

RAMAN SPECTRA OF CRYSTALS AND THEIR INTERPRETATION

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1. Introduction

ITS universal applicability, the simplicity of the technique, the precision of the results obtained and the ease of their interpretation make the Raman effect a powerful instrument for the study of the structure of matter. The information yielded by Raman spectra has been of great value in the investigation of relatively simple molecules as well as of the more complicated polyatomic ones. Its utility in the investigation of the physico-chemical problems set by the crystalline state of matter is equally great. An appreciation of this fact was no doubt responsible for the late Lord Rutherford having stated in his Presidential Address to the Royal Society in December 1930 that the Raman effect "has proved and will prove an instrument of great power in the study of the theory of solids". If this prophecy has not been fulfilled to the maximum extent, it is because the physics of the solid state has been dominated for many years by theories which had their birth before the discovery of the effect, and which, it is safe to say, would probably not have been put forward or received general acceptance if the experimental information furnished by Raman spectra regarding crystals had been available at the time. The reference here is to the well-known theories of solid behaviour originally put forward about the same time (1912) by Debye and by Max Born and which have a common central core in their structure of thought.

It is a significant fact that, subject to some noteworthy qualifications and exceptions, the modes of atomic vibration appearing in the Raman spectra of crystals are represented by sharp lines irrespective of the nature of the substance or of the nature or frequency of the vibrations. In his Faraday Society address of September 1929, Sir C. V. Raman pointedly drew attention to this feature and suggested that the monochromatism of the atomic vibrations is a characteristic consequence of the regular ordering of the ultimate particles in the crystalline state of matter. More recently (1941), he has returned to this subject and put forward a new theory of the specific heat

of crystals in which the basic notions of the Debye and Born treatments are rejected as untenable. In the introductory paper (Raman, 1943) of the present symposium, this new theory has been given a precise mathematical form, and it is shown that every crystal has $(24p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies. Of this number, $(3p - 3)$ modes may be described as oscillations of the p interpenetrating atomic lattices of which the crystal is composed, while the remaining $21p$ modes are oscillations with respect to each other of various important planes of atoms in the crystal. The number of distinct frequencies is considerably reduced when the crystal has a high degree of symmetry. Both the number of frequencies and the geometry of the modes can be fully worked out from symmetry considerations in the case of simple structures. For instance, diamond has eight fundamental frequencies, rock-salt has nine, fluorspar has fourteen, and so forth.

The Raman dynamics of crystal lattices has now reached a form in which it can be worked out and developed in various directions. It is important, however, to show that the ideas on which it is based are well founded, and that on the other hand, the alternative theories which now hold the field are irreconcilable with the experimental facts. It is here that the evidence of the spectroscopist is of the highest importance. In another paper appearing in the present symposium, Mr. Pant (1943) has reviewed the extensive and entirely independent evidence available from the published studies on the luminescence and absorption spectra of crystals at very low temperatures. In the present paper, the Raman effect evidence will be marshalled and discussed in its relation to the theories of crystal dynamics.

The numerous papers which have appeared on the Raman spectra of crystals may be placed broadly in two divisions, namely those in which the emphasis is respectively on the chemical and on the physical aspects of the subject. Many more investigations belong to the former group than to the latter, but they have nevertheless yielded data of great significance to crystal physics. The researches on the Raman effect designed expressly to elucidate the fundamental aspects of crystal physics are not very numerous. As we shall see, however, the results they have furnished are quite sufficient to yield a decisive answer to the theoretical issues now under consideration.

2. *The Case of Rock-Salt*

The Debye theory assumes from the start that the atomic vibrations are of the same general nature as the elastic vibrations of the solid. The Born theory rests on a fundamentally similar assumption, which appears as the so-called "postulate of the cyclic lattice". It is scarcely necessary to discuss

here the Debye theory in detail, as it has no explanation whatever to offer for the appearance of discrete lines in the Raman spectra of crystals. According to Born, the vibration spectrum of the crystal may be divided into branches which he classifies respectively as the "optical branches" and the "acoustic branches", all these, however, being essentially continuous spectra. The experimental fact that the Raman spectra exhibit sharply defined frequencies stands in obvious contradiction with these assumptions. To escape this fundamental difficulty, an ingenious argument has been put forward which we shall examine in detail later in this paper. Before doing so, we shall proceed to consider the actual experimental facts in the case of the rock-salt lattice, which is a particularly suitable substance in view of the fact that much of the work of Born and his collaborators has centred round this substance and its analogues, the alkali halides.

