constant.  $V_0$ ,  $\chi_0$  and  $C_v$  have the usual significance, namely volume, compressibility and specific heat of the crystal. Further, the quantity  $\frac{d(\log \nu)}{d(\log V)}$  should be independent of temperature. These conclusions have an important bearing on the theory of the solid state. It is therefore necessary to see how far they are in agreement with facts in any particular case. No attempt appears to have been made to test the validity of the above conclusions in any particular case. The present investigation was therefore undertaken with a view to get reliable data on the thermal variation of the Raman frequencies in diamond, the thermal expansion of which has already been studied in detail by the author (Krishnan, 1946 a).

## 2. PREVIOUS WORK

Ramaswamy (1930) who was the first to photograph the Raman spectrum of diamond investigated the effect of temperature on the principal Raman frequency ( $1332\text{ cm.}^{-1}$ ) of diamond. He reported that the Raman line was not perceptibly shifted or decreased in intensity and sharpness when the diamond was heated up to  $250^\circ\text{ C}$ . His negative result may be attributed either to the unsuitable way of heating the crystal or to the relatively small dispersion of the spectrograph employed by him. Robertson, Fox and Martin (1934) reported similar negative results on cooling the crystal to  $-180^\circ\text{ C}$ .

Using the  $\lambda\ 4046$  and  $\lambda\ 4358$  excitation, Nayar (1941) measured the frequency shift of the principal line of diamond and its variation with temperature over the range of temperature from  $-180^\circ\text{ C}$ . to  $860^\circ\text{ C}$ . From the observed variation of the characteristic frequency, Nayar evaluated the thermal expansion coefficient of diamond and compared the same with the available data on thermal expansion which, however, covered only a short range of temperature. The experimental value was definitely higher than the theoretical value. Nayar's frequency-temperature curve in the region of high temperatures is not very reliable as it was based on observations made at three temperatures only in the range from  $250^\circ$  to  $850^\circ\text{ C}$ .

## 3. DETAILS OF THE EXPERIMENT

As is well known, the first order Raman spectrum of diamond exhibits only a single, sharp and intense line with a frequency shift of  $1332\text{ cm.}^{-1}$ . The other fundamental modes of oscillation of the diamond lattice are forbidden to appear in the first order spectrum. Some of them manifest themselves as octaves and combinations in the second order Raman spectrum (Krishnan, 1944 *a*, 1946 *b*). The temperature variations of the frequencies of the forbidden modes have therefore to be estimated from the observed thermal behaviour of the Raman lines appearing in the second order spectrum. As the second order lines are necessarily weak and not so sharp as the first order line ( $1332\text{ cm.}^{-1}$ ), it is not possible to determine their temperature variations with the same degree of accuracy and over short ranges of temperature as could be attained in the case of the principal line at  $1332\text{ cm.}^{-1}$ . Two independent sets of experiments had therefore to be carried out. In order to utilise the high resolving power of a quartz spectrograph in the ultra-violet and to take spectrum photographs with reasonably short exposures, the intense  $\lambda\ 2536.5$  mercury resonance radiation was used for exciting the Raman spectrum. Diamonds of the ultra-violet transparent type were employed.

*High Temperatures.*—For work above room temperature a specially designed heater was constructed. It consisted of a thin rectangular steel tube ( $4" \times \frac{1}{2}" \times \frac{1}{2}"$ ) provided with three circular holes ( $\frac{1}{4}"$  in diameter) covered with quartz windows on three of its sides in the central portion of the tube. These served for illumination of the crystal supported inside the tube and for observation of the scattered light. The steel part of the heater was covered with a thin layer of mica and was closely wound over with nichrome wire set in a mixture of alumina and sodium silicate solution. To reduce losses due to radiation, an aluminium foil was stuck on to the outside of the furnace. Steady current was supplied to the heater from a set of accumulators. During an exposure the heater current was maintained at a constant value. The top of the furnace was closed by a disc to which was attached a thin metal tube. The tube supporting the furnace was clamped vertically to an adjustable stand.

