

The eigenvibrations of crystal structures*

1. Introduction

As is well known, the atomic architecture of a crystal may be described as a three-dimensionally periodic distribution of matter in space on a very fine scale. The regularity of such arrangement is, however, liable to be disturbed in various ways and especially by the thermal agitation in the crystal or by the incidence of radiations on it, and the atoms then vibrate about their respective positions of equilibrium. A knowledge of the modes and frequencies of the vibrations thus arising is of the greatest possible importance for the theory of the solid state. For, it enables us to evaluate the strength of the interatomic forces and thus to obtain a quantitative physical picture of the structure of the crystal, supplementing the geometric description furnished by X-ray analysis. Further, such knowledge is the basis for a development of the theory of the physical properties of crystals, including especially all those which depend on or are influenced by the temperature of observation.

The volume of papers under review is intended to furnish a definitive answer to the problem of ascertaining the modes and frequencies of vibration of the atoms in a crystal in relation to their geometric distribution in space and the forces holding them together as a rigid structure. Of the 19 papers forming the symposium, 9 describe new experimental results obtained from investigations specially designed to throw light on this fundamental problem. These experimental papers are richly illustrated, no fewer than 65 separate spectrograms and 35 microphotometer records besides numerous diagrams being reproduced to aid the reader's understanding and appreciation of the results of the researches. The introductory paper of the symposium furnishes the necessary theoretical background, while the remaining nine papers are devoted to the consideration of the consequences of the theory in particular cases and their comparison with the facts of experiment. Before entering into a discussion of the theoretical aspects of the subject, it appears desirable to present the reader with a review of the experimental situation as it emerges from the symposium.

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2. The scattering of light in crystals

Many investigations on the vibration spectra of crystals have been made during the past twenty years by the method first employed in 1928 by the present writer, viz., illuminating the crystal by monochromatic light and recording the spectrum of the scattered radiations emerging from it. While much empirical knowledge of value has accumulated as the result of such studies, they left untouched the fundamental problem of ascertaining what the *complete* vibration spectrum of any crystal is and of how it is related to the structure of the crystal. Investigations designed to resolve this problem were undertaken at Bangalore a few years ago by Dr R S Krishnan. Numerous crystals have been studied with the utmost possible thoroughness and a rich harvest of results obtained in every one of the cases investigated, viz., calcite, quartz, barytes, gypsum, fluorspar, corundum, topaz, diamond, rock-salt, sylvine, ammonium chloride, ammonium bromide. We shall presently proceed to take note of such of these studies as are now reported on. As an example of the results which previously found publication, we may mention the case of calcite, with which no fewer than 16 frequency shifts were recorded by R S Krishnan as against a maximum of 7 by earlier workers. The following facts observed with this crystal may be regarded as typical of those noticed with inorganic crystals generally. (a) The frequency shifts recorded with small or moderate exposures represent the *first-order* spectrum, namely, the fundamental eigenfrequencies of atomic vibration in the crystal which are active in light scattering. (b) In strongly exposed spectrograms, frequency shifts are recorded with appreciable intensity which represent the vibration-spectra of higher orders, viz., the overtones and summationals of the eigenfrequencies, including those not recorded as fundamentals. (c) The frequency shifts of all orders are recorded as

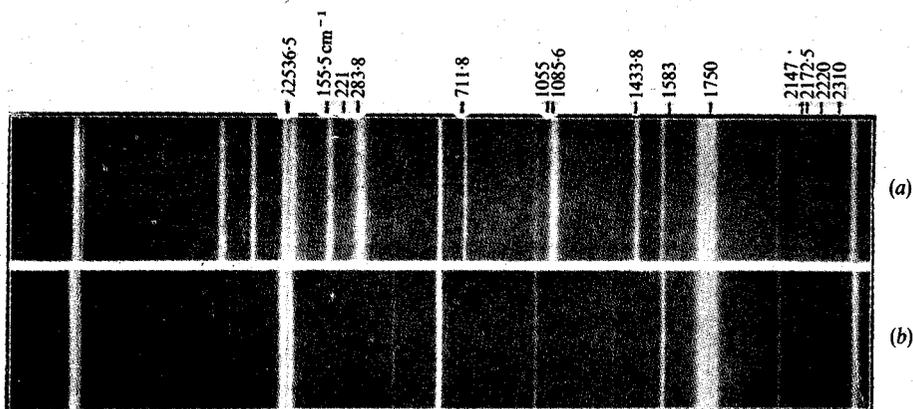


Figure 1. (a) Raman spectrum of calcite. (b) Mercury spectrum (after Dr R S Krishnan).