We owe to Rasetti (1929, 1930) the development of a remarkably useful technique for the study of the Raman effect, the value of which has been demonstrated by the resounding success with which he himself applied it in several cases of fundamental interest. In this field of research generally, and especially in investigating substances such as gases or vapours which scatter light only feebly, or crystals which exhibit only feeble Raman spectra, it is essential to employ a light source which emits the most intense possible and highly monochromatic radiation, and that there should be no unwanted radiations and especially no continuous spectrum accompanying the same. Further, it is highly desirable that the exciting radiation (but not the excited ones) should be removed from the light scattered by the medium before its entry into the spectrograph, as otherwise the photographic plates would be fogged by its general diffusion within the instrument. Rasetti secured all these advantages and in addition the enormously increased scattering power of short wave-length radiations arising from the λ^{-4} law, besides enabling the high resolving power which even small quartz spectrographs possess in the ultra-violet region to be utilized, by employing the 2537 A.U. monochromatic radiations of mercury vapour under special conditions which ensured that *only* this radiation and *none* other would give an observable Raman effect. The technique consists in using a low-pressure quartz mercury arc in which the mercury vapour is prevented from reaching any considerable density, and from absorbing the 2537 radiation emitted by itself. This is accomplished firstly by very effective water-cooling, and secondly by squeezing the discharge against the walls of the quartz tube by the field of a specially designed electromagnet. A filter of mercury vapour at room temperature is placed in the path of the scattered light emerging from the substance under study to absorb the 2537 radiation. This filter works so effectively that

some of the feeble mercury lines which have intensities negligibly small in comparison with the 2537 radiations and which therefore give no observable Raman effect nevertheless appear stronger than the 2537 line in the recorded spectra. This is in particular noticeable with regard to the neighbouring 2535 A.U. line which appears adjacent to the 2537 line in the recorded spectra. In no case, however, does it give any detectable Raman shifts, indeed not even those excited most intensely by the 2537 excitation.

Rasetti investigated many crystals using his technique and with notable success. His greatest achievement in this field was the successful recording of the Raman spectrum of rock-salt which previous investigators had reported as giving no observable effect. The feebleness of the phenomenon can be judged from the fact that with a large prism of rock-salt 5 centimetres thick, an exposure of 8 hours reinforced by internal reflections within the prism had to be given, while a few minutes under the same conditions sufficed for recording the spectrum of quartz. In his preliminary report in *Nature* (1931), Rasetti remarked on the "very peculiar structure" of the Raman spectrum of rock-salt. A rather poor reproduction of the spectrogram appears with his paper in the *Nuovo Cimento* (1932). There is a better reproduction accompanied by a microphotometer record in the joint paper by Rasetti and Fermi (1931) in the *Zeitschrift für Physik*. But the most satisfactory reproduction is that appearing on page 139 of the German translation of Fermi's book *Moleküle und Krystalle* (1938). In this reproduction, the discrete character of the spectrum is quite evident, and the positions of the intensity maxima can be read off from it directly with a glass scale. The details of the structure as thus seen and measured are confirmed by their complete correspondence with the peaks or kinks seen in the microphotometer record appearing immediately above the reproduced spectrogram. A further striking confirmation is furnished by the fact that the pattern is also visible in the reproduction as an "antistokes" Raman spectrum in the extremely clear region lying on the short wave-length side of the 2537 exciting radiation. The details of this region also appear quite distinctly in the microphotometer record.

One notices that the spectrum consists of nine discrete and clearly resolved Raman lines. Their frequency shifts from the exciting 2537 radiation and their approximate widths are recorded in Table I. This shows both the "Stokes" and "antistokes" Raman shifts as determined from the spectrograms and microphotometer records. From the latter records, rough computations have been made of the relative intensities of both the Stokes and antistokes Raman lines. These results are also included in the table. The observed value of the ratio of the intensities of the Stokes

to the antistokes Raman lines is in reasonable agreement with that to be expected from Placzek's well-known formula, as will be seen from the comparison made in the table.