The specimen of diamond which was in the form of a thin plate ( $10 \times 6 \times 0.6$  mm.) was fixed on the top of a silica rod  $\frac{1}{4}"$  in diameter with its flat faces vertical and facing the most intense portion of a water-cooled magnet-controlled quartz arc. The light scattered through one of the straight edges of the diamond in the end—on position was focussed on the slit of the spectrograph. After the preliminary adjustments were made, the furnace was lowered into position. To determine the temperature of the diamond during exposures, a calibrated nichrome-constantan thermocouple was fixed permanently inside the furnace almost touching the diamond. Diamond being a good conductor of heat, its temperature was taken to be that of the air inside the furnace. At the highest temperature used, namely,  $700^{\circ}$  C., after switching on the current, it took about 20–30 minutes for the furnace to come to a steady state.

*Low Temperatures.*—For work below room temperature a demountable vacuum flask with an inner vessel of metal and an outer vessel of glass was employed. The lower end of the outer vessel was provided with two quartz windows. Through one of these windows the diamond was irradiated with the light from the mercury arc, while the observation of the scattered light was made through the second window. The thin plate of diamond was held in a copper block fixed to the bottom of the inner brass tube of the flask which formed the container for the refrigerant. The flanged joint between the inner and outer tubes at the top was sealed with Apiezon sealing compound, "Q". The flask was kept evacuated continuously with the aid of a Cenco Hyvac pump.

*Principal Raman Frequency ( $1332$  cm.<sup>-1</sup>).*—For measuring the temperature variation of the principal Raman line, a Hilger E1 quartz spectrograph

having a dispersion of about  $44 \text{ cm.}^{-1}/\text{mm.}$  in the  $\lambda 2625$  region was used. With a slit-width of  $0.01 \text{ mm.}$ , exposures of the order of two hours were required to get the line recorded with a reasonable intensity. With the furnace in position, the temperature of the diamond was  $55^\circ \text{ C.}$  when no current was passed through the heater coil. With the low temperature apparatus, the temperature of the diamond was the same as that of the room temperature, *viz.*,  $27^\circ \text{ C.}$ , when no refrigerant was poured into the flask. It was therefore necessary to make accurate measurements of the frequency shift of the principal Raman line for these two temperatures. For each temperature a couple of photographs of the Raman spectrum was taken with an iron arc comparison spectrum partially overlapping the Raman spectrum. The plates were measured with a Hilger cross-slide micrometer reading up to  $1/1000 \text{ mm.}$  The mean values of the frequency shift at  $27^\circ$  and  $55^\circ$  were evaluated in the usual way.

Using a Hartmann diaphragm, two photographs of the Raman spectrum were recorded in juxtaposition on the same plate, one without any current passing through the heating coil, *i.e.*, the crystal being maintained at  $55^\circ \text{ C.}$  and the other with the crystal heated to a known temperature. During the high temperature exposure, the furnace current was continuously regulated by hand in order to keep the temperature constant. It did not vary by more than  $2^\circ$  from the desired temperature.

The use of the high dispersion E1 spectrograph presented some difficulties in the beginning. Being of an all-metal type, it was susceptible to small variations of temperature. The spectrograph was housed in a separate double-walled cabin and the furnace, arc, etc., were placed outside. In between two exposures, the cabin door had to be opened for shifting the Hartmann diaphragm. While doing this, warm air from outside rushed into the cabin. Consequently the temperature of the spectrograph varied to such an extent as to produce a noticeable drift of the mercury lines in the spectrogram recorded subsequently. In order to minimise this trouble, the spectrograph was covered with two layers of woollen blankets which proved to be very effective. As a further check, the frequency change of the 1332 line was evaluated not from the observed shift of this line, but from the relative shift with reference to the nearest mercury lines on either side.

The frequency changes of the principal Raman line were determined for 13 different temperatures above  $55^\circ \text{ C.}$ , namely,  $117^\circ$ ,  $152^\circ$ ,  $211^\circ$ ,  $242^\circ$ ,  $285^\circ$ ,  $345^\circ$ ,  $396^\circ$ ,  $452^\circ$ ,  $500^\circ$ ,  $550^\circ$ ,  $600^\circ$ ,  $654^\circ$  and  $703^\circ \text{ C.}$  Two low temperature measurements were also obtained by using liquid air as refrigerant in one case and solid carbon dioxide-acetone mixture in the other case.

