

# THE RAMAN SPECTRUM OF ROCKSALT AND ITS INTERPRETATION

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## 1. INTRODUCTION

It is characteristic of crystals that their Raman spectra consist of discrete lines which are very sharp, particularly when recorded with the crystal held at a low temperature. The obvious and most natural interpretation of this fact is that the vibration spectra are themselves of that nature, in other words, that the regularly ordered three-dimensional structure of a crystal has a set of eigenvibrations with corresponding eigenfrequencies which are monochromatic. Basing himself on quite elementary and well-established dynamical principles, Sir C. V. Raman (1943) showed theoretically that this is the case and derived the result that a crystal with  $p$  atoms in a unit cell has  $(24p-3)$  such eigenvibrations, and that the number of distinct eigenfrequencies would be further reduced if the crystal has other symmetries besides the three simple translations. The experimental confirmation of this proposition is obviously a matter of fundamental importance for the progress of crystal physics, and the cases that naturally suggest themselves as suitable material for a thorough investigation are those in which  $p$  is as small as possible, *e.g.*, diamond and rocksalt, where  $p=2$ .

According to the theory, the number of distinct eigenfrequencies for rocksalt is nine. Whereas in diamond one of the eigenfrequencies is active and gives a sharp and intense line as the first-order Raman spectrum, in rocksalt all the nine are inactive, and the study has therefore to be based solely on the second-order spectrum consisting of 9 octaves and 36 combinations of the primary vibrational frequencies. If all the 45 lines thus theoretically possible appeared in the spectrum with approximately equal intensities and were distributed uniformly over the narrow range of frequencies, and if their inevitable thermal broadening were also taken into consideration, the resulting spectrum could easily be mistaken for a continuous one, and it would have been a hopeless task to derive any useful results from its study. Fortunately, however, neither such equality of intensities nor such uniformity of distribution of frequencies is to be expected theoretically. The possibility is thereby opened up, by the use of refined spectroscopic technique, of

analysing the spectrum into its constituent lines and thereby establishing its true nature. In undertaking such analysis, it would clearly be an advantage to know, not merely that there are 9 fundamental frequencies whose overtones and combinations may appear in the spectrum, but also to know what these frequencies are, and to have an idea of the relative intensities with which the various overtones could be expected to appear in the second-order spectrum. These necessary preliminaries have been furnished in two theoretical papers respectively by K. G. Ramanathan (1947) and by Sir C. V. Raman (1947), appearing in these *Proceedings*, and the interpretation of the experimental results on an assured basis has thereby been made possible.

The earliest attempts of various authors to record the Raman spectrum of rocksalt using the  $\lambda$  4358 excitation of the mercury lamp were unsuccessful. Later, Rasetti (1931) using the  $\lambda$  2536.5 radiation successfully recorded the second-order spectrum. The reproductions of the spectrogram and its microphotometer record appearing with the paper of Fermi and Rasetti (1931) showed just such a structure for the spectrum as would be expected if it were an unresolved aggregate of lines unequally distributed, some of them being more intense than the others. Accordingly, in an earlier paper (R. S. Krishnan, 1943) the present author ventured to suggest that Rasetti's spectrum could be explained as representing mainly the octaves of the nine fundamental frequencies of rocksalt. Since, however, Rasetti had not given any measurements, and also in the hope of obtaining a more clearly resolved spectrogram, the experimental work of Rasetti was repeated using an instrument of the same type but with a finer slit. The results (Krishnan, 1945; 1946 *a, b*) confirmed the suggestion made previously, the microphotometer records showing clearly the existence of a number of sharply defined lines. In particular, the most intense line with a frequency shift of  $235 \text{ cm.}^{-1}$  stood out clearly, appearing quite as sharp and intense as one of the lines of the mercury spectrum and being recorded both as a positive and negative frequency shift. Subsequently also, the author succeeded in recording the rocksalt spectrum with the large Hilger quartz E1 spectrograph and the resulting spectrogram was reproduced with a note in *Nature* (Krishnan, 1947). Since then, several fresh spectrograms and microphotometer records have been obtained. It is the purpose of the present paper to present the results together with a critical discussion of their interpretation.

## 2. THE STRUCTURE OF THE SPECTRUM

As is well-known, in order to obtain a correct idea of the structure of any spectrum, it is necessary to examine it with a spectrograph of suitable

dispersion and resolution. In the case of molecular spectra which usually consist of a very large number of closely spaced lines, it is a familiar experience that spectrograms taken with a smaller instrument exhibit a system of unresolved broad bands showing little or no structure, whereas when examined with bigger spectrographs having sufficient resolution, the closely spaced lines are recorded clearly resolved from one another, thereby exhibiting unambiguously the discrete character of the spectra. Let us consider the case of spectra which consist of a few bright lines far apart from each other and superposed on a background composed of a great many feebler lines which are very close together and thereby appear unresolved. If examined under a spectrograph of small dispersion, such a spectrum would appear continuous, and the presence of the brighter discrete lines could easily be overlooked as they would be overpowered by the continuum. On the other hand, if an instrument of high dispersion is employed, the background would be weakened relatively to the individual lines, and the latter would then appear more prominently in the spectrograms. It is well-known also, that in heavily exposed spectrograms the photographic contrasts are greatly diminished and the presence of discrete lines is therefore less easily observed. In such cases, in order to gauge correctly the structure of the spectrum, it is necessary to take weakly or moderately exposed spectrograms. It may also be pointed out that if a spectrum is truly continuous, in other words, if it does not contain any detail beyond the power of a smaller instrument, the use of a larger instrument would not bring out any new detail but would, on the other hand, make even such detail as is present less obvious to inspection.

