

RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part III. Quartz

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1. REVIEW OF THE PREVIOUS WORK

As clear pieces of quartz are readily available, it is one of the most frequently examined crystals in Raman effect studies. The earliest investigations were those of Landsberg and Mandelstam (1928) at Moscow and of K. S. Krishnan (1928, 1929) at Calcutta. Subsequent studies of the Raman effect in quartz were carried out in many laboratories, notably by Rao (1928), Daure (1929) and Nisi (1929). The last two authors recorded the maximum number of Raman lines, namely ten. A little later, Gross and Romanova (1929) made a comparative study of the Raman and infra-red absorption spectra of crystalline and amorphous quartz. With the λ 4358 radiation of the mercury arc and exposures of the order of 120 hours, they succeeded in recording 19 Raman lines, including 7 very faint ones, and catalogued the frequency shifts and their estimated relative intensities. Using the λ 2536.5 mercury resonance radiation as exciter and giving an exposure of only 20 minutes, Rasetti (1932) recorded a spectrum which exhibited 14 lines with frequency shifts 128.6, 207.3, 265.9, 356.5, 394.4, 403.9, 466.4, 696.8, 796.9, 809.3, 1063.1, 1082.5, 1160.2 and 1227.1 cm^{-1} . He was the first to establish the doublet structure of the Raman lines at about 400, 800 and 1075 cm^{-1} . Kujumzelis (1935, 1936) carried out a detailed and comparative study of the Raman spectra of fused and crystalline quartz and of different optical glasses. Besides confirming the results obtained by Rasetti for crystalline quartz, Kujumzelis reported the existence of some fainter lines with frequency shifts 530, 570-600, 740, 860-950, 1100 and 1400-1600 cm^{-1} . Nedungadi (1940) and Saksena (1940) independently carried out a careful and detailed investigation of the Raman spectrum of crystalline quartz using the 4046 and 4358 radiations of the mercury arc as exciter. These authors were unable to record the feebler lines reported by Gross and Romanova and by Kujumzelis. Using the Rasetti technique and giving long exposures, Roop Kishore (1942), however, succeeded in observing a set of feeble Raman lines in the region 860-950 cm^{-1} .

The effect of temperature on the intensity of the Raman line at 466 cm.^{-1} in crystalline quartz has been studied by several workers, viz., Landsberg and Leontowitsch (1929), Brickwedde and Peters (1929), Landsberg and Mandelstam (1929, 1930), Ornstein and Went (1935), and Venkateswarlu (1941). They showed that the ratio of the intensities of the Stokes and the anti-Stokes lines was in accordance with the modified Boltzmann formula. Sharp disagreements with the existing theories have been reported as regards the individual intensities of the Stokes and anti-Stokes lines. The influence of temperature on the frequency shift and width of the Raman lines in quartz has been studied by Ney (1931) over the range of temperature from 18° to 500° C. and by Nedungadi (1940) over the range from -180° C. to 530° C. Nedungadi drew attention to the extraordinary behaviour of the line 207 cm.^{-1} . It broadens enormously at higher temperatures and in an unsymmetrical manner with respect to its original position and ultimately disappears into a continuum as the transition temperature (575° C.) is approached. Raman and Nedungadi (1940) suggested that the remarkable behaviour of the line 207 with rise of temperature has a special significance for the α - β transformation of quartz which takes place at 575° C.

Cabannes (1929), Menzies (1929), Bouhet (1937), Cabannes and Bouhet (1937), Michalke (1938) and Saksena (1940) investigated the effect of crystal orientation on the intensity and polarisation of the Raman lines in quartz. On the basis of the results obtained from such studies, they have attempted to classify the frequency shifts of the Raman lines. Cabannes, Menzies and Michalke used incident unpolarised light, whereas Cabannes and Bouhet worked with incident circularly polarised light. Saksena who made a thorough investigation of the problem used incident light polarised in different azimuths. He has given a more or less correct and complete classification of the principal lines observed in the spectrum of quartz and also identified the corresponding fundamental modes of internal vibration of the atoms in the unit cell. The results obtained by Saksena will be referred to in detail later in this paper.