*Second order Raman lines*.—Using a Hilger E3 medium quartz spectrograph which had a dispersion of about 140 cm.<sup>-1</sup>/mm., a heavily exposed Raman spectrum of diamond showing the second order lines was recorded with the specimen (N.C. 89) maintained at room temperature (30°) by fan cooling. Similar photographs were also taken on different plates with the crystal maintained successively at 390° C. and 620° C. The constant temperature furnace described earlier in the section was used for this purpose. The negatives were microphotometered, and from the microphotometric records the frequency shifts of the prominent second order lines were estimated.

4. RESULTS

The frequencies of the principal Raman line at different temperatures are given in Table I and the variation with temperature is graphically represented by the curve in Fig. 1. The ordinates represent the decrease or

TABLE I  
*Frequencies of the principal Raman line in diamond at different temperatures*

Temperature of	Frequency shift in cm. <sup>-1</sup>
85	1333.2
195	1332.7
300	1331.8
328	1331.5
390	1330.4
425	1329.6
484	1327.7
515	1327.3
558	1327.0
618	1325.6
669	1324.4
725	1323.1
773	1322.2
823	1320.8
873	1318.9
927	1317.6
976	1316.0

increase in frequency shift from the value at 300° T. It will be noticed that the rate of decrease, *i.e.*,  $-\frac{d\nu}{dT}$  is greater at higher temperatures. As the temperature is lowered the curve tends to flatten up. Comparing the results reported here with those of Nayar (1941), it is seen that although the general features of the ( $\Delta\nu - T$ ) curve are similar in both cases, the actual values of the frequency shifts at higher temperatures are not in agreement. For example, when the temperature of the diamond was raised from room