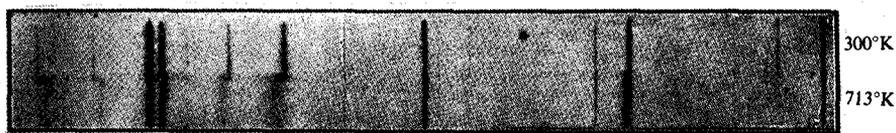


Figure 2. Variation with temperature of the Raman spectrum of calcite (after P K Narayanaswamy).

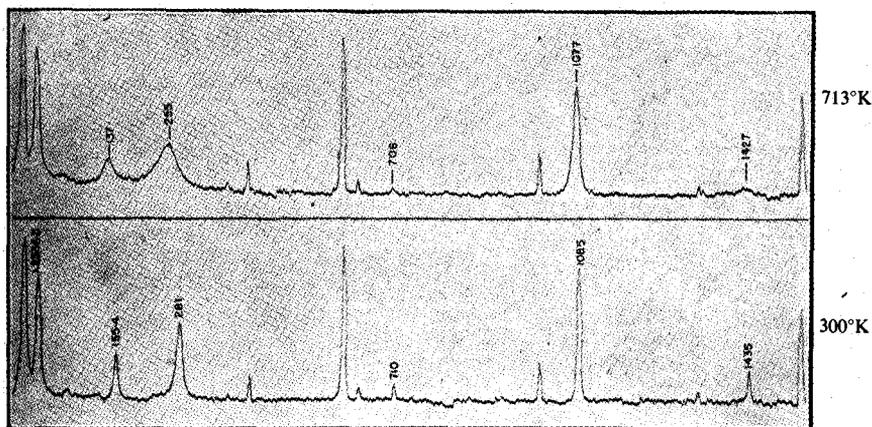


Figure 3. Microphotometer records of the Raman spectrum of calcite at two different temperatures (after P K Narayanaswamy).

sharply defined lines on a clear field, the apparent spectral width of such lines in many cases being no greater than that of the mercury arc lines registered on the plates with comparable intensities. (d) When the crystal is heated, the spectral lines broaden and shift towards the position of the exciting radiation and their peak intensities diminish notably. (e) Vice-versa, if the crystal is cooled to liquid-air temperature, the spectral lines sharpen and shift away from the exciting radiations while their peak intensities increase. But these effects are by no means so conspicuous as those of the opposite kind noticed on heating (see figures 1, 2 and 3).

3. The cases of corundum and topaz

These are two well known crystals found in nature, while the former can also be prepared synthetically. Corundum is of much simpler composition and structure than topaz, and is a crystal of the trigonal class, while topaz is orthorhombic. These differences are reflected in the degree of complexity of their vibration spectra, 7 frequency shifts being recorded by Dr R S Krishnan with corundum

and 32 with topaz, as compared with a maximum of 2 and 11 frequency shifts respectively reported by earlier authors. The lower crystal symmetry of topaz evidently results in a much larger proportion of the possible modes of vibration being active in light-scattering than in the case of corundum. Figure 4 reproduces, in part, the spectrogram of pure topaz obtained in light-scattering, while figure 5 is the *luminescence* spectrum of topaz containing a trace of chromic oxide

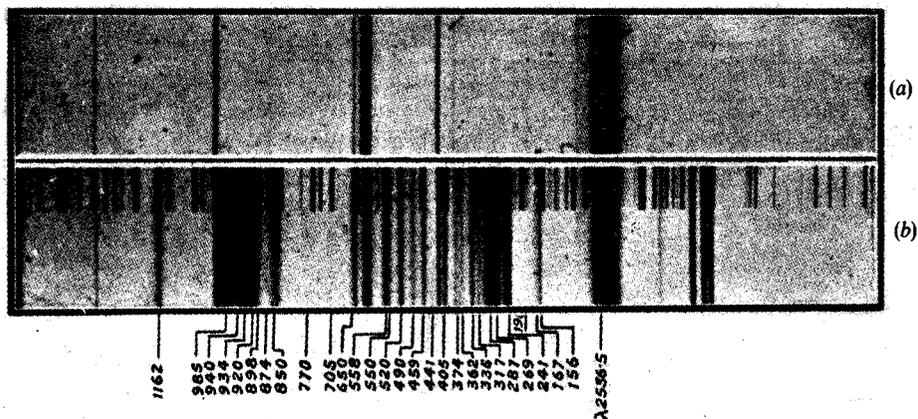


Figure 4. (a) Mercury spectrum. (b) Raman spectrum of topaz (in part) (after Dr R S Krishnan).