The foregoing remarks are relevant in relation to the facts noticed in the Raman spectrum of rocksalt. Even the spectrograms taken with the Hilger medium quartz spectrograph exhibited the characteristic features of the spectrum quite clearly. A typical spectrogram is reproduced in Fig. 1 (c) in Plate (XIII) and its microphotometer record is reproduced below as Fig. 2 with the more prominent peaks marked with the respective frequency shifts. The sharpness of some of the peaks, especially 235 and 350  $\text{cm.}^{-1}$ , is comparable to that of any mercury line, showing thereby that these peaks represent Raman lines with discrete frequency shifts. This conclusion is further supported by the fact that the intense lines with frequency shifts 235 and 350  $\text{cm.}^{-1}$  are more prominently visible on the anti-Stokes side of the microphotometer record owing to the lightly exposed nature of the spectrum in this region. They are also seen clearly as lines on the anti-Stokes side of the spectrogram and are so sharp that they may be mistaken for mercury lines.

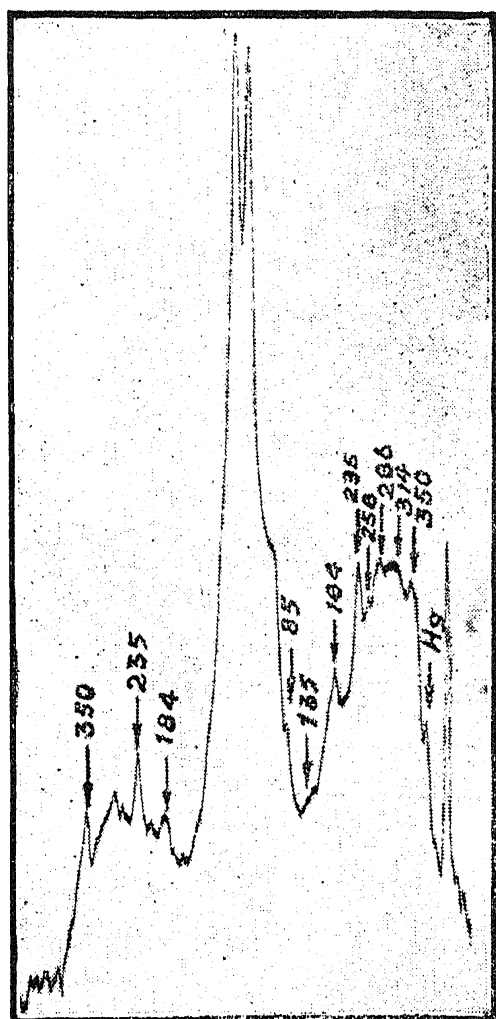


FIG. 2. Microphotometer record of the Raman spectrum of rock-salt taken with the medium quartz spectrograph.

A lightly exposed spectrogram of the Raman effect in rock-salt taken with the Hilger large quartz spectrograph is reproduced in Fig. 3 in Plate (XIV). Figs. 4(a) and 4(b) represent photographs enlarged to the same extent of the spectrograms taken with the large and medium quartz spectrographs respectively. A comparison of the two figures shows at once that the details of the spectrum are more clearly seen in Fig. 4(a) evidently due to the higher dispersion and resolution of the larger spectrograph. A few salient features may be mentioned. The 235 line is definitely sharper and relatively more intense in the photograph taken with the larger instrument than in the other one. The doublet  $343\text{--}50\text{ cm.}^{-1}$  is seen more clearly separated from the rest of the spectrum in Fig. 4(a) than in the other figure. The sharpness and the discrete character of the 235 line in particular become self-evident from a comparison of the microphotometer record of the spectrogram taken with the E1 spectrograph and reproduced in Fig. 5 below with that taken with the medium spectrograph and reproduced in Fig. 2. In the latter the line appears to be of the same intensity as some of the other prominent lines in the spectrum, whereas in the record shown in