TABLE I
Raman Spectrum of Rock-Salt

Serial Number	Frequency shifts of the Stokes line in cm.^{-1}	Approximate breadth in cm.^{-1}	Relative intensity taking the intensity of 235 Stokes line as 10	Frequency shift of the anti-stokes line in cm.^{-1}	Approximate breadth in cm.^{-1}
1	134	diffuse	3.3	150?	
2	183	25	5.8	189	
3	235	5	10	239	6
4	256	13	8.9	265	
5	281	15	9.9	278	15
6	294	14	10.3	288	15
7	317	14	10	311	15
8	340	8	8.9	339	10
9	350	8	9.2	349	10

Serial Number	Relative intensity taking the intensity of 235 Stokes line as 10	Observed intensity ratio of the Stokes to antistokes line	Calculated intensity ratio using Placzek's formula	Fundamental frequency in cm.^{-1}
1	2.4	1.4	1.9	67
2	2.9	2.0	2.3	91
3	3.2	3.1	3.0	117
4	2.4	3.7	3.3	128
5	2.7	3.7	3.7	140
6	2.8	3.7	3.9	147
7	2.6	3.9	4.3	158
8	2	4.5	4.8	170
9	2	4.6	5.0	175

As will be seen from the figures in the third column of the table, some of the observed lines are quite sharp while others are only moderately so. The line having a frequency shift of 235 cm.^{-1} exhibits exceptional sharpness and intensity both on the Stokes and antistokes sides, and being situated in a clear region and well separated from the remaining lines is a conspicuous feature in the spectrogram. The agreement of the frequency shifts as measured from the Stokes and the antistokes regions, as also of their approximate widths on the two sides, and the fair agreement of the observed intensity ratio of the Stokes to the antistokes lines with that calculated from Placzek's formula leave no room for doubt that the figures shown in the second column are a correct description of the Raman spectrum of rock-salt.

We shall now proceed to examine the facts stated above in the light of the existing theories. As is well-known, the crystal structure of rock-salt is made up of two interpenetrating face-centred cubic lattices. The unit cell is a rhombohedron with one sodium ion and one chlorine ion contained in it. According to Born's theory, a crystal with p non-equivalent atoms in the unit cell would in general have $(3p - 3)$ "limiting frequencies" in the optical branch, the remaining 3 degrees of freedom going to the acoustic branch of the vibration spectrum. The former number may, however, be reduced by the symmetry properties of the crystal to a smaller figure. In the present case $p = 2$, and the crystal belongs to the highest class of cubic symmetry. The 3 possible "limiting frequencies" of the optical branch are therefore reduced by degeneracy to one. As the result of the manner in which the sodium and chlorine ions are grouped around each other, the oscillation of the two sets of ions with respect to each other which has this frequency, would be active in infra-red absorption and would correspond to the reststrahlen frequency of 52μ observed in rock-salt. For the same reason, this vibration should be inactive in the Raman effect. This explains the inability of some of the earlier workers, notably Schæfer (1929) to record any Raman line with rock-salt, and indeed also in the other alkali halides.

Accepting the view-point of the Born dynamics, Fermi attempted to give a theoretical explanation of the observed Raman spectrum of rock-salt in the joint paper by himself and Rasetti (1931) and succeeded to the extent of showing why the high-frequency limit of the Raman spectrum agrees with twice the known reststrahlen frequency of rock-salt. He frankly, however, admitted his inability to explain the other features observed in the spectrum in the following words (translated from the original German):—"In order to calculate the intensity distribution in the Raman spectrum, special assumptions are necessary regarding the influence of the polarisability of the crystal atoms by the elastic displacements. It appears therefore impossible for the present to explain the fine structure of the observed spectrum."

The appearance of nine discrete frequencies in the Raman spectrum of rock-salt, on the other hand, finds a natural and ready explanation in the new theory of the dynamics of crystal lattices put forward by Sir C. V. Raman in the introductory paper in this symposium. In a paper appearing elsewhere in this symposium, Chelam (1943) has worked out the complete vibration spectrum of rock-salt basing himself on the Raman theory of crystal dynamics. The main results of his paper are summarised below. The number of non-equivalent atoms in the rock-salt lattice is 2. Hence the total number of degrees of freedom will be $2 \times 8 \times 3$ or 48, of which 45 will appear as the atomic frequencies and the remaining 3 go over into the

“elastic spectrum”. The 45 frequencies would be reduced by degeneracy to 9 distinct ones as shown below:

	Degeneracy
(1) The sodium and chlorine lattices vibrating against each other	4
(2) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(3) The alternate planes of the chlorine atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(4) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, parallel to themselves	8
(5) The alternate planes of chlorine atoms parallel to the octahedral planes oscillating against each other, parallel to themselves	8
(6) & (7) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces, normal to these faces	3 each.
(8) & (9) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces along these planes	6 each.