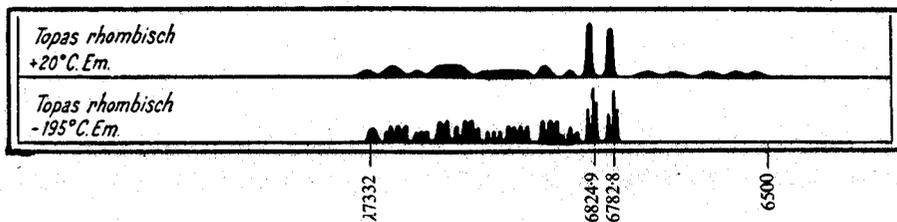


Figure 5. Luminescence spectrum of topaz (after Deutschbein).

as impurity recorded with the crystal held at liquid-air temperature. A comparison of the frequency shifts λ 2536.5 as observed in light-scattering and from λ 6824.9 (the principal chromium line) as observed in luminescence shows a most remarkable concordance. The bands observed in the luminescence spectrum of ruby and also those observed in its absorption spectrum are successfully explained on similar lines in terms of the vibration frequencies of the corundum crystal observed in light-scattering and in infra-red absorption.

It is obvious that the mechanism of the diffusion of light by a crystal and the mechanism of its impurity-activated luminescence are very far from being identical. That nevertheless there is a concordance between the vibration-spectra as observed by the two methods is theoretically significant. It indicates that the vibration spectrum of a crystal as observed in light-scattering is not fundamentally different in its general character from the *complete* vibration-spectrum. In other words, the latter is essentially a *line-spectrum* exhibiting a discrete set of frequencies. This conclusion is reinforced by a vast array of other evidence furnished by critical studies of the spectroscopic behaviour of numerous crystals by diverse methods reported in the literature during the last twenty years. It will not, however, be necessary for us to enter into a description or discussion of such evidence, since the facts regarding magnesium oxide discussed in *Current Science* for December 1947, and those regarding diamond and the alkali halides which we shall presently consider completely clinch the issue.

4. The case of diamond

Five of the papers in the symposium deal exclusively with the spectroscopic behaviour of diamond, and we may here briefly summarise their contents. Dr R S Krishnan reports, in continuation of his earlier studies, a thorough investigation on the scattering of light in diamond, examined spectroscopically. The frequency shifts observed are of three kinds as indicated against them in figure 6; the

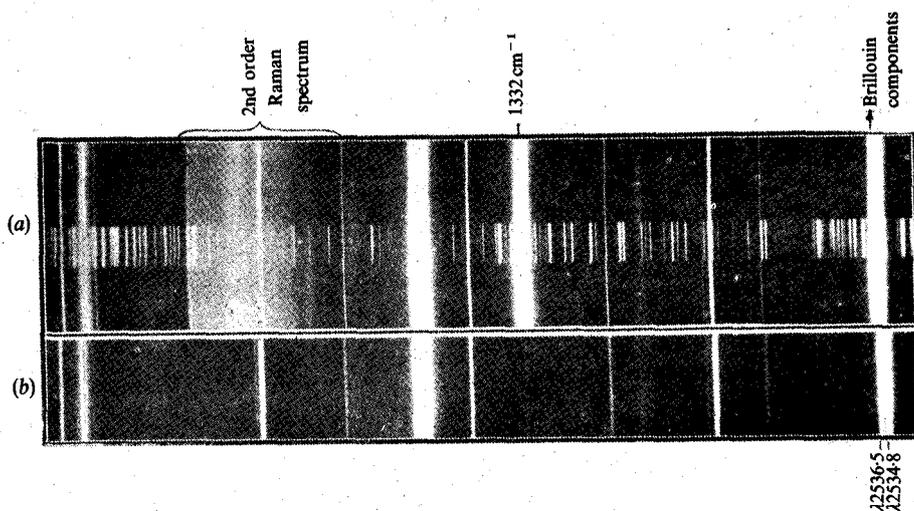


Figure 6. (a) Mercury spectrum. (b) Raman spectrum of diamond (after Dr R S Krishnan).