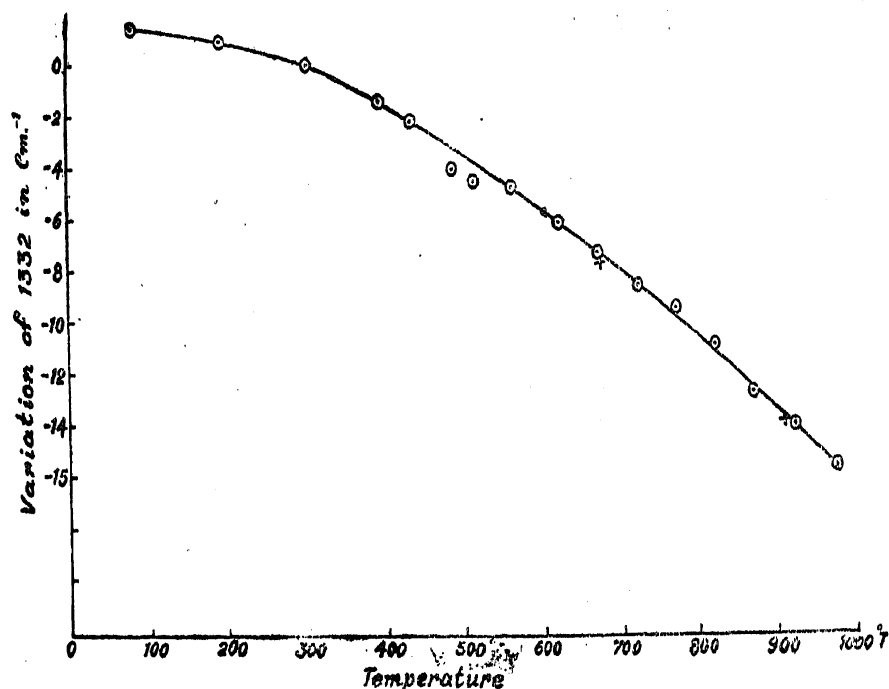


FIG. 1

FIG. 1. Frequency-Temperature curve for the principal Raman line of diamond

temperature to 632° C., Nayar recorded a change in the frequency equal to 10.2 wavenumbers. Actually, for the same range of temperature the author has observed a frequency change of 13.4 wavenumbers. The deviation increases with increasing temperature. In order to be sure that the observed deviation had nothing to do with the type of diamond used in the present investigation, the experiment was repeated for two temperatures using the same specimen of diamond with which the thermal expansion measurements were made (Krishnan, 1946 *a*) and which belonged to the ultraviolet opaque type. In an earlier publication (Krishnan, 1944) the author had shown that at room temperature there is no difference in the frequency shifts of the principal Raman line for the two types of diamond. Using the constant temperature furnace described in the previous section, a Hilger two prism spectrograph and  $\lambda$  4358 excitation, the frequency changes for the ultraviolet opaque diamond were measured for two ranges of temperature, namely, 55°-398° C. and 55°-640° C. The values are plotted in Fig. 1. They are indicated by crosses and fall on the smooth curve, showing thereby that the temperature variations of the principal Raman frequency are the same for the two types of diamond in the range of temperature covered by the present investigation.

The smaller values for the frequency changes reported by Nayar (1941) may be attributed to the fact that in his experiments the thermo-couple might not have recorded the correct temperature of the diamond. As the specimen was kept at one end of the furnace, its temperature was in all

probability lower than the temperature inside the furnace. The thermo-couple which was supported inside the heater recorded the correct temperature of the latter and not of the crystal. In the present experiment the diamond which was only 1 cm. in length was supported inside the furnace which was about 4" long. In order to eliminate air currents passing through the furnace, the top was completely closed by a metal disc, while the bottom was partially covered by the supporting quartz rod. The calibration curve for the thermo-couple was checked against the readings taken with a standard thermometer.

Table II gives the values of the frequency shifts of some of the prominent second order Raman lines at three different temperatures. It is evident from the figures given in Table II that for the same increase of temperature,

TABLE II

*Frequency shifts in wavenumbers of the prominent second order Raman lines in Diamond*

30°	390°	620°
2666	2652	2640
2502	2494	2486
2460	2449	2438
2176	2171	2158

the proportional change in the frequency shift is different for different second order Raman lines.

5. DISCUSSION OF RESULTS

The quantity  $\frac{d(\log \nu)}{d(\log V)}$  can be written in the form:—

$$\frac{d(\log \nu)}{d(\log V)} = \frac{d\nu}{\nu} \cdot \frac{V}{dV} = \frac{\Delta \nu}{\nu} \cdot \frac{1}{\bar{\alpha} (T_2 - T_1)}, \tag{3}$$

where  $\Delta \nu$  is the diminution in frequency  $\nu$  in the temperature range  $T_1$  to  $T_2$  and  $\bar{\alpha}$  is the mean coefficient of thermal expansion over the same range. In column 3 of Table III are given the observed values of the mean coefficient of thermal (volume) expansion for the different temperature ranges entered in column 1. The values below the horizontal line are those reported by the author (Krishnan, 1946 *a*), while those above the horizontal line were taken from Röntgen's (1912) measurements. The corresponding values of  $\Delta \nu$  in wavenumbers for the principal Raman line ( $1332 \text{ cm.}^{-1}$ ) in diamond are read off from the curve reproduced in Fig. 1 and are given in column 4.

The quantity  $\gamma_{1332} \left\{ = \frac{d(\log \nu)}{d(\log V)} \right\}$  has been evaluated using equation (3).

The values for the different temperature ranges are entered in column 5 of Table III.

TABLE III

Temperature range ° T	Mean Temperature ° T.	$\bar{\alpha} \times 10^6$	$\Delta \nu_{1332}$ in $\text{cm.}^{-1}$	$\gamma_{1332}$	$\gamma = \frac{\alpha V_0}{\chi_0 C_p}$
84.8-194.1	139.5	0.54	0.5	6.4	1.19
194.1-273.2	233.6	1.74	0.6	3.3	1.03
273.2-296.2	284.7	2.91	0.3	3.4	1.10
296.2-351.1	323	3.87	0.9	3.2	1.15
301-378	339.5	4.36	1.3	2.9	1.20
378-478	428	6.51	1.9	2.7	1.27
478-573	525	8.52	2.0	1.9	1.31
573-678	625	9.84	2.45	1.8	1.3
678-778	728	10.86	2.5	1.7	1.3
778-878	828	11.76	2.7	1.7	1.3