Because of the symmetry properties of the rock-salt structure, all these nine modes of vibration would be inactive in Raman effect. But it has been pointed out from theoretical considerations by Placzek (1934) and recently by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal vibration is active in the Raman effect, irrespective of whether the fundamental is permitted or forbidden. The observed nine frequencies in the Raman spectrum of rock-salt are therefore the overtones of the nine fundamental modes of vibration enumerated above. The values of these fundamental frequencies calculated from the observed Raman shifts are given in the last column in Table I.

3. *The Structure and Sharpness of the Raman Lines*

In the Raman dynamics of crystal lattices, the monochromatism of the $(24p - 3)$ modes of vibration possible appears as a natural consequence of the fundamental property of crystal structure that it is a three-dimensional repetition pattern in space of practically infinite extension. Any

circumstance that modifies or alters the periodic structure of the crystal must modify the monochromatism of the vibration frequencies to an extent depending on the particular circumstances of the case. An imperfection or mosaicity of the crystal structure and the disturbing influence of thermal agitation may be mentioned as such circumstances. The extent of their influence on the character of the spectra would depend on the individual case, including especially the nature and strength of the binding forces within the crystal, the geometric character of the particular mode of vibration and the masses of the vibrating atoms, ions or molecules. In agreement with these indications of the theory, we find that though Raman spectra of crystals usually consist of well-defined lines with accurately measurable frequency shifts, their sharpness varies from crystal to crystal and even in the same crystal, it may be different for the different lines. It may be and usually is also a function of temperature. Speaking broadly, it may be said that the lines with small frequency shifts are less sharp than the lines with high frequency shifts, but there are numerous exceptions to this rule. Further, there are many examples which suggest that vibrations controlled by valence forces appear as extremely sharp lines in the Raman spectrum, while vibrations controlled by ionic or molecular attractions, appear as rather broad and diffuse lines.

The explanations which have been offered for the appearance of sharp lines in the Raman spectra of crystals on the basis of the Born lattice dynamics may now be briefly stated and examined. They rest on the idea that only the "limiting frequencies" of the lattice, *viz.*, those having great phase-wavelengths could appear in the observed spectra. As a consequence of the postulate of the cyclic lattice, however, vibrations with smaller phase-wavelengths are enormously more numerous than those with longer phase-wavelengths, and they would give frequencies different from the latter, and thereby build up a continuous spectrum. What is actually observed in light-scattering, however, is something very different, and to remove this obvious contradiction between the theory and the experimental facts, it is suggested that the frequencies of the vibrations of shorter phase-wavelengths disappear from the spectrum by reason of the optical interference of the effects due to them arising from different elementary volumes in the crystal. While this argument is no doubt ingenious, it is obvious that it assumes that the atomic vibrations in the lattice have perfectly ordered phase-relations over volume elements sufficiently large for such interference to give, on the one hand the frequencies actually observed with the sharpness and intensities found in experiment, and on the other hand to extinguish completely the frequencies assumed to exist but to be unobservable.

Perhaps the most appropriate comment which could be made is that while, as we have seen in the case of rock-salt, the Born theory does not on the one hand, explain the features actually observed in the spectra, it postulates on the other hand a whole spectrum of frequencies for which there is no observational evidence. Further, to remove the conflict between fact and theory, a hypothetical assumption is made for which there is no experimental justification. In fact, it may be said that the entire approach made in the theory is artificial in character. It should be added that neither *a priori* considerations or any actual facts of observation compel us to assume the existence of coherent phase-relationships of the lattice vibrations of high frequency over extended volumes of the crystal. The mosaicity of most actual crystals, the existence of thermal agitation and above all, the known facts about the thermal conductivity of solids indeed make it difficult to accept such an assumption without large reservations.