Some miscellaneous investigations have also been reported in the literature concerning the Raman effect in quartz. Weiler (1932) examined the Raman spectra of a series of silicic acid esters and gels and compared the characteristic frequencies of the SiO_2 group in these compounds with those of crystalline and fused quartz. Ornstein and Went (1935) investigated the dependence of the intensity of the Raman lines of quartz on the wave-length of the exciting line. The λ^{-4} law was found to be obeyed.

It is evident from what has been said above that neither Rasetti (1932), nor Roop Kishore (1942) fully utilised the power of the Rasetti technique. By using

the λ 2536.5 mercury radiation as exciter and giving exposures of the order of 48 hours for a crystal 15 cm. long, the author (Krishnan, 1945) recorded a very intense spectrum of quartz in which 41 distinct frequency shifts were observed and measured. In the preliminary report which appeared in *Nature*, provisional assignments were given for most of the lines. Since then the subject has been further investigated by the author and more complete results are presented in this paper.

2. DETAILS OF THE EXPERIMENT

A few transparent and practically colourless specimens of quartz with well developed faces were selected for the present study from Sir C. V. Raman's personal collection. The biggest one was about 7" long and $2\frac{1}{2}$ " thick. One end of each specimen was cut normal to the optic axis. This end face was then ground and polished. The construction of the mercury arc and the optical arrangement used for investigations on the Raman spectra of crystals have already been described in Part I (Krishnan, 1945) of this series.

The crystal to be examined was mounted with its optic axis vertical and with one of its long hexagonal sides facing the most intense portion of the arc. The light scattered along the optic axis was focussed on to the slit of a quartz spectrograph with the aid of an aluminised mirror and a condensing lens.

As in the case of calcite and gypsum, two quartz spectrographs (Hilger E1 and E3) were used for recording the Raman spectrum. The higher dispersion instrument was employed in order to measure the frequency shifts and widths of the principal Raman lines very accurately. For this purpose, an iron arc comparison spectrum was photographed at the centre of the Raman spectrum. With a slit-width of 0.03 mm. and using a crystal 2" long, exposures of the order of three days were given to get a satisfactory spectrum with the high dispersion instrument.

The E3 spectrograph was employed for recording an intense spectrum of quartz showing as many second order Raman lines as possible. For this purpose, the biggest crystal was used. With a slit-width of 0.03 mm., exposures of the order of three to four days were given to obtain intense photographs.

All the negatives were measured under a Hilger cross-slide micrometer.

3. RESULTS

First Order Spectrum.—The spectrogram taken with the high dispersion instrument showing the first order spectrum of quartz is reproduced in Fig. 1. The microphotometer record of the same is reproduced in Fig. 2.

The spectrum consists in the main of 12 first order or principal Raman lines including two doublets. The frequency shifts together with relative intensities of the lines are given in Table I. The values reported earlier by Rasetti (1932) and Saksena (1940) are also included for purposes of comparison. The author's results agree closely with those of Rasetti except for the doublet at about 800 cm.^{-1} . The intensity and width of the pair of lines at about 800 cm.^{-1} are found to be markedly influenced by crystal orientation (Saksena, 1940). It is quite probable that the orientation of the crystal in Rasetti's experiment was different from the one adopted in the present investigation.

TABLE I

Frequency Shifts of the First Order Raman Spectrum of Quartz

No.	Rasetti	Saksena	Author	Class
1	128	128	127.7 (20)*	E ₁
2	207.3	207	206.4 (15)	A ₁
3	265.9	267	266.1 (8)	E ₂
4	356.5	358	357.2 (7)	A ₂
5	{ 394.4	391	394.8 (6)	E ₃
	{ 403.9			
6	466.4	466	466.0 (30)	A ₃
7	696.8	695	696.4 (5)	E ₄
8	{ 796.9	806	805.8 (6)	E ₅
	{ 809.3			
9	1063.1	1063	1063.7 (5)	E ₆
10	1082.5	1082	1081.9 (4)	A ₄
11	1160.2	1160	1159.3 (8)	E ₇
12	1227	1228	1228.0 (4)	E ₈

* The figures enclosed in brackets represent the relative intensities of the lines on an arbitrary scale. They were estimated from the micro-photometric record of the spectrogram (reproduced in Fig. 3) which was taken with the optic axis of the crystal perpendicular to the incident and parallel to the scattered rays, the illuminating beam being unpolarised.