The last column in the above table gives the values of the Grüneisen number  $\gamma \left( = \frac{\alpha V_0}{\chi_0 C_p} \right)$  taken from another paper by the author (Krishnan, 1946a) appearing in this symposium. It is evident that  $\gamma_{1332}$  far from being a constant, *decreases* steadily from a value of 6.4 at 85° T. to about 1.8 at 600° T. Above 600° T. its value remains constant. The temperature dependence of  $\gamma_{1332}$  is graphically represented in Fig. 2. The portion of the curve below

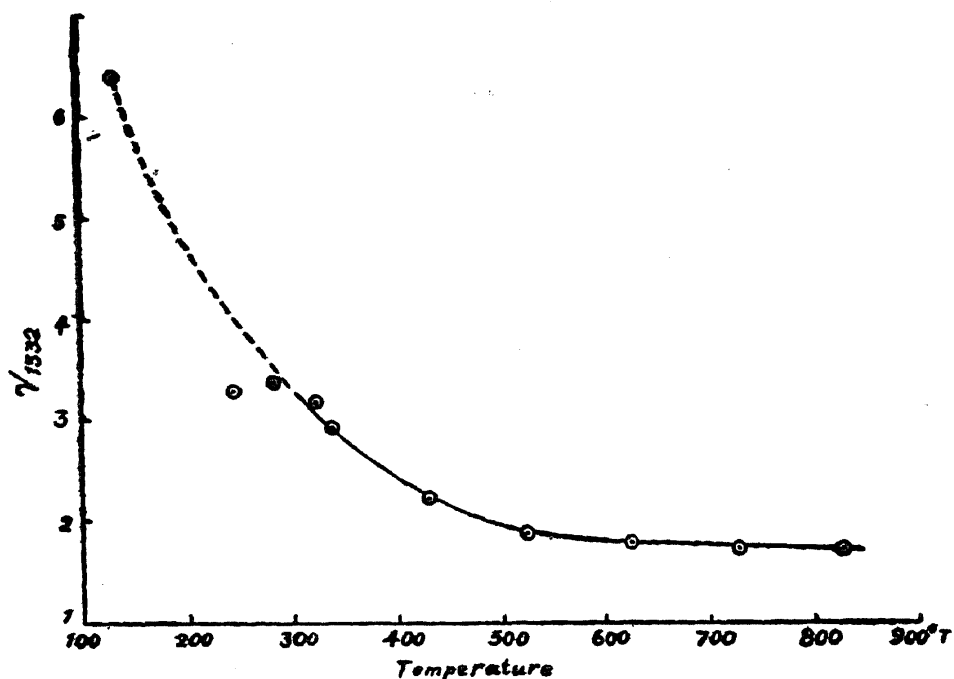


FIG. 2. Temperature dependence of  $\gamma_{1332}$ , i.e., the ratio of the relative change of frequency to the relative change of volume



273° T. is shown by a broken line as the values of  $\gamma_{1332}$  are not so accurate as those at high temperatures owing to the small values of  $\bar{a}$  and  $\Delta\nu$ . Comparing the values given in columns 5 and 6 in Table III one finds that throughout the range of temperature investigated here  $\gamma_{1332}$  is not equal to the Grüneisen number  $\gamma$ .

The mean values of  $\gamma_i$  for the prominent second order Raman lines for the temperature ranges 30–390° C. and 30–620° C. have been evaluated from the observed displacements of the lines. The results are entered in Table IV. As is to be expected,  $\gamma_i$  is the same for the 1332 line and its octave at 2666 cm.<sup>-1</sup> Different frequencies have in fact different  $\gamma_i$ 's, that for the principal Raman line (1332 cm.<sup>-1</sup>) being the highest. It is interesting to

TABLE IV

Raman line	$\bar{\gamma}_i$	$\bar{\gamma}_i$
	30–390°	30°–620°
1332	2.0	1.9
2666	2.0	1.9
2502	1.2	1.2
2460	1.7	1.7
2176	0.8	1.6

note that  $\gamma_i$  for the line 2176 increases with temperature. This line is evidently the octave of the prominent lattice line with a frequency shift of 1088 cm.<sup>-1</sup> appearing in the luminescence and absorption spectra of diamond.