Brillouin shifts in the vicinity of the exciting radiation λ 2536.5 are less intense than the first-order frequency shift of 1332 cm^{-1} , but both are recorded with short exposures, while the second-order spectrum requires much heavier exposures. Under the high resolution provided by the Hilger E_1 quartz spectrograph, the Brillouin components due to the longitudinal and transverse sound-waves which reflect the light waves are successfully resolved from each other (figure 7), the transverse sound-waves for some unexplained reason giving

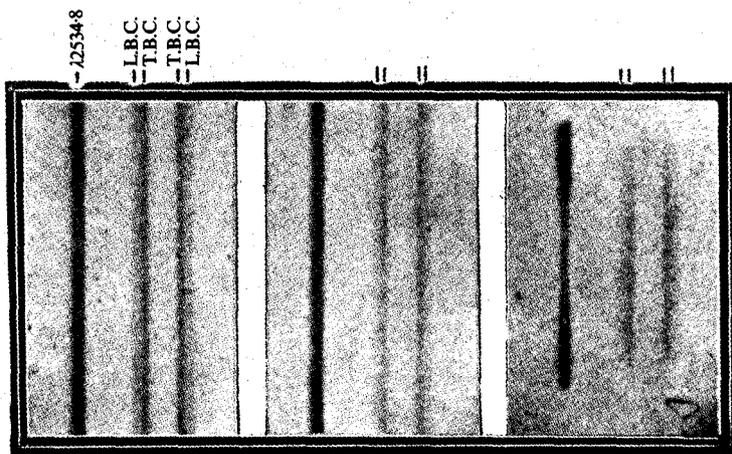


Figure 7. Scattering of light by longitudinal and transverse sound-waves in different directions in diamond (after Dr R S Krishnan).

the more intense components. That sound velocities of both kinds determined from the frequency shifts are found to vary with the direction of their travel [*vide* figures 7(a), (b) and (c)] is to be expected theoretically. Their numerical values for the different directions agree fairly well with those determined by Bhagavantam and Bhimasenachar by the ultrasonic method. The same high-resolution spectrograph also suffices to resolve the spectrum recorded in the region of frequency shifts between 2665.4 cm^{-1} and 2015 cm^{-1} into discrete lines. The shift 2665.4 cm^{-1} which stands out very clearly in the spectrum as a distinct line is clearly the octave of 1332 cm^{-1} . It is much less intense than the close doublet $2460\text{--}2470\text{ cm}^{-1}$, adjacent to which there are also several other lines (see figure 8). The terminal line at 2015 cm^{-1} is so feeble that it is not seen in the reproduced spectra but is quite clearly shown by a microphotometer record. The apparently continuous background seen in the second-order spectrum appears under high resolution as an aggregate of closely spaced lines which is part of the *third-order spectrum* and which appears superposed on it.

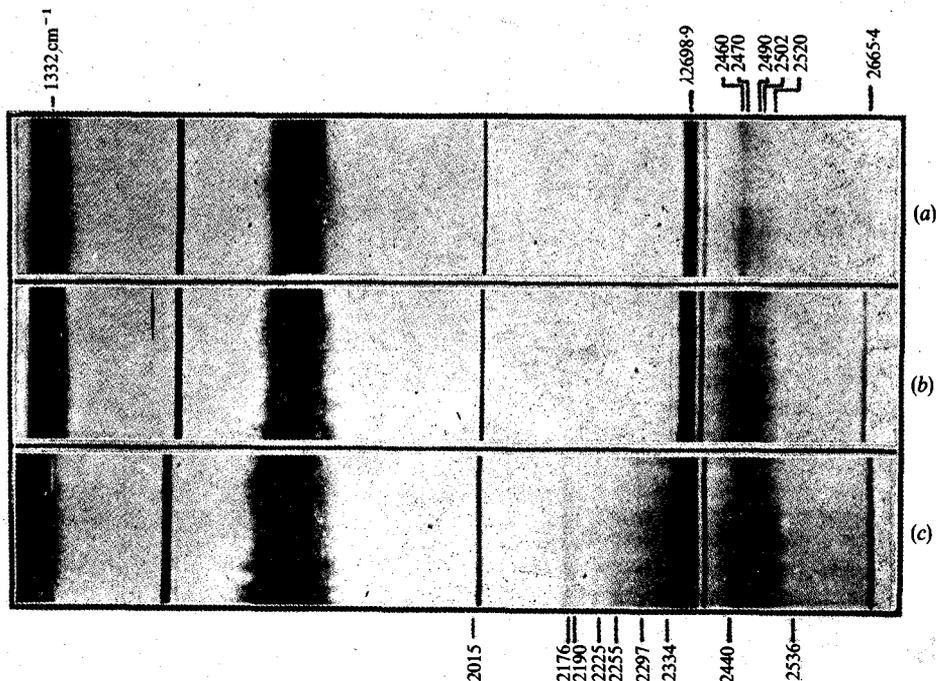


Figure 8. Raman spectrum of diamond under high resolution (after Dr R S Krishnan).