Second Order Spectrum.—A heavily exposed photograph of the Raman spectrum of quartz taken with the E3 spectrograph is reproduced in Fig. 3 together with a photograph of the direct arc. The microphotometric records of the same are shown in Fig. 4. The second order Raman lines can be clearly seen in the microphotometric record. Most of them can also be identified in the reproduced photograph. In addition to the first order Raman lines already listed in Table I, the spectrum of quartz as recorded here consists of 29 Raman lines, some of which have intensities comparable with those of the first order lines. The positions as well as the frequency shifts of most of them have been marked in Fig. 4. Some of the lines fall very close to the very intense principal Raman lines and as such, they are not seen resolved either in the photograph reproduced in Fig. 3, or in its

microphotometric record reproduced in Fig. 4. Such lines are, however, clearly discernible in the photograph taken with the high dispersion instrument. Their positions are indicated in Figs. 1 and 2.

The frequency shifts of the more intense second order Raman lines were evaluated from measurements made on the negatives, whereas those of the feebler ones were estimated from the microphotometric records. In order to be sure of the existence of each and every second order line reported here, microphotometric records not only of different spectrograms, but also of different regions in the same spectrogram were taken and compared. Care was taken to eliminate those Raman lines which could reasonably be assigned as first order Raman shifts excited by other mercury lines.

The 29 second order Raman lines have been classified into two groups and their frequency shifts have been listed separately in Tables II and III.

TABLE II
Second Order Raman Lines explicable as Octaves and Combinations of the Fundamentals listed in Table I

No.	Frequency Shifts in cm.^{-1}	Assignment	Calculated Frequency Shifts
1	488	$A_3 + E_1$	485
2	530	$2E_2; E_1 + E_3$	532, 527
3	730	$A_3 + E_2$	732
4	864	$A_2 + E_3$	866
5	890	$E_2 + E_3$	888
6	925	$E_1 + E_5$	928
7	961	$E_2 + E_4$	962
8	980	$2B_2$	976
9	1269	$A_1 + E_6; A_3 + E_5$	1269, 1266
10	1290	$A_1 + A_4$	1288
11	1394	$2E_4$	1393
12	1444	$A_2 + A_4$	1439
13	1495	$E_2 + E_3$	1494
14	1630	$E_3 + E_8; A_3 + E_7$	1628, 1625
15	2126	$2E_6$	2128
16	2240	$A_4 + E_7$	2241
17	2420	$B_4 + E_8$	2418

TABLE III
Raman Lines not explicable as Octaves and Combinations of the Fundamentals Listed in Table I (Super-Lattice Lines)

No.	1	2	3	4	5	6	7	8	9	10	11	12
Frequency shifts	39	95	145	170	240	452	509	548	588	842	944	1040
Relative intensity	1	2	3	2	2	7	4	2	0	1	0	0

The lines with frequency shifts 509, 530, 588, 730 and 944 cm.^{-1} have already been reported by Gross and Romanova (1929). The existence of the line at 452 cm.^{-1} (see Table III) was first reported by Cabannes and Bouhet (1937), and later confirmed by Nedungadi (1940). Saksena showed that by suitably polarising the incident light, the 466 line could be greatly weakened and the two companions at 452 and 488 cm.^{-1} could then be clearly observed. The two lines with frequency shifts 95 and 145 cm.^{-1} came next in the order of intensities (see Table III). The existence of these two low frequency shifts was first pointed out by Norris (1941) after a careful scrutiny of the spectrograms taken by Nedungadi and Saksena, and his findings have been confirmed. The remaining lines listed in Tables II and III have been recorded for the first time.

4. DISCUSSION OF RESULTS

α -Quartz belongs to the trigonal subdivision of the hexagonal system, the symmetry class being trigonal enantiomorphous hemihedral. The space group is represented by D_3^4 . The unit cell contains three molecules of SiO_2 . Each silicon atom is surrounded by four oxygen atoms, and each oxygen atom has two silicon atoms as near neighbours. The four oxygen atoms round a silicon atom do not form a regular tetrahedron.