Curves showing the relation between the increase of lattice spacing with increase of temperature and the corresponding decrease of frequency have been reproduced in Fig. 3 for the Raman lines 1332, 2502, 2460 and 2176 cm.<sup>-1</sup> The data on the lattice spacing variation were taken from the author's paper on the thermal expansion of diamond. Above room temperature, *i.e.*, 300° T. the relationship is nearly linear for the lines 1332, 2460 and 2502 cm.<sup>-1</sup>, but with different slopes. The variation of the frequency of the 2176 line is represented by a more complicated curve. The relative decrease in frequency shift of this line is smaller at low temperatures, and increases rapidly above 400° C. The difference in the thermal behaviour of the Raman lines is due to the fact that the inter-atomic forces inside the diamond lattice are affected by temperature to varying extent. On the basis of the lattice lines observed in luminescence, the Raman lines 2502 cm.<sup>-1</sup> and 2176 cm.<sup>-1</sup> can be assigned as the octaves of the fundamentals with frequency shifts 1251

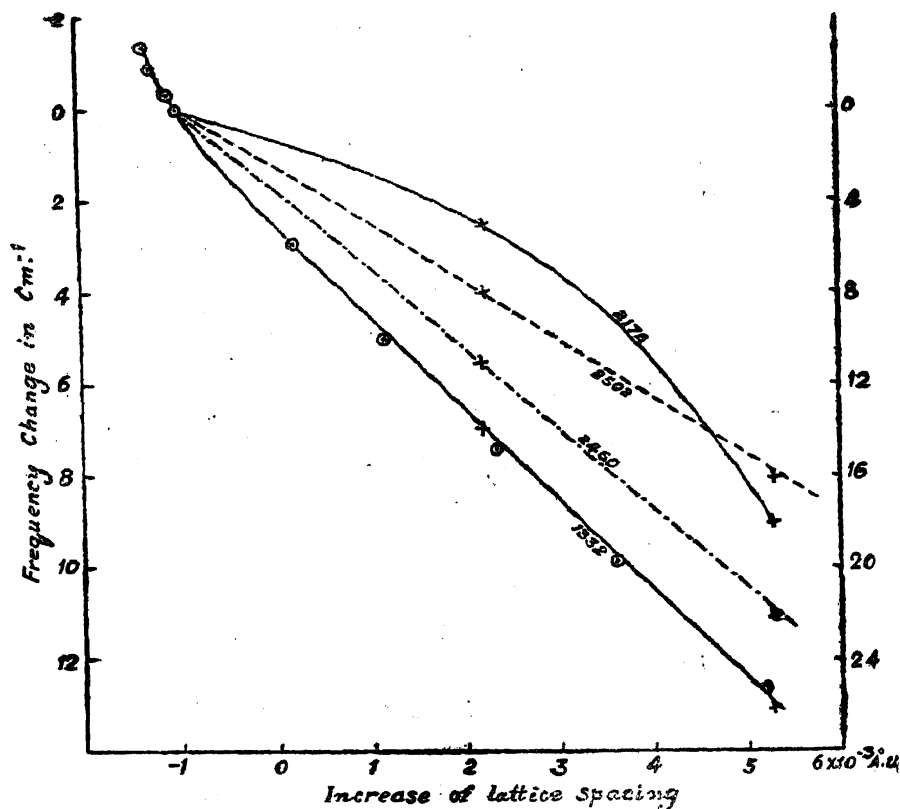


FIG. 3. Dependence of frequency on lattice spacing

and  $1088 \text{ cm.}^{-1}$ . The lattice lines with frequency shifts 1332, 1251 and 1088 correspond to the modes  $F_2$ ,  $H_4$  and  $K_3$  as designated by Bhagavantam (1943). The expressions for the frequencies are given in Table V.