The infra-red absorption by diamond in the frequency range between 900 cm^{-1} and 4000 cm^{-1} has been surveyed by K G Ramanathan and a set of ten curves showing much significant detail obtained with different diamonds is reproduced with his paper. The plates employed were of not very different thicknesses, but they differed much in their physical properties such as ultraviolet transparency, luminescence, birefringence, and photoconductivity. The ten infra-red absorption curves exhibit a practically continuous sequence of variation, ranging from complete transparency in the region $900\text{--}1350\text{ cm}^{-1}$ to nearly complete opacity in the same region, and such variation also shows a complete correlation with the variations of the other properties referred to. With another paper by the same author, the emission and absorption spectra of blue-luminescent diamonds and their microphotometer records are reproduced. The discrete character of the blue-luminescence spectrum is evident from the reproductions (see figure 9), and the measured frequency differences from the principal emission line at $\lambda\ 4152$ indicate very clearly that we are concerned here with the characteristic vibration frequencies of the diamond structure.

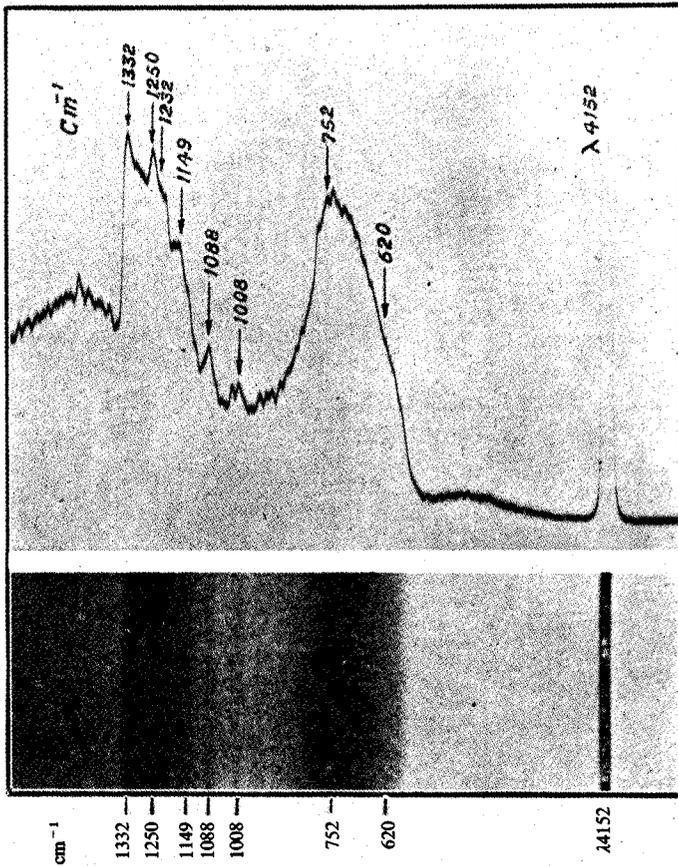


Figure 9. Blue-luminescence spectrum of diamond and its microphotometer record (after K G Ramanathan).

Thus, in the case of diamond, we have a wealth of experimental material regarding the nature of the vibration spectrum obtained by diverse methods of observation, viz., first and second order scattering of light, infra-red absorption of the first and second orders – the former varying from diamond to diamond while the latter remains invariable – luminescence of various types, as also the related absorption. An intercomparison of the results obtained by different methods taking into account the different circumstances of observation, shows a remarkable concordance, which is exhibited diagrammatically in figure 10. The observations themselves clearly indicate that the diamond structure has a set of discrete modes and frequencies of vibration which are finite in number, these appearing in the first-order spectra as fundamentals and in the second-order