Principal Frequencies of Quartz.—On the basis of the above structure and on the assumption that the repeating unit in the dynamic crystal is the simple unit cell. Went (1935) discussed the $(3p - 3)$ so-called fundamental modes of oscillation of the quartz lattice. Since p , the number of non-equivalent atoms in the unit cell, is 9 for quartz, the number of modes is 24. Owing to the degeneracy of some of the modes of oscillation, the number of distinct frequencies is reduced to 16, distributed as follows:—4 coming under the A class active only in Raman effect, 4 of the B class active only in infra-red absorption, and 8 of the E class active in both. But Went's assignments of the observed frequencies were not correct as they were based on the insufficient polarisation data presented by the earlier workers.

A complete group-theoretical analysis of the normal modes of internal oscillation of the quartz lattice has been worked by Saksena (1940, 1942). According to his analysis, the group of 3 silicon and 6 oxygen atoms present in the unit hexagonal cell has 16 principal modes of vibration with distinct frequencies. The assignments of the observed principal Raman frequencies are shown in column 5 of Table IV. They have been made on the basis of their relatively large intensities and also on the polarisation data given by Saksena. These assignments are in agreement with those of Saksena except as indicated in the following paragraphs.

TABLE IV

Class	<i>ni</i>	Raman	Infra-red	Observed frequencies in cm. ⁻¹
A	4	P	f	206.4; 357.2; 466.0; 1081.9
B	4	f	P	385; 488; 800; 1111-1190
E	8	P	P	127.7; 266.1; 394.8-403.8; 696.4; 794.7-805.8 1063.7; 1159.3; 1228.0

The notations have the usual significance as understood in group theoretical analysis.

The four principal frequencies coming under class B (see Table IV) have been assumed from the infra-red measurements of Plyler (1929) as $B_1 = 385$, $B_2 = 488$, $B_3 = 800$ and $B_4 = 1111-1190$ cm.⁻¹ Saksena took them as 364, 508, 777 and 1149 cm.⁻¹ on the basis of the observed positions of infra-red reflection maxima.

The line 1228.0 cm.⁻¹ has been taken by the author as one of the principal frequencies coming under the E class for the reason that it appears with very high intensity for some orientations of the crystal and that it is one of the twelve principal frequencies recorded by Rasetti. Moreover, the frequency shift of this line cannot be reasonably accounted for as an octave or a combination of the other principal frequencies listed in Table I. Saksena, on the other hand, has taken a line at 479 cm.⁻¹ as one of the E class fundamentals in place of the line 1228 cm.⁻¹ and is inclined to treat the latter as a combination Raman line on the following scheme:

$$B_3 (777) + 2A_3 (466) - E (479) \sim 1228.$$

Thus, according to Saksena's assignment, the 1228 line is a quaternary combination. Apart from the fact that such an assignment is far fetched, if we take the correct value of B_3 , namely 800 cm.⁻¹ and not 777 cm.⁻¹ as taken by Saksena, the calculated frequency shift would be in excess of the observed value by 25 wave numbers.

In the infra-red absorption spectrum, the high frequency oscillation appears as a doublet with frequency shifts 1111 and 1190 cm.⁻¹ It is probably correct to take the fundamental as 1150 cm.⁻¹ which has suffered a Fermi splitting on account of the fact that the combination $B_1 (385) + B_3 (800)$ and the infra-red active $E_7 (1159)$ fall in the region of the doublet. Analogous explanation has already been offered by Saksena for the appearance of the pairs of lines at 394.8, 403.8 cm.⁻¹ and 794.7, 805.8 cm.⁻¹ in the Raman effect.

Combinations of the Principal Frequencies.—Applying the ordinary selection rules, it can be shown that in the second order Raman spectrum,

besides the overtones of the principal frequencies, the following combinations, namely $A_l + E_m$, $B_l + E_m$, $A_l + A_m$, $B_l + B_m$ and E_l and E_m are allowed to appear. The subscripts l and m can take the values 1 to 4 in the case of A and B and 1 to 8 in the case of E. On this basis, satisfactory assignments have been given to the 17 Raman lines appearing in the second order spectrum of quartz and listed in Table II. The assignments as well as the calculated frequency shifts are included in the same table.