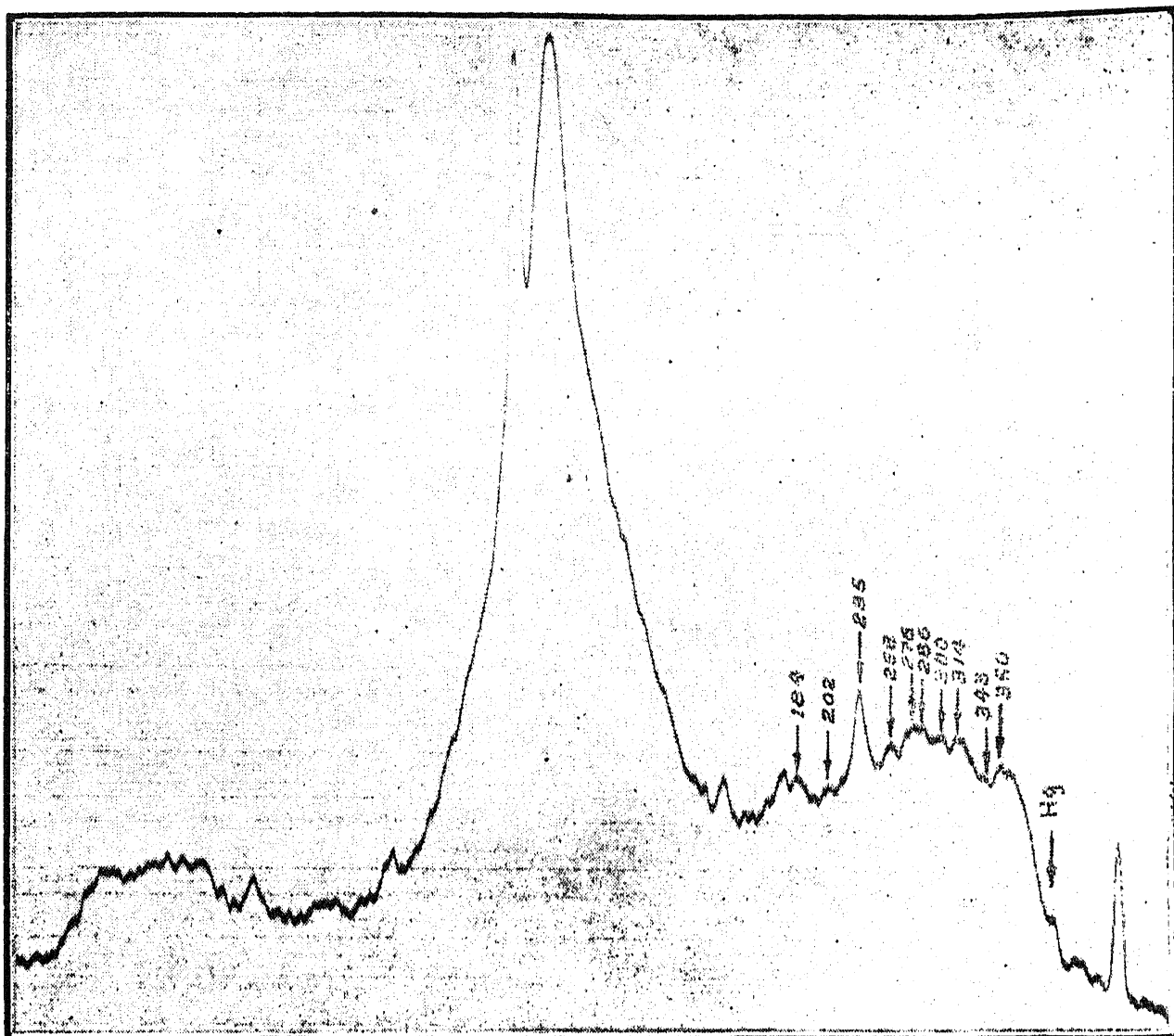


FIG. 5. The microphotometer record of the Raman spectrum of rocksalt taken with the E1 large quartz spectrograph.

Fig. 5, the line appears to be the most intense one. The explanation is obvious. Because of the better definition of the bigger instrument and the monochromatic character of the Raman line, the energy of the line is concentrated over a very small region in spite of the high dispersion, and in consequence the peak intensity of the line is enhanced relatively to some of the other lines which are not so sharp and fall in a region bunched up with lines.

From the above analysis, the structure of the Raman spectrum of rocksalt has been clearly established. The spectrum consists of a series of distinct Raman lines of which nine could be distinguished without difficulty in the photograph reproduced in Fig. 3. They are the prominent lines of the spectrum. There are three more lines with frequency shifts 202, 135 and  $85\text{ cm.}^{-1}$  which are comparatively feeble and are just discernible in the spectrogram taken with the medium spectrograph [see Fig. 1 (c)] in Plate (XIII). They are more clearly seen in the microphotometer record,

reproduced as Fig. 6. Besides the lines mentioned above, the microphotometer record (Fig. 5) of the spectrogram taken with the larger instrument

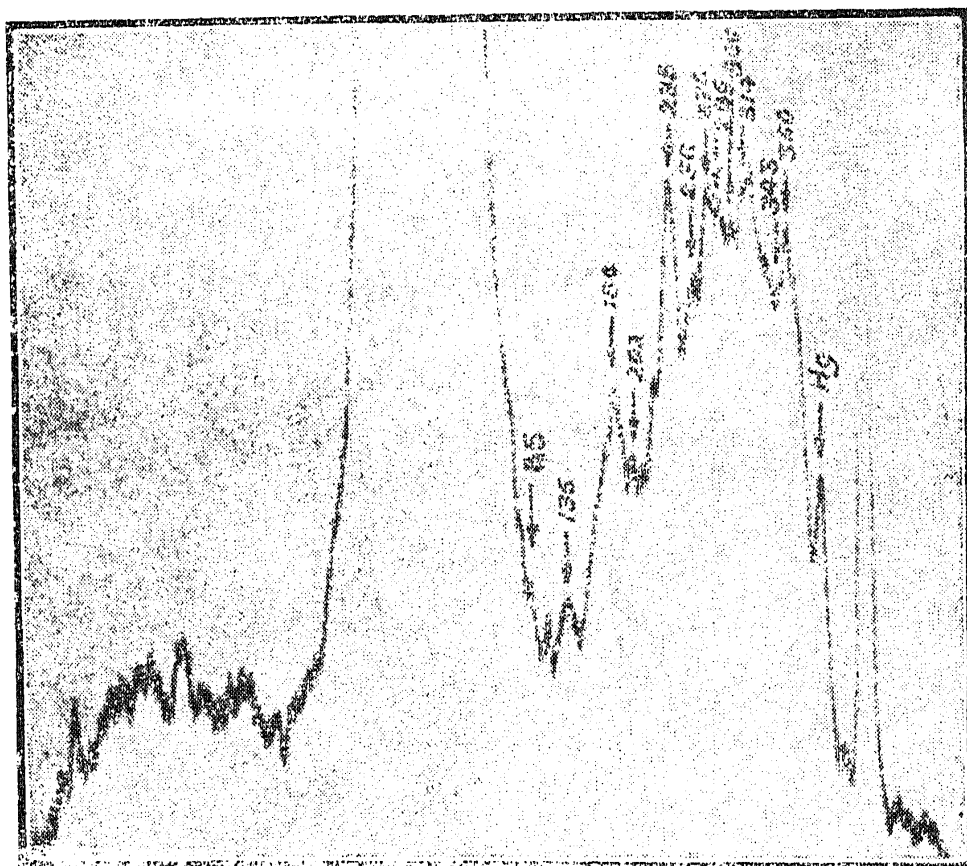


FIG. 6. Microphotometer record of the positive of the spectrogram taken with the medium spectrograph.

shows a large number of minor kinks. By a careful and critical examination of a couple of microphotometer records, the kinks due to graininess of the photographic plate were eliminated and only those which appeared in every record at the same place were taken into consideration. Table I gives the frequency shifts in wavenumbers from the exciting line of the Raman lines of rocksalt, the prominent ones being given in *italics*. Rough estimates of the relative intensities of the lines have also been made and their values are entered in Table I.