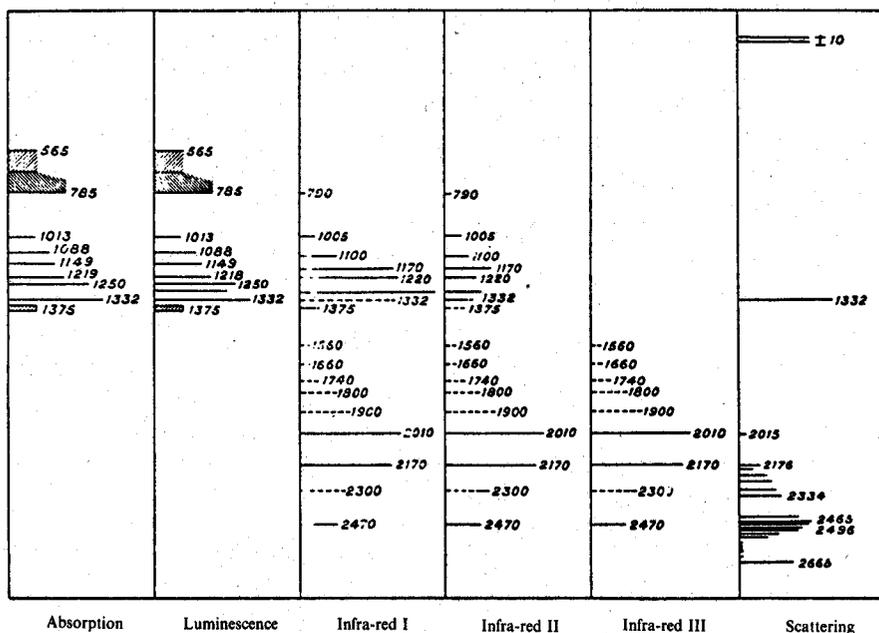


Figure 10. Spectral frequencies of diamond in cm^{-1} as observed by various methods.

spectra as their overtones and summationals. The fundamental frequencies deduced from the observations are in cm^{-1} , 1332, 1250, 1232, 1149, 1088, 1008, 752 and 620, being just 8 in number. The dynamical theory set out in the introductory paper of the symposium leads to the result that the structure of diamond has nine characteristic modes of vibration of which the fifth and the sixth are indistinguishable, thus giving us only eight eigenfrequencies. The identification of these with the eight experimentally observed frequencies therefore naturally suggests itself, but such identification evidently demands an independent proof before it can be accepted as convincing. The two other papers on the case of diamond appearing in the symposium, respectively by the present writer and by Mr K G Ramanathan, furnish the required demonstration.

The nine eigenvibrations of the diamond structure are readily described. Eight of them arise from the existence of three sets of alternative possibilities, namely, an oscillation of the cubic (octahedral) planes in a direction normal (tangential) to those planes, the nearest layers of carbon atoms being in the same (opposite) phase of motion. The ninth mode is a movement of the two sets of carbon atoms forming the structure against each other. Owing to the high symmetry of the structure, the number of independent force-constants required to evaluate the frequency of any one of these modes is very considerably reduced. Actually, three

force-constants (P, Q, R) which express the interactions with the nearest four atoms are sufficient to give a fair approximation to the facts, while eight constants (P, Q, R, S, U, W, Σ , Ω) which take account of the 28 nearest atoms are all that are needed. The values of P, Q, R which fit the experimental data are found to be related to each other in a manner which one would expect from the known physico-chemical structure of diamond (viz., $P > 4Q$ and $2Q > 2R > Q$). The values of the remaining five constants which express the interactions with distant atoms come out very small as is to be theoretically expected. Tables 1 and 2, reproduced from the paper by K G Ramanathan, exhibit this situation very clearly.

The agreement of the frequencies computed theoretically with those observed and the reasonable values of the force-constants which have to be assumed to fit the data are both impressive. But even a more striking confirmation of the correctness of the identifications comes to hand when we consider the *activity* of the various modes in light-scattering and infra-red absorption on the basis of the

Table 1. Numerical values of the force-constants $\times 10^{-5}$ dynes per cm

Atom 0	Atoms 1 to 4			Atoms 5 to 14			Atoms 17 to 28	
P	Q	R	S	U	W	Σ	Ω	
7.35	-1.39	-0.858	-0.005	-0.131	-0.114	-0.06	+0.005	