The overtones of the four infra-red active B class frequencies should be expected to appear in Raman effect with appreciable intensity. In the recorded spectrum, the overtone of 488 cm.^{-1} appears as a separate line with frequency shift 980 cm.^{-1} . The appearance of the octave of 385 cm.^{-1} is indicated by the presence of a point of inflexion on the slope of the intense doublet at about 800 cm.^{-1} (see Fig. 4). Two additional lines with frequency shifts 1596 cm.^{-1} and 2225 cm.^{-1} have been marked in Fig. 4, although they are not listed in Table II. The former one can be assigned as the octave of B_3 (800 cm.^{-1}) and/or as an anti-Stokes Raman shift 128 cm.^{-1} excited by $\lambda 2652.0$, while the latter can be assigned as the first order Raman shift 466 cm.^{-1} excited by $\lambda 2655.1$ and/or the octave of the infra-red frequency B_4 (1111 cm.^{-1}). The octave of 1190 cm.^{-1} even if present, would not be detected as it would fall roughly on the mercury line $\lambda 2698.9$.

Besides the 29 Raman lines already accounted for, there are no fewer than 12 Raman lines the frequency shifts of which are listed in Table III. The intensities of some of them are comparable to those of the less intense principal lines. Attempts have been made to explain these lines as combinations. None of them could be reasonably assigned as a summational since the values of the observed frequency shifts do not correspond to the sums of the principal frequencies taken two by two. A differential can appear in the Raman effect only if the corresponding summational is allowed (*viz.*, Herzberg, 1945). The intensity ratio of the differential to the corresponding summational is roughly given by the Boltzmann factor. Herzberg has drawn attention to the important result that the wave number of a differential should be exactly equal to the difference of the wave numbers of the constituent Raman lines even if anharmonicity is taken into account, whereas the wave number of a summation line is not exactly the sum of the wave numbers of the individual lines. In the light of the above principles, it is impossible to explain any of the frequency shifts of the Raman lines listed in Table III as differentials of the 16 principal frequencies of internal oscillation of the quartz lattice.

Super-Lattice Frequencies.—The fact thus emerges that a whole series of frequency shifts in the Raman spectrum of quartz are incapable of being

assigned either as one of the $(3p - 3)$ so-called fundamental modes of oscillation of the lattice or as octaves or combinations thereof. The appearance of these Raman lines which cannot be understood on the basis of the usual theories of crystal dynamics, however, finds an explanation in the new theory of crystal dynamics put forward by Sir C. V. Raman (1943). According to this theory, every crystal has not $(3p - 3)$ but $(24p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies. Of this number, $21p$ modes are oscillations of the lattice in which the equivalent atoms in adjacent cells along 1, 2 or 3 crystallographic axes vibrate in opposite phases. In the case of quartz, $p = 9$ and hence, there should be 189 such modes of super-lattice oscillations. The actual number of distinct frequencies would be considerably less because of the symmetry of the crystal and consequent degeneracy of some of the modes of oscillation. In the super-lattice oscillations, the equivalent atoms in the adjacent cells vibrate in opposite phases and the variations of optical polarisability produced in different cells therefore cancel out to a first approximation. Consequently, the super-lattice oscillations would be inactive as fundamentals in the Raman effect. They can, however, manifest themselves as octaves and as allowed combinations in the second order Raman spectrum. But a great majority of them would be extremely weak because of the very nature of these oscillations. It is not surprising therefore, that the recorded spectrum exhibits only a very limited number of super-lattice lines. In this connection, it is noteworthy that out of the 12 lines observed, the lines with frequency shifts 95, 145, 170, 240, 452, 509 and 842 cm.^{-1} appear in the vicinity of some of the extremely intense principal frequency shifts, viz., 128, 206, 466 and 800 cm.^{-1} and it appears not at all unlikely that the former have borrowed intensity from the latter by a kind of *Fermi resonance*.