### 3. THE EXTENSION OF THE SPECTRUM

Rasetti had reported the existence of a low frequency band starting from zero frequency shift and extending up to about  $60 \text{ cm.}^{-1}$  in the spectrum of rocksalt. Investigations carried out by the author definitely showed that there was no such band in the Raman spectrum. The band in this region appearing in the photograph taken by Rasetti is evidently due to optical coma in the instrument used by him. This fact will become evident from a comparison of the photographs reproduced in Fig. 1 in Plate (XIII). Figs. 1 (a) and 1 (c) are the photographs of the Raman spectrum of rocksalt taken with the E1 and medium quartz spectrographs respectively.

TABLE I  
Second-order Spectrum

Sl. No.	Frequency shift in $\text{cm.}^{-1}$ observed	Relative intensity	Assignment
Second-order Spectrum			
1	85	1	Octave $2\nu_9$
2	135	1	Octave $2\nu_8$
3	140	..	Combination $\nu_7 + \nu_9$
4	162	..	Combination $\nu_6 + \nu_9$
5	184	4	Combination $\nu_6 + \nu_8$
6	199	..	Combination $\nu_5 + \nu_8$
7	202	3	Octave $2\nu_7$
8	220	..	Combination $\nu_6 + \nu_7$
9	235	10	Octave $2\nu_6$
10	258	6	Octave $2\nu_5$
11	270	..	Combination $\nu_4 + \nu_5$
12	276	10	Combination $\nu_2 + \nu_6$
13	286	10	Octave $2\nu_4$
14	300	8	Octave $2\nu_3$
15	314	9	Octave $2\nu_2$
16	320	..	Combination $\nu_1 + \nu_4$
17	326	..	Combination $\nu_2 + \nu_3$
18	343	7	Octave $2\nu_1$
19	350	8	
Third-order Spectrum			
1	390	Very feeble	$2\nu_5$ ; $2\nu_6 + \nu_2$
2	443	do	$2\nu_3 + \nu_4$
3	459	do	$2\nu_2 + \nu_4$ ; $2\nu_4 + \nu_1$
4	475	do	$2\nu_3 + \nu_1$ ; $3\nu_2$
5	507	do	$2\nu_1 + \nu_2$

Figs. 1 (b) and (d) represent the spectra of the mercury arc taken with the same instruments. The coma is present in the bigger spectrograph also. The spurious band appears with the same intensity in the mercury spectrum.

On the higher frequency shift side, the rocksalt spectrum shows an abrupt fall in intensity after the 350 line. The photograph of the Raman spectrum does not indicate the presence of any band beyond this point. But the microphotometer record reproduced in Fig. 7 (a) below shows the existence of a weak tail extending up to about  $520 \text{ cm.}^{-1}$  the intensity decreasing continuously with increasing frequency shift. The tail is not made up of a smooth curve but shows some structure. By critical examination of a couple of microphotometer records, it was possible for the author to identify the existence of at least five peaks with frequency shifts 390, 443, 459, 475 and  $507 \text{ cm.}^{-1}$  These are included in Table II. The intensities of these are about 1/20th the intensities of the prominent lines in the main second-order spectrum. This observation is very significant. The feebleness of these

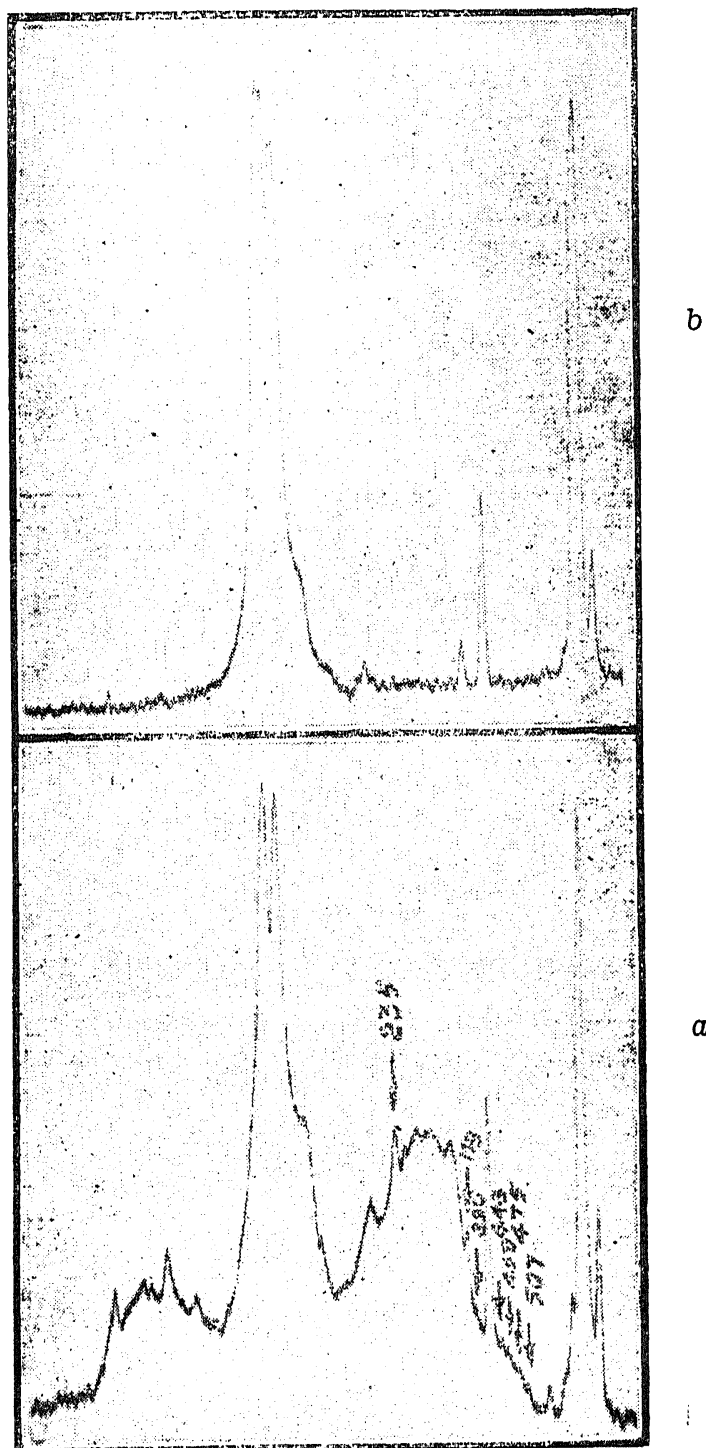


FIG. 7. (a) The microphotometer record of the Raman Spectrum of rocksalt taken with the medium quartz spectrograph. (b) The microphotometer record of the mercury spectrum.

lines and the magnitude of their frequency shifts indicate that they represent the third-order spectrum of rocksalt.