Table 2. Calculated value of the frequencies of diamond

Sequence	Degeneracy	Operative force-constant	Frequencies from abbreviated formulae			
			P only	P, Q, R	P, Q, R S, U, W	Complete formula
I	3	$P - 4Q + 4S + 8U - 12\Sigma$	cm ⁻¹ 1020	cm ⁻¹ 1 51	cm ⁻¹ 1294	cm ⁻¹ 1332
II	8	$P - 2Q - 2R + 4W + 6\Sigma + 6\Omega$	1020	1294	1269	1250
III	6	$P - 4R - 4S - 12\Omega$	1020	1234	1236	1232
IV	4	$P + 2Q - 4R - 8W - 6\Sigma + 12\Omega$	1020	1064	1123	1149
V & VI	3 + 3	$P + 4S - 8U$	1020	1020	1088	1088
VII	4	$P - 2Q + 4R - 8W + 6\Sigma - 12\Omega$	1020	973	1038	1008
VIII	6	$P + 4R - 4S + 12\Omega$	1020	744	746	752
IX	8	$P + 2Q + 2R + 4W - 6\Sigma - 6\Omega$	1020	635	582	620

known structure of diamond and compare the same with the facts of observation. This is done at considerable length in the second paper of the symposium, and the concordance which emerges is so satisfying as to leave no doubt whatsoever of the correctness of the theoretical approach made to the problem.

5. The alkali halides

The symposium under review includes papers by Dr R S Krishnan describing and discussing the results of his investigations on the scattering of light in two of the alkali halides, namely, rock-salt and ammonium chloride, which are both cubic crystals. Figure 11(a) and (b) reproduce the spectrum of rock-salt as recorded by him respectively with the larger and small Hilger quartz spectrographs, but enlarged in both cases to the same size. It will be noticed that the

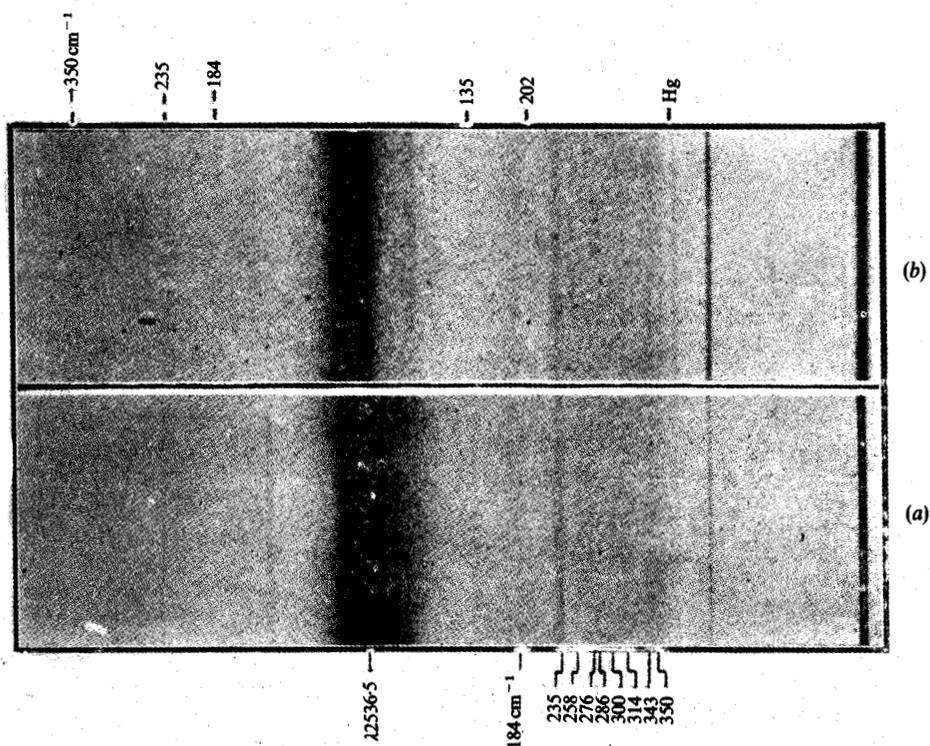


Figure 11. (a), (b) Raman spectrum of rock-salt recorded under high and low resolving powers (after Dr R S Krishnan).

frequency shift of 235 cm^{-1} appears distinctly sharper and that the other details are also seen more clearly in the spectrum recorded with the larger instrument. This is also evident from the microphotometer records reproduced with the paper which show significant differences in the distribution of intensity as recorded with the two instruments. In particular, the frequency shift 235 cm^{-1} shows a large gain in intensity relatively to the other features and indeed overtops all of them in the microphotometer record of the spectrum (see figure 12) which is not the case