5. THERMAL ENERGY OF QUARTZ

On the assumption that quartz has only sixteen fundamental vibration frequencies as suggested by Saksena, the specific heat of quartz between 25.8° T. and 808.6° T. has been recalculated, taking the values of the frequency shifts as those given in Table IV. The second column in Table V gives the sum-total of the contributions of the 24 Einstein terms. Column 3 gives the Debye correction term for the remaining three degrees of freedom. The limiting frequency for the Debye function is assumed to be that obtained by Norris (1941) from the data on elastic constants of quartz. Column 4 gives the calculated value of the total C_v . The observed values of C_v at various temperatures were taken from Norris' paper and shown in column 5 of Table V. It is seen from the table that there is no satisfactory agreement between the observed and the calculated values of the specific heat throughout

the range of temperature investigated. This suggests that the fundamental assumption on which the calculation of the specific heat is based is wrong the fundamental modes of vibration of the quartz lattice are not $(3p - 3)$ *i.e.*, 24, but $(24p - 3)$, *i.e.*, 213 in number. Before a proper evaluation of the specific heat could be made, it is necessary to know the frequencies of the various possible modes of super-lattice oscillation and their respective degeneracies.

TABLE V

Temperature T°	Einstein Term Contribution $\sum_{i=1}^{24} RE\left(\frac{h\nu_i}{kT}\right)$	Debye Term Contribution according to Norris	Total C_v Calculated	Total C_v Observed	Deviation
25.8	0.17	0.39	0.56	1.25	.69
28.75	0.29	0.53	0.82	1.56	.74
36.1	0.70	0.96	1.66	2.38	.72
53.4	2.03	2.14	4.17	4.65	.48
60.3	2.67	2.57	5.24	5.56	.32
80.0	4.55	3.57	8.12	8.58	.46
98.9	6.47	4.20	10.67	11.04	.37
122.1	8.82	4.72	13.54	14.29	.75
156.2	12.10	5.14	17.24	18.69	1.45
184.8	14.63	5.36	19.99	21.99	2.00
216.1	17.28	5.52	22.80	25.07	2.27
252.1	20.11	5.62	25.73	28.34	2.61
272.0	21.63	5.68	27.31	30.34	3.03
296.1	23.31	5.71	29.02	31.49	2.47
381.1	28.57	5.81	34.38	36.84	2.46
428.8	30.96	5.84	36.80	39.16	2.36
475.8	33.04	5.86	38.90	41.25	2.35
565.3	36.25	5.88	42.13	44.54	2.41
670.0	38.99	5.91	44.90	46.82	1.92
777.3	40.71	5.92	46.63	48.68	2.05
808.6	41.16	5.92	47.08	49.09	2.01

6. BRILLOUIN COMPONENTS

A comparative study of the photographs and microphotometric records reproduced in Figs. 3 and 4 shows that the width of the exciting line λ 2536.5 and its intensity relative to that of its neighbour λ 2534.8 are enhanced in the spectrum of the scattered light from quartz. The increase has to be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour. Although they have a finite wave number separation from the unmodified line, they are not seen separated from the latter because of the low resolving power of the spectrograph used. Similar observations have already been reported by the author in the case of calcite and gypsum. Quartz, however, shows the phenomenon most prominently. It was therefore thought desirable to examine the so-called unmodified scattered radiation in quartz with the aid of a high resolving power interferometer, namely, a Fabry-Perot etalon. Unlike the λ 4680,

722 and 4810 zinc arc lines, the λ 2536.5 mercury resonance radiation has very equally intense hyperfine structure components close to one another which give the line a width of about 0.75 cm.^{-1} . This fact precludes the mercury resonance radiation being used for quantitative studies of the Doppler effect in light-scattering in crystals.

Using the Rasetti technique and an aluminised Fabry-Perot etalon (1 mm. separation), the author has successfully photographed the Brillouin components in quartz. Photographs (a) and (e) in Fig. 5 show the interference pattern of the 2536.5 radiation taken through the intermediate spectrograph. Photographs (b), (c) and (d) show the patterns of the same radiation after scattering in a crystal of quartz. The Brillouin components* can be clearly seen in the photographs. The first is for the case of backward scattering along the optic axis, the second for backward scattering perpendicular to the optic axis, and the third one for the case of transverse scattering, the illumination being perpendicular to the optic axis and the observation along the optic axis. Because of the finite width of the exciting line and of the 1 mm. separation used in the present case, the positive and negative components from two consecutive orders partly overlap. The extent to which the overlapping takes place depends on the orientation of the crystal. The Brillouin components in (d) are definitely broader than those in (b). For longitudinal scattering along the optic axis which corresponds to case (b) the calculated value of the shift of the Brillouin components = 2.59 cm.^{-1} the separation of the successive orders being equal to 5 cm.^{-1} . The width of the unmodified line is 0.75 cm.^{-1} . For this case, therefore, the overlapping of the positive Brillouin component of one order and negative Brillouin component of the next higher order would be complete. For transverse scattering represented by case (c) the calculated value of the shift of the Brillouin components is 2.02 cm.^{-1} . The Brillouin components from two consecutive orders would therefore be adjacent to each other and appear as a single broad band. The observed features of the interference patterns for different orientations of the crystal are thus qualitatively accounted for.