#### 4. THE FUNDAMENTAL FREQUENCIES

In order to evaluate the fundamental frequencies using the expressions for the frequencies given by Ramanathan (1947) reproduced in Table II below, it is necessary to identify some of the second-order lines appearing in the Raman spectrum of rocksalt. Sir C. V. Raman (1947) has remarked



TABLE II

Sl. No.	Description of mode	Symbol	De- generacy	Formula	Frequency in cm. <sup>-1</sup> calculated	Frequency cm. <sup>-1</sup> observed
I	Cubic planes oscillating normally, Na and Cl in same phase	$\nu_1$	3	$\frac{P-8T}{m_1} + \frac{P'-8T'}{m_2} + \frac{16(T+T')}{m_1+m_2}$	173	175
II	Cubic planes oscillating tangentially, Na and Cl in opposite phases	$\nu_2$	6	$\frac{1}{2} \frac{P}{m_1} + \frac{P'}{m_2} + \frac{8(T+T')}{m_1+m_2}$	166	157
III	Na and Cl lattices vibrating against each other	$\nu_3$	3	$\frac{P+8T}{m_1} + \frac{P'+8T'}{m_2}$	159	150
V	Octahedral Na planes vibrating normally	$\nu_4$	4	$\frac{P-8T}{m_1}$	143	143
IV	Octahedral Na planes vibrating tangentially	$\nu_5$	8	$\frac{P+4T}{m_1}$	129	129
VI	Octahedral Cl planes vibrating normally	$\nu_6$	4	$\frac{P'-8T'}{m_2}$	117	117
VII	Octahedral Cl planes vibrating tangentially	$\nu_7$	8	$\frac{P'+4T'}{m_2}$	104	101
VIII	Cubic planes vibrating normally, Na and Cl in opposite phases	$\nu_8$	3	$-\frac{16(T+T')}{m_1+m_2}$	66	67
IX	Cubic planes vibrating tangentially, Na and Cl in same phase	$\nu_9$	6	$-\frac{8(T+T')}{m_1+m_2}$	46	42

Note.—P and P' represent the force on any atom proportional to its own displacement. T and T' represent the force on any atom proportional to the displacement of the next nearest neighbours, force and displacement being along the same cubic axis and the plane containing the two being the cubic plane containing the two atoms. The undashed quantities refer to sodium ions and the dashed ones to chlorine ions.  $m_1$  and  $m_2$  are the respective masses of sodium and chlorine ions.  $P \approx P'$ ;  $T \approx T'$ ;  $P \gg T$ .

that because of the high refractivity of the chlorine ions, the oscillation of the chlorine layers against each other normally to the octahedral planes, *i.e.*,  $\nu_6$  in Table II, should appear with great intensity in the second-order spectrum. The 235 line is the most intense one and is therefore identified as the octave of  $\nu_6$ . The normal oscillation of the corresponding layers of sodium ions, *i.e.*,  $\nu_4$  should also appear with a moderate intensity in the second-order spectrum. Moreover, the expressions for the frequencies are such that  $\nu_4/\nu_6$  should be roughly equal to  $\sqrt{m_2/m_1}$ . The line with the

frequency shift  $286 \text{ cm.}^{-1}$  satisfies the above relation. The tangential oscillations of the (111) sodium and chlorine layers (*i.e.*,  $\nu_5$  and  $\nu_7$ ) should only appear feebly in the second-order spectrum and their frequencies should also be roughly in the same ratio as  $\nu_4$  and  $\nu_6$ . The lines 258 and 202 satisfy this relation. Therefore the lines 286, 258, 235 and  $202 \text{ cm.}^{-1}$  can be identified as the octaves of  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$  and  $\nu_7$  respectively. As will be evident from Table II, in order to evaluate the four constants P, P', T and T', it is enough if three frequencies are assumed, since there is a relation connecting the four force constants, namely  $(P + 8T) = (P' + 8T')$ . Accordingly, the frequencies of  $\nu_4$ ,  $\nu_5$  and  $\nu_6$  are taken as 143, 129 and  $117 \text{ cm.}^{-1}$  respectively. The force constants have been evaluated.