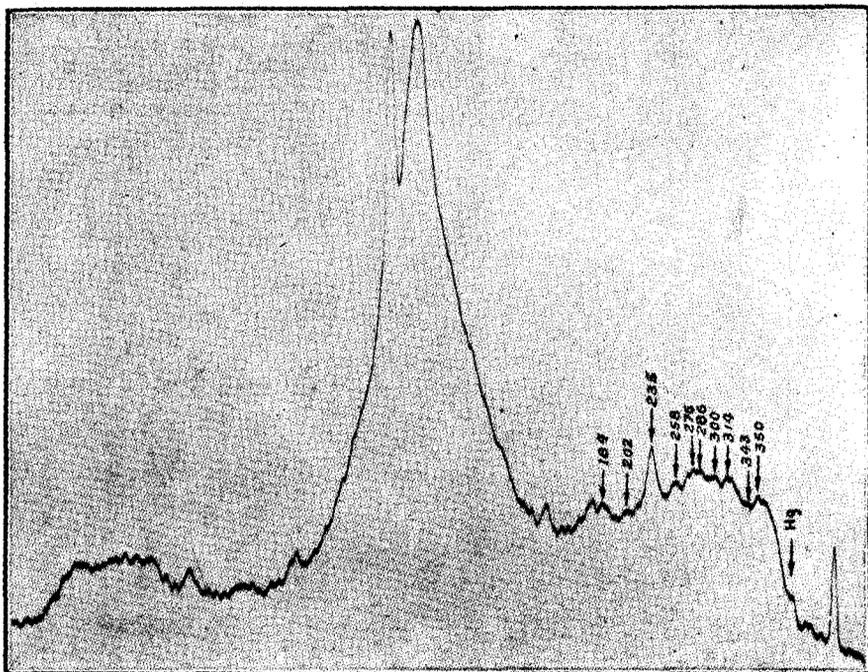


Figure 12. Microphotometer record of the rock-salt spectrum under high resolution (after Dr R S Krishnan).

when the smaller instrument is used. This is precisely what we should expect to find when a higher resolving power is brought to bear upon a closely spaced aggregate to spectral lines of differing intensities. In other words, the comparative microphotometric study reveals that the rock-salt spectrum is an aggregate of discrete lines and that the frequency shift of 235 cm^{-1} shows up a distinct line even under a low resolution just because its intrinsic intensity is much greater than that of the other lines crowded together in the spectrum.

The large intensity with which the frequency shift of 235 cm^{-1} appears finds a simple explanation in the theory of the vibrations of the rock-salt structure developed and discussed in the symposium. One of the nine possible eigen-

vibrations of the structure represents an oscillation of the chlorine ions contained in the octahedral planes of the crystal in a direction normal to these planes, the intervening layers of sodium ions remaining at rest. Owing to the large mass of the chlorine ions, this particular oscillation has a low frequency, being in fact the sixth among the modes in the descending sequence of frequency. The chlorine ions have, however, a large refractivity, indeed very much larger than that of the sodium ions, and hence the alternate approach and recession of the octahedral layers containing them results in much greater variations of optical polarisability than in the case of any other mode. These variations in the successive layers cancel each other's effects in the first approximation, but in the second approximation a residue is left over which results in a frequency shift of double the frequency appearing with quite notable intensity. It is evident from figure 12 that the spectrum also contains numerous other lines, most of which are barely resolved from each other. This is scarcely surprising when we recall that the second-order spectrum of rock-salt should exhibit 45 separate shifts, to say nothing of the third-order spectrum which is also in part superposed on it.

The results obtained with ammonium chloride are also of great interest in view of the remarkable changes which occur in the spectrum of this substance when the temperature is varied. We have, however, no space here to refer to them in detail, and the interested reader will no doubt, consult the original paper.

6. Some concluding remarks

The spectroscopic behaviour of diamond as observed in light-scattering which has been described and discussed above, and the behaviour of crystalline magnesium oxide as observed in infra-red absorption, described and discussed in *Current Science* for December 1947, clearly demonstrate that the complete vibration spectrum of a crystal in the higher ranges of frequency is a discrete *line-spectrum*. In view of the thoroughness with which these two cases have been investigated, and the simplicity of the structure and composition of both the crystals, the experimental facts which have been observed with them are acid tests for any theory which concerns itself with the atomic vibrations in crystals and claims to be able to explain the physical phenomena resulting from such vibrations; any theory which cannot account for the facts noticed with these two crystals or leads to results different from those observed must necessarily stand discredited. *Per contra*, a theoretical approach to the subject which leads to a simple and natural explanation of the facts observed with diamond and magnesium oxide must at least be on the right lines. This is the claim made on behalf of the theory of the eigenvibrations of crystal structures set out and discussed in the introductory paper of the symposium.

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