7. INFRA-RED SPECTRA

Quartz is one of the few crystals most frequently examined in infra-red studies. The numerous investigations reported in the literature have already been reviewed by Saksena (1940). It was therefore thought unnecessary to summarise the existing infra-red data in the present paper. However, a

* Only the components due to the longitudinal sound waves in the crystal have been recorded. Those due to the two sets of transverse sound waves are not recorded owing to their comparatively feeble intensity.

complete bibliography of the infra-red studies on quartz is appended to this paper.

The author takes this opportunity to express his respectful thanks to Professor Sir C. V. Raman for the loan of the quartz crystals and for his inspiring interest in the work. The author is also grateful to the authorities of the Annamalai University for the loan of the E3 quartz spectrograph employed in the present investigation.

8. SUMMARY

A detailed study has been made of the Raman effect in quartz using the λ 2536.5 mercury radiation as exciter. The spectrum consists of 43 Raman lines, nearly half of them have been recorded for the first time. Of these, fourteen Raman lines including two doublets constitute the internal oscillation spectrum of the unit cell of the quartz lattice. The frequency shifts of these have been very accurately determined. Of the remaining 29 lines which constitute the second order spectrum of quartz, 17 have been satisfactorily explained as octaves and combinations of some of the principal frequencies. The 12 Raman lines which are not explicable as combinations and overtones of the principal frequencies, constitute in part the super-lattice spectrum of quartz to be expected on the basis of the Raman theory of crystal dynamics.

The specific heat of quartz has been evaluated on the assumption that the vibration spectrum consists of only 16 principal frequencies, 12 appearing in the Raman effect and 4 in the infra-red absorption. The calculated values of the specific heat were lower than the observed values over the range of temperature from 25.8° T. to 803.6° T. It is pointed out that the neglect of the super-lattice frequencies is responsible for the above discrepancy.

The Brillouin components due to longitudinal sound waves in quartz have been successfully photographed using an aluminised Fabry-Perot etalon. The dependence of the form of the interference pattern on crystal orientation has been qualitatively accounted for on the basis of the variation of acoustic velocity with direction inside the crystal.

A complete bibliography on the Raman effect and infra-red studies in quartz is also appended.