$$P = 2.43 \times 10^4 \quad \text{dynes/cm.}$$

$$P' = 2.475 \times 10^4 \quad \text{,,}$$

$$T = -0.043 \times 10^4 \quad \text{,,}$$

$$T' = -0.049 \times 10^4 \quad \text{,,}$$

Using the above values of the force-constants, the fundamental frequencies of all the modes have been evaluated and the results are shown in column 6 of Table II. Comparing the theoretical results with the frequency shifts of the prominent Raman lines listed in Table I, identification of the lines can be easily made. The lines with frequency shifts 350, 314, 300, 202, 135 and 85 are the octaves of  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  respectively. The fundamental frequencies calculated from the observed frequencies of the octaves are shown in column 7 of Table II. The agreement between the theoretical and observed values of the fundamental frequencies is fairly satisfactory. As is to be expected on theoretical grounds (Raman, 1947), the line  $314 \text{ cm.}^{-1}$ , *i.e.*, the octave of  $\nu_2$  is more intense than either the 300 line ( $2\nu_3$ ) or the 350 line ( $2\nu_1$ ), and the octaves of  $\nu_8$  and  $\nu_9$  are the weakest in the whole spectrum. The remaining lines listed in Table I can be satisfactorily explained as combinations and the respective assignments are given in the last column of Table I. The intensity of the 184 line is increased by the presence of a feeble mercury line falling adjacent to it. The intensity of the 276 line is also rather high for a combination. It is probable that because of its nearness to  $2\nu_4$ , its apparent intensity is enhanced. The line with the frequency shift of  $343 \text{ cm.}^{-1}$  may be explained as arising from degeneracy splitting of the octaves of  $\nu_1$  or as due to a kind of Fermi resonance since the third harmonic of  $\nu_6$  falls on the top of the octave of  $\nu_1$ . If one puts down all the 36 combinations which can appear in the second-order spectrum, no fewer than 20 of them are bunched together in the region of frequency shifts from 260 to  $350 \text{ cm.}^{-1}$ . This would account for the strong unresolved continuum appearing in this region of the observed spectrum.

The tail end of the spectrum to which reference has been made in the last section exhibits five lines which are satisfactorily explained as third-order combinations, and their tentative assignments are shown in column 4 of Table I.

Thus, in all its details, the spectroscopic behaviour of rocksalt as manifested in the Raman effect is fully and satisfactorily explained on the basis of the new theory of crystal dynamics put forward by Sir C. V. Raman.

#### 6. REMARKS ON BORN'S THEORY

Soon after the publication of the author's detailed paper on the Raman spectrum of rocksalt in the *Proceedings of the Royal Society*, a paper on the theory of the Raman effect in crystals by Born and Bradburn (1947) appeared in the same journal, in which these authors attempted to work out theoretically the Raman spectrum of rocksalt, and claimed that their results satisfactorily explained the facts as reported by Rasetti and by the author. This publication was received here only after sending the last communication to *Nature* (Krishnan, 1947) and therefore the author did not have any opportunity to reply to the remarks made therein. In subsequent communications to *Nature*, Born (1946, 1947) did not make any reference to the author's detailed paper, but persisted in the original claim of having satisfactorily explained the observed facts on the basis of his theory. The writer has carefully gone through the theoretical paper by Born and Bradburn and wishes to make the following comments.

For their theoretical calculations, Born and Bradburn have used the vibration spectrum of the rocksalt lattice as deduced by Kellermann on the basis of the Born-Karman theory of the cyclic lattice. The fundamental postulate of the latter theory is that all atomic vibrations can be considered as sets of waves traversing the crystal from end to end. The very appearance of the second-order spectrum is, however, inconsistent with this wave picture for two reasons. Firstly, it can be shown quite rigorously that if these waves extend over the entire volume of the crystal as postulated in the Born theory, the second-order effects in light-scattering from the individual cells of the lattice would cancel out by optical interference and therefore no Raman spectrum could be observed. This would be the case even if the waves are supposed to extend only to volume elements having the size of a few wavelengths of light. Secondly, the second-order effects, if any, are obtained by taking into consideration the anharmonicity arising from the finite amplitude of the atomic vibrations. These amplitudes should be a sensible fraction of the distance between Na and Cl ions, since otherwise the optical effects of anharmonicity would be quite negligible. The energy of any vibration

is  $h\nu$  and that of its octave is  $2h\nu$ . If this energy is distributed over a very small number of atoms, as in the case of polyatomic molecules, the amplitude of vibration of every atom would be sufficiently large to give rise to second-order effects. If, on the other hand, each vibration is considered as a wave extending over the entire volume of the crystal or a volume element which is macroscopically small but large enough to include a great many lattice cells, the energy  $2h\nu$  would be shared by an immense number of atoms, and the resulting amplitude of vibration would be too small to give any such effects of the second and higher orders. In the case of diamond, the observed intensity of the second-order spectrum is about 1/250th the intensity of the first order. In rocksalt, one does not observe any first-order spectrum but finds instead a second-order spectrum of appreciable intensity, and a weak third-order spectrum is also recorded. The very appearance of the higher order spectra indicates that as in the case of polyatomic molecules, the vibrations are localised, being restricted to the atoms in the individual cells of the lattice, or a very few of them. It follows therefore that the very basis of the theoretical calculations of Born and Bradburn is untenable.

Born and Bradburn admit that according to their theory the second-order Raman spectrum of rocksalt should be in the nature of a continuum exhibiting a few broad peaks. It is therefore not surprising that they misinterpret the observed spectrum as a continuous one with small superimposed peaks to suit their theory. Any one possessing a practical knowledge of spectroscopy would, however, have no difficulty in recognizing that the Raman shift of  $235\text{ cm.}^{-1}$  is actually a very sharp and comparatively intense line. Born and Bradburn have no explanation to offer for the appearance of this line, which even taken by itself, is a complete refutation of their theoretical ideas.

Born and Bradburn have given no explanation whatsoever for the activity or otherwise in the Raman effect of the various branches of combinational frequencies. They have arbitrarily chosen the coupling constants and the intensity factors in an attempt to fit the facts. In this process, they succeed in getting an intensity distribution curve which exhibits four broad peaks in the region of frequency shifts 200 to  $370\text{ cm.}^{-1}$ . As will be evident from the microphotometer record reproduced in Fig. 5, of the present paper, apart from the extremely sharp line at  $235\text{ cm.}^{-1}$ , the recorded spectrum exhibits no less than 18 observable peaks about the reality of which there can be no question, since they are perfectly reproducible. Their theoretical intensity distribution curve does not therefore resemble even remotely what has been recorded experimentally.