TABLE V

Mode	$4\pi^2\nu^2$	Observed $\nu$ in $\text{cm.}^{-1}$
$F_2$	$\frac{8K \times 64K_\alpha}{3m}$	1332
$H_4$	$\frac{8K \times 4K_\alpha + 12K''}{3m}$	1251
$K_3$	$\frac{6K + 24K''}{3m}$	1088

$K$ ,  $K_\alpha$  and  $K''$  are the respective force constants arising from the primary valence bond, the directed valence bond and the repulsion between the next nearest neighbours. Their values are according to Dayal (1944):—

$$K = 0.314 \times 10^6 \text{ dynes/cm.}$$

$$K'' = 0.039 \times 10^6 \text{ ,,}$$

$$K_\alpha = 0.0197 \times 10^6 \text{ ,,}$$

From the observed variations of the frequencies of  $F_2$ ,  $H_4$  and  $K_3$  with lattice spacing the corresponding changes in the force constants have been estimated. When the temperature of the diamond is raised from  $300^\circ T.$  to  $800^\circ T.$  the values of  $K$  and  $K_a$  decrease by  $3.7 \times 10^3$  dynes/cm. and  $2.5 \times 10^2$  dynes/cm. respectively, whereas the value of  $K''$  increases by  $3.4 \times 10^2$  dynes/cm. The decrease in the value of  $K$  is of the same order of magnitude, but definitely greater than that of the force constant of the C—C bond with increase in the equilibrium nuclear distance as deduced from band spectrum data.

6. WIDTH OF THE 1332 LINE AND ITS INTERPRETATION

The author had remarked in one of the earlier papers (Krishnan, 1944 *b*) that the principal Raman line in diamond, though sharp, had a finite width at room temperature. As the temperature is raised, this line is found to broaden, the aggregate intensity of the line being greater at the higher temperature. The widths of the line at different temperatures have been estimated from the microphotometric records of the corresponding spectrograms. Typical microphotometric curves showing the variation of line width with

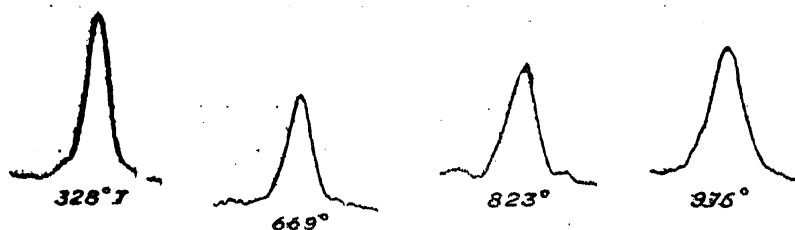


FIG. 4. Microphotometric records of the 1332 line at different temperatures

temperature are reproduced in Fig. 4. The relation between the half width of the 1332 line at half intensity and the temperature of the diamond is illustrated by the curve reproduced in Fig. 5. The values entered as ordinates are the measured half widths without making any allowance for the finite

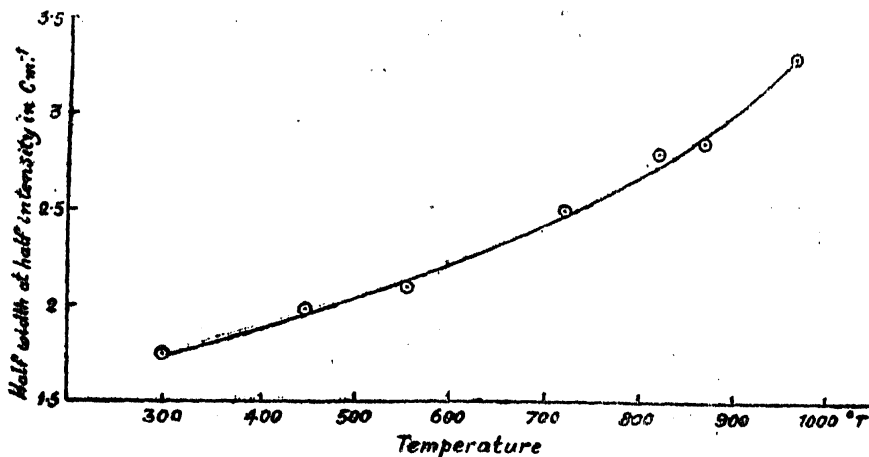


FIG. 5. Temperature dependence of the half width at half intensity of the 1332 line