REFERENCES

1. Raman Effect

- Landsberg and Mandelstam .. *Naturwissenschaften*, 1928, 16, 557; *Comp. Rend.*, 1928, 187, 109; *Zeit. f. Phys.*, 1928, 50, 769.
- Krishnan, K. S. .. *Nature*, 1928, 122, 477; *Ind. Journ. Phys.*, 1929, 4, 131.
- Rao, I. R. .. *Ind. Journ. Phys.*, 1928, 3, 123.
- Pringsheim and Rosen .. *Zeit. f. Phys.*, 1928, 50, 741.
- Wood .. *Phil. Mag.*, 1928, 6, 729.
- Daure .. *Ann. de Physique*, 1929, 12, 375.
- Gross and Romanova .. *Zeit. f. Phys.*, 1929, 55, 744.
- Nisi .. *Proc. Imp. Acad. (Tokyo)*, 1929, 5, 127.
- Rasetti .. *Nuovo Cimento*, 1932, 9, 72.
- Kujumzelis .. *Zeit. f. Phys.*, 1935, 97, 561; 1936, 100, 221.
- Nedungadi .. *Proc. Ind. Acad. Sci.*, A, 1940, 11, 86.
- Saksena .. *Ibid.*, 1940, 12, 93.
- Roop Kishore .. *Ibid.*, 1942, 16, 36.
- Landsberg and Leontowitsch .. *Zeit. f. Phys.*, 1929, 53, 439.
- Brickwedde and Peters .. *Phys. Rev.*, 1929, 33, 116.
- Landsberg and Mandelstam .. *Zeit. f. Phys.*, 1929, 58, 250; 1930, 60, 364.
- Ney .. *Ibid.*, 1931, 68, 554.
- Ornstein and Went .. *Physica*, 1935, 2, 503.
- Went .. *Doctorate Thesis*, Utrecht, 1935.
- Raman and Nedungadi .. *Nature*, 1940, 145, 147.
- Venkateswarlu .. *Proc. Ind. Acad. Sci.*, A, 1941, 14, 529.
- Cabannes .. *Comp. Rend.*, 1929, 188, 249.
- Menzies .. *Phil. Mag.*, 1929, 8, 504.
- Bouhet .. *Comp. Rend.*, 1937, 204, 1661.
- Cabannes and Bouhet .. *Ibid.*, 1937, 205, 768.
- Michalke .. *Zeit. f. Phys.*, 1938, 108, 748.
- Weiler .. *Helv. Phys. Acta.*, 1932, 5, 302; *Nature*, 1932, 130, 893; *Zeit. f. Phys.*, 1933, 80, 617.
- Krishnan, R. S. .. *Nature*, 1945, 155, 452.
- Saksena .. *Proc. Ind. Acad. Sci.*, A, 1942, 16, 270.

2. General

- Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, A, 1945, 22, 182.
- Norris .. *Ibid.*, 1941, 14, 499.
- Herzberg .. *Raman and Infra-red Spectra of Polyatomic Molecules*, New York, 1945.
- Raman, C. V. .. *Proc. Ind. Acad. Sci.*, 1943, 18, 237.

3. Infra-red

- Merritt .. *Wied. Ann.*, 1895, 55, 49.
- Bormann .. *Zitt Verst. Kon. Akad. Wet. Amsterdam*, 1896, 43, 8, 1896.
- Nichols .. *Wied. Ann.*, 1897, 60, 401.

- Rubens and Nichols .. *Phys. Rev.*, 1897, **4**, 314.
 Rosenthal .. *Wied. Ann.*, 1899, **68**, 783.
 Rubens .. *Phys. Zeit.*, 1903, 4.
 Coblentz .. *Phys. Rev.*, 1906, **23**, 125 ; *J. Franklin Institute*, 1914, **177**,
 445 ; *Bull. Bur. Stds.*, 1914, **11**, 471.
 Reinkober .. *Ann. Phys.*, 1911, **34**, 343.
 Liebisch and Rubens .. *Preus. Akad. Wiss. Phys. Klasse*, 1919, 198.
 Dreisch .. *Zeit. f. Phys.*, 1927, **42**, 426.
 Reinkober and Kipcke .. *Ibid.*, 1928, **48**, 205.
 Plyler .. *Phys. Rev.*, 1929, **33**, 48.
 Czerny .. *Naturwissenschaften*, 1929, **17**, 12 ; *Zeit. f. Phys.*, 1929, **53**, 317.
 Mcginnety .. *Proc. Univ. Durham Phil. Soc.*, 1931, **8**, 337.
 Drummond .. *Nature*, 1932, **130**, 928 ; 1934, **134**, 739 ; 1936, **138**, 248 ;
Proc. Roy. Soc., 1936, **153**, 328.

DESCRIPTION OF PLATES

PLATE XI

- Fig. 1. Raman spectrum of crystalline quartz taken with the E1 spectrograph.
 Fig. 2. Its microphotometric record.

PLATE XII

- Fig. 4a. The microphotometric record of the Raman spectrum of quartz taken with the E3 spectrograph.
 Fig. 4b. The microphotometric record of the mercury spectrum.

PLATE XIII

- Fig. 3a. The Raman spectrum of quartz taken with E3 spectrograph (heavily exposed photograph).
 Fig. 3c. Do. (lightly exposed photograph).
 Fig. 3b. The comparison spectrum of the mercury arc.
 Fig. 5a & e. The interference pattern of the 2536.5 line of mercury.
 Fig. 5b, c & d. The interference patterns of the same radiation scattered by a crystal of quartz showing the Brillouin components for three different orientations.