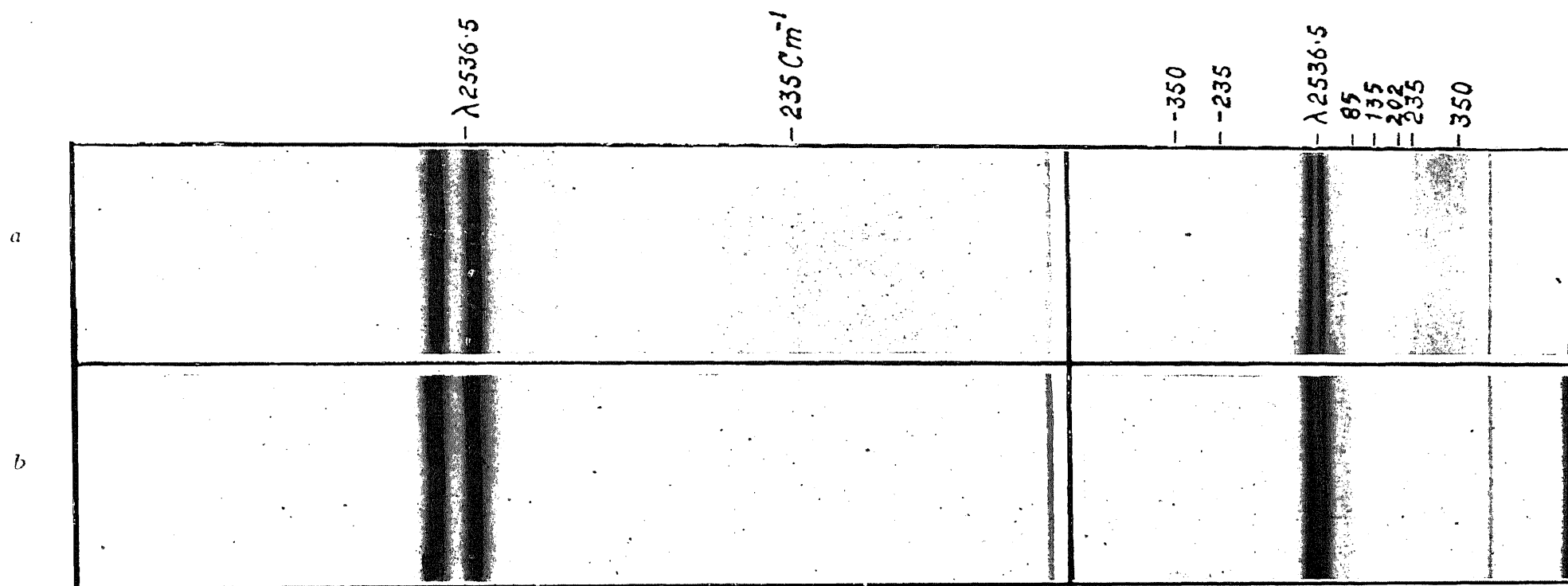


FIG. 1. (a) Raman spectrum of rock-salt taken with the large quartz Spectrograph  
(b) Comparison Spectrum of the mercury arc  
(c) Raman spectrum of rock-salt taken with the medium quartz Spectrograph  
(d) Comparison mercury Spectrum taken with the same instrument

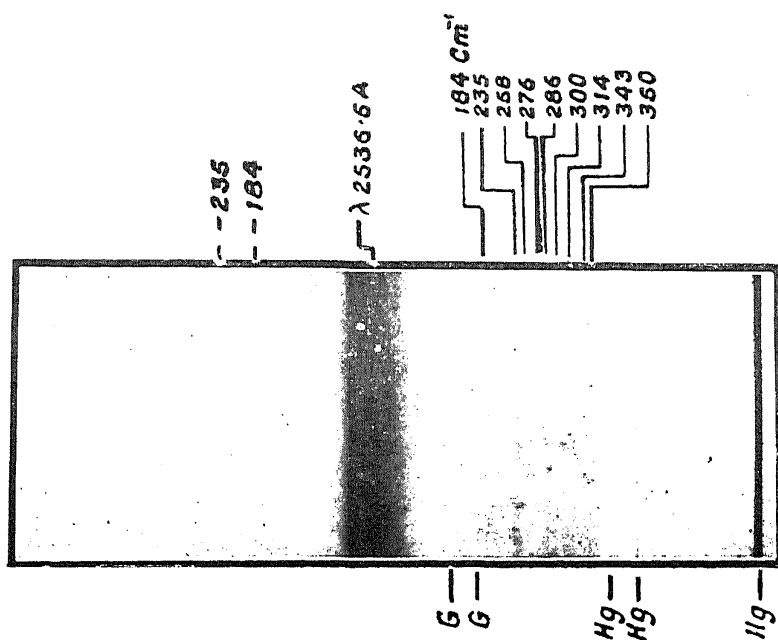


FIG. 3. Raman spectrum of rock-salt taken with a Hilger E1 large quartz Spectrograph