4. *The Force-Fields in Crystals*

In not a few cases, the experimental facts established by Raman effect studies with molecular systems, *e.g.*, gases and vapours at ordinary and at higher pressures, liquids, solutions, mixtures and fused melts, form a useful starting point for the interpretation of the phenomena observed with crystals. The greater density and consequently increased magnitude of the force-fields, as also the regular ordering of the units characteristic of the crystalline state have, of course, to be taken into account in this connection. It is obvious also that the classification of molecular movements into three classes as translations, rotations and vibrations, which is quite appropriate for gases and which is not quite so appropriate for liquids ceases to have a strict scientific significance in a crystal. All movements should be considered as atomic displacements and described as time-periodic variations from the standard atomic configurations prescribed by the crystal structure. Indeed no other way of describing the movements is open to us in the case of those crystals in which no specific molecular or ionic configurations can be recognized. With typically molecular or ionic lattices, however, it is convenient to speak of "internal vibrations", "rotational oscillations" and "translatory oscillations", and these descriptions may even roughly correspond to specifiable ranges of vibration frequency. In using these terms, however, it should be remembered that they cannot be an accurate description of the actual displacements in the crystal.

Subject to the limitations indicated, we may consider "ionic" and "molecular" crystals and discuss in turn each of the three classes of vibration. Raman effect studies with liquids, mixtures, solutions and melts show

that the internal vibrations are only influenced in a secondary degree by the state of aggregation. When the irregular arrangements existing in fluids is replaced by the regular ordering characteristic of a crystal, the force-fields surrounding individual ions or molecules become definite. *In consequence, we should expect the "internal frequencies" of the ions or molecules in crystals to become as precisely specifiable as in gases, but with definite changes due to the influence of the force-fields. Indeed, it should be possible to evaluate the changes in these frequencies as between the gaseous, fluid and crystalline states by considering the magnitudes of the force-fields, and vice-versa from the observed frequency changes to evaluate the force-fields.* This principle has been applied with success at this Institute and its utility thereby established.

Raman effect studies in fluid media show that the freedom of rotation of the ions or molecules is greatly hindered in fluids by the density of the aggregation and by the viscosity of the medium. In crystals the molecules or ions occupy specific orientations and the force-fields in which they lie should therefore be exactly definable. Hence the ions or molecules in crystals should have precisely definable frequencies of rotational oscillation about their positions of equilibrium. *From the frequencies of rotational oscillation of optically anisotropic groups as observed in the Raman effect, it should be possible to determine the nature and strength of the force-fields in which they are located. Vice-versa if the force-fields are known, the frequencies of such rotational oscillation could be computed.* This idea again has been applied with success to a number of cases.

Since as stated above, the force-fields in which molecules or ions are located in a crystal are definite, *their translatory oscillations about their positions of equilibrium should also have exactly specifiable frequencies, determined by the masses of the particles and the strength of the fields in which they lie.* In view of the indefiniteness of the force-fields in liquids, we could hardly expect such "translatory oscillations" of the molecules or ions to be observable in the majority of fluid media. Nevertheless, in a few cases, *e.g.*, water and formic acid, they have been observed in the Raman effect as diffuse bands with small frequency shifts. The idea that such translatory movements in crystals should have well-defined frequencies is thereby strengthened. Indeed, there is observational evidence which shows that this is actually the case.

Finally, we may refer to the vibrations of lowest frequency which are essentially mass-movements and are naturally to be regarded as pertaining to the elastic spectrum of the crystal. There would be an immense number of such modes possible in a crystal which would be the more closely crowded together, the lower we go down in the scale of frequency.

Summary

An examination of the spectrograms of the Raman effect in rock-salt obtained by Rasetti reveals the existence of nine distinct Raman lines both on the Stokes as well as on the antistokes sides. The frequency shifts of these lines have been estimated. From the microphotometer record reproduced in Rasetti's paper, the relative intensities of the lines as well as the intensity ratios of the Stokes to the antistokes lines have also been evaluated. These nine frequencies have been identified as due to the nine distinct modes of vibration of the sodium chloride lattice to be expected on the basis of the Raman dynamics of crystal lattices. Though these vibrations are forbidden in the Raman effect as fundamentals, they are allowed as octaves and appear as such in the spectrum. It is pointed out that the Born theory of crystal dynamics is not capable of offering any satisfactory explanation for the observed facts.

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