width of the slit and other factors connected with the spectrograph. A mercury line which was recorded on the plate with roughly the same intensity as the Raman line had a half width at half intensity of 1.5 wavenumbers. The rate of increase of the breadth of the 1332 line increases with temperature. The enhanced width of the 1332 line at high temperatures cannot be attributed to temperature variations of the furnace as the latter never exceeded 2° either way.

The finite width of the Raman line at any particular temperature may be attributed to the thermal fluctuations in density inside the crystal. On the basis of the new lattice dynamics, if the atoms within an element of volume in the crystal of sufficient extension are arranged with perfect regularity in the lattice, their vibrations would be strictly monochromatic. But due to thermal agitation the lattice spacings undergo fluctuations. As the domain gets compressed, the atomic vibration frequency increases and when it expands, the frequency gets diminished. As the compressions and expansions are of varying magnitude, the frequency will vary continuously about the mean value, giving rise to a finite width for the Raman line. The mean square of the fluctuations in volume is given by the well-known formula

$$(\overline{\Delta V})^2 = kT\chi V \quad (4)$$

where  $k$  is the gas constant,  $\chi$  compressibility and  $V$  is the volume of the domain. The relative mean fluctuation in volume is given by

$$\frac{\sqrt{(\overline{\Delta V})^2}}{V} = \sqrt{\frac{kT\chi}{V}} \quad (5)$$

From the observed variations of the frequency shift of the 1332 line with increase in lattice spacing, the half width of the line arising from the relative mean fluctuation in a volume element at any desired temperature can be evaluated. The values of the half width for three different sizes of the volume element, namely,  $V_1 = 8$  times,  $V_2 = 64$  times and  $V_3 = 512$  times the volume of the unit cube, and for different temperatures are given in Table VI.

TABLE VI

Temperature °T.	Calculated mean half width in cm. <sup>-1</sup>			Observed value of half width*
	$V_1$	$V_2$	$V_3$	
300	10.8	4.3	1.7	1.7
500	13.7	5.1	2.1	2.1
700	16.4	6.1	2.5	2.4
900	18.0	6.9	2.8	2.9
970	18.8	7.1	2.9	3.6

\* No correction has been made for the width arising from the finite width of the exciting line, width of slit used and other factors connected with the spectrograph.

Comparing the figures given in Table VI, it is evident that for a volume element which has 8 times the linear dimensions of the unit cubic cell, the calculated half width of the 1332 line is of the same order of magnitude as the observed half width at half intensity.

In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman for useful discussions during the progress of these investigations.

#### SUMMARY

With a high dispersion spectrograph, a diamond of the ultraviolet transparent type and the mercury  $\lambda$  2536.5 excitation, the principal Raman frequency has been measured and is found to decrease from 1333.2  $\text{cm.}^{-1}$  at 85° T. to 1316.0  $\text{cm.}^{-1}$  at 975° T. Identical results are obtained with a diamond of the ultraviolet opaque type and the  $\lambda$  4358 excitation. The temperature dependence of the more prominent second order Raman frequencies has also been investigated. The relative change of the principal frequency with relative change of volume decreases from a high value at 85° T. to a constant small value above 500° T. and differs greatly from the so-called Grüneisen constant. The different lattice and superlattice frequencies behave differently in respect of their temperature variation and this has been explained as due to differences in the rate of change with temperature of the different force constants which determine the vibration frequencies of the diamond lattice.

The 1332 line has a finite width which increases with temperature. This may be explained as due to the changes of lattice frequency arising from the thermal fluctuations of density in the volume elements of the crystal, if the effective linear dimensions of a volume element are assumed to be about 8 times as large as the edge of the unit cubic cell.

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