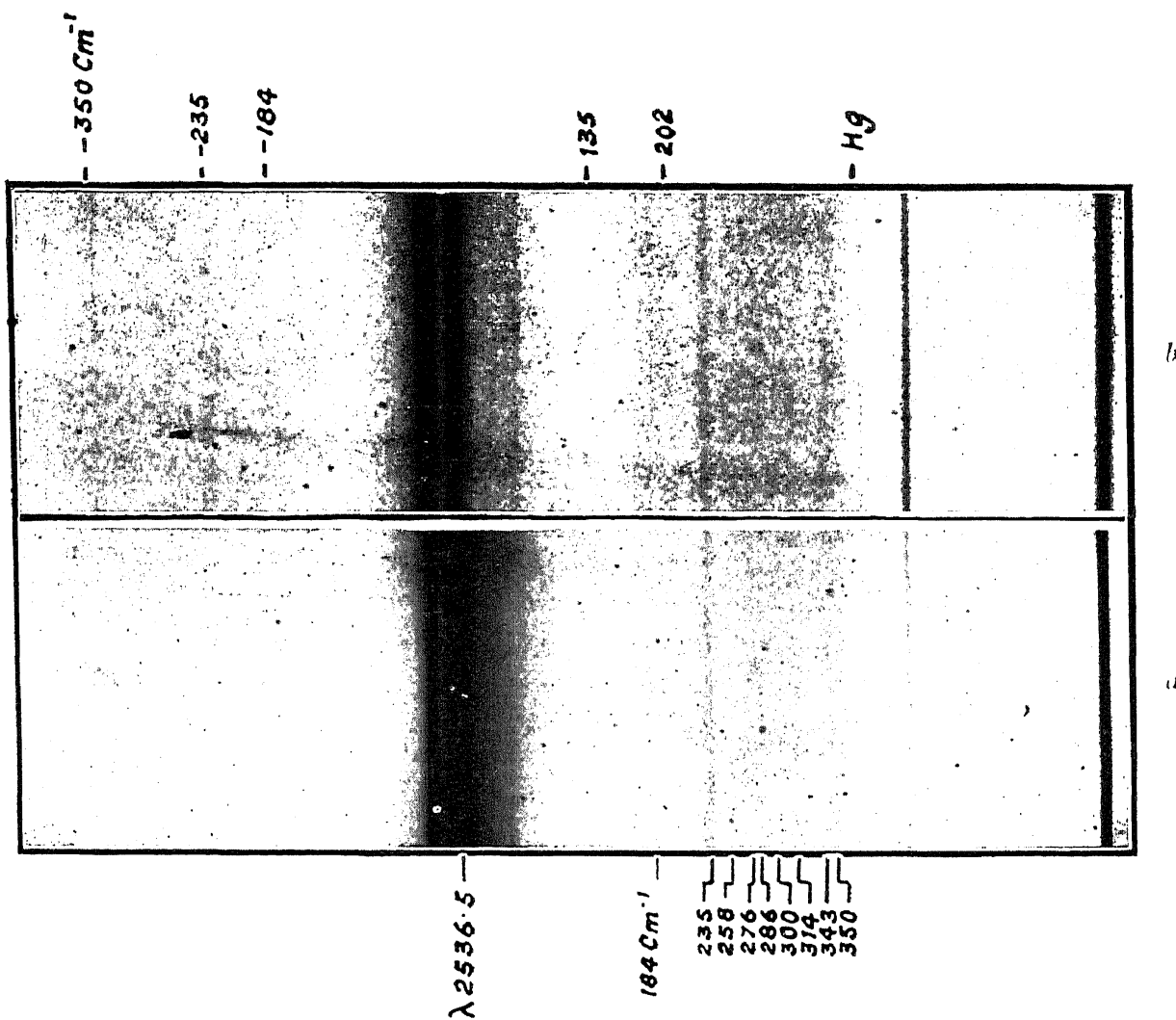


FIG. 4. Raman Spectrum of rock-salt (a) and (b) spectrograms taken with the large and medium quartz spectrographs respectively and enlarged to the same size.

Again, in trying to account for the broad band adjacent to the exciting line and extending up to  $60 \text{ cm.}^{-1}$  reported by Fermi and Rasetti, Born and Bradburn have obtained two strong low frequency bands at 15 and  $50 \text{ cm.}^{-1}$  which they ascribe to the activity of some differential branches of frequencies. The present investigation has, however, shown that there is no such band in the Raman spectrum, and that what has been reported by Fermi and Rasetti is patently due to optical coma in the instrument. If one proceeds on the basis adopted by Born and Bradburn, viz., to adjust the theoretical calculations to fit the facts, one has necessarily to drop out their differential branches 12, 15, 17 and 18 which give rise to the low frequency bands, as they have no existence in the actual spectrum. Then one has necessarily also to drop out the corresponding summational branches, namely 6, 9 and 10. The theoretical curve would then be materially altered. This is only one illustration of the completely artificial character of the whole procedure adopted by Born and Bradburn.

The author is grateful to Prof. Sir C. V. Raman, F.R.S., for useful discussions.

#### 7. SUMMARY

By a careful microphotometric study of the spectrograms taken under high dispersion, it has been shown that the Raman spectrum of rocksalt consists of an aggregate of discrete lines some of which are more intense than the others. With the aid of the indications given by the theory regarding the vibration frequencies and their relative activities in light-scattering, nine of the more prominent lines in the spectrum have been identified as the octaves and the rest as combinations of the nine fundamental frequencies of oscillation of the rocksalt lattice. The views expressed by Born and Bradburn regarding the nature of the rocksalt spectrum and the explanations offered by them for its appearance have been examined and shown to be untenable.

#### REFERENCES

- |                       |  |
|-----------------------|--|
| Born, M.              | .. <i>Nature</i> , 1946, <b>157</b> , 810; 1947, <b>159</b> , 267.                 |
| ——— and Bradburn, M.  | .. <i>Ibid.</i> , 1945, <b>156</b> , 567.  |
| ——— ———               | .. <i>Proc. Roy. Soc., A</i> , 1947, <b>188</b> , 161.                             |
| Fermi and Rasetti, F. | .. <i>Zeits. f. Physik.</i> , 1931, <b>71</b> , 689.                               |
| Krishnan, R. S.       | .. <i>Proc. Ind. Acad. Sci., A</i> , 1943, <b>18</b> , 298.                        |
| —————                 | .. <i>Nature</i> , 1945, <b>156</b> , 267; 1946 <i>a</i> , <b>157</b> , 623.       |
| —————                 | .. <i>Proc. Roy. Soc., A</i> , 1946 <i>b</i> , <b>187</b> , 188.                   |
| —————                 | .. <i>Nature</i> , 1947, <b>159</b> , 266.   |
| Raman, C. V.          | .. <i>Proc. Ind. Acad. Sci., A</i> , 1943, <b>18</b> , 237; 1947, <b>26</b> , 370. |
| Ramanathan, K. G.     | .. <i>Ibid.</i> , 1947, <b>26</b> , 493.   |
| Rasetti, F.           | .. <i>Nature</i> , 1931, <b>127</b> , 626.   |