THE VIBRATION SPECTRA OF CRYSTALS

Part II. The Case of Diamond

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CONTENTS

1. INTRODUCTION

OF recent years, there has been a great accession of exact knowledge regarding the spectroscopic behaviour of crystals. Much of this knowledge has been gained by the method of investigation introduced by the present writer in the year 1928, namely, the spectral examination of the scattered radiations from crystals illuminated by monochromatic light. Valuable information has also come to hand from the study of luminescence spectra and of absorption spectra in the visible and ultra-violet regions at low temperatures. Considerable progress has also been made in the study of infra-red absorption by crystals. By working with thin films, and also by using the highest possible resolving powers, the inherent difficulties and imperfections of infra-red spectroscopy as applied to solids have been minimised. Critical investigations by these diverse methods concur in showing that the vibration spectrum of a crystal held at a sufficiently low temperature as observed in the infra-red region of frequency is effectively *a line spectrum*. From the fact that several procedures of experimental study which are wholly different in principle agree in their indications, it is clear that the spectra of crystals are inherently of this nature and not by virtue of any particular method of observing them.

The earlier theories of the subject which were based on ideas derived from the behaviour of elastic solids identified the atomic vibrations in a crystal with an immense number of " waves " of diverse wave-lengths and frequencies assumed to be present in it. This hypothesis led to a conception of the nature of the vibration spectrum of a crystal radically different from that stated above, viz., that it is *a continuous spectrum*, both in the acoustic

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and in the infra-red ranges of frequency. That such a view gained currency was perhaps not surprising at a time when experimental knowledge of the spectroscopic behaviour of crystals was of a meagre description. It is, however, altogether inconsistent with the facts known at present as the result of recent research, as will be shown in this paper and the others following it.

The case of diamond which we shall proceed to consider in detail is by far the most suitable test for any theory of the spectroscopic behaviour of crystals. For, it is the solid of the simplest structure and composition of which the vibration spectrum is amenable to theoretical calculation as well as to experimental study. Indeed, all the possible different methods of spectroscopic investigation—five in number—which can be applied to the study of a crystal have been successfully employed in the case of diamond. A further special advantage presented by diamond is that its vibration spectrum appears spread out over a wide range of frequency. This makes it possible with only instruments of moderate power to ascertain and establish the true nature of its spectrum unambiguously, while with the aid of more powerful instruments, it is possible to discover and demonstrate the finest details of its spectral behaviour. A further and notable advantage which arises from the high frequencies of atomic vibration in diamond is that the secondary effects due to thermal agitation are unimportant in its case even at ordinary temperatures. Such effects are markedly present in the majority of crystals and disturb the intrinsic simplicity of their spectra.

2. The Eigenvibrations

As is well known, the structure of diamond may be described as consisting of two similar Bravais lattices of carbon atoms of the face-centred cubic type interpenetrating each other. Each atom in one of the lattices is linked to four atoms in the other lattice by valence bonds along the four trigonal axes of symmetry of the crystal. The atoms in the two lattices appear in distinct layers in the octahedral as well as in the cubic planes. In the former set of planes, they are alternately nearer and further apart, while in the cubic planes they are equidistant. This disposition of the layers is a consequence of the quadrivalence of the carbon atoms and is represented in Fig. 1, for the octahedral planes and in Fig. 2 for the cubic ones. A_1 and A_2 represent successive layers of carbon atoms belonging to one lattice, while B_1 and B_2 represent successive layers belonging to the other.

In Part I of this series of papers, we have already derived the nine possible eigenvibrations of diamond, and they may be readily visualised with the help of a model of its structure. Figs. 1 and 2 above are also helpful in this connection. The principal oscillation of the structure is the one in
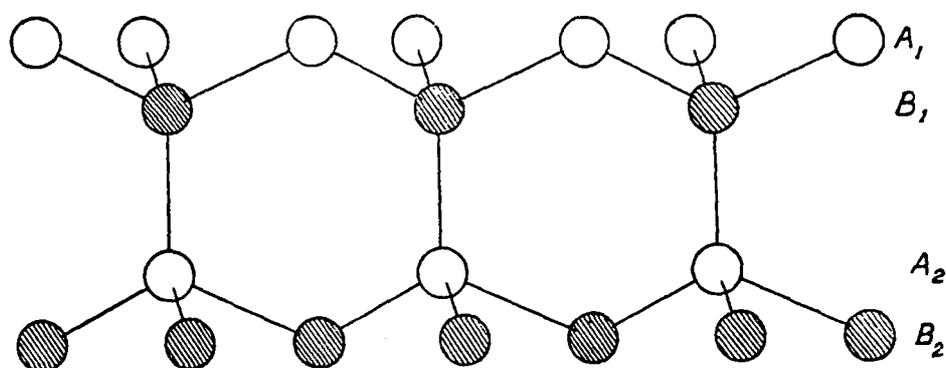
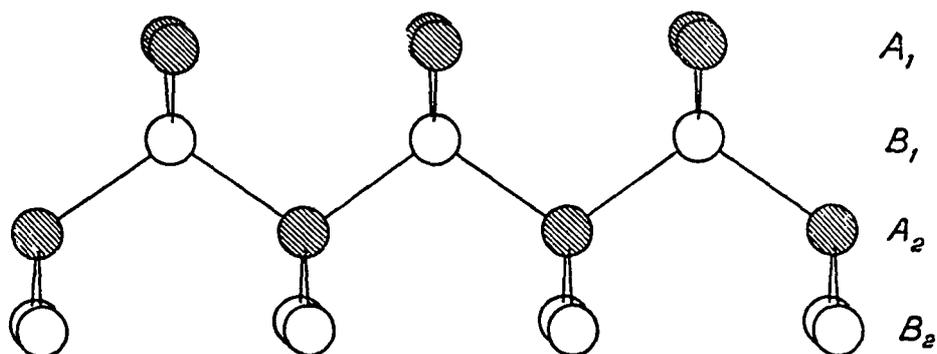Fig. 1. Structure of Diamond viewed perpendicular to a trigonal axis

Fig. 2. Structure of Diamond viewed perpendicular to a cubic axis

which the atoms of each lattice move together in the same phase against the atoms in the other lattice moving together in the opposite phase. It is a triply degenerate oscillation, and hence the direction of motion may be either normal or tangential to the atomic planes in either of the two figures, *viz.*, up and down the printed page or horizontally across it. The other eight possible movements arise from the three pairs of possible alternatives; the oscillations may be of the octahedral or of the cubic planes of atoms; the oscillations may be normal or tangential to these planes; the oscillations may be symmetric or antisymmetric, adjacent layers of the structure belonging to the two lattices moving in the same phase in the symmetric modes, and in opposite phases in the antisymmetric ones. Thus, for instance, in the tangential symmetric oscillation of the octahedral planes, the layers A_1 and B_1 in Fig. 1 move together horizontally across the page against the layers A_2 and B_2 moving together in the opposite direction. Similarly, in the tangential antisymmetric oscillation of the cubic planes, the layers A_1 and

B_2 in Fg. 2 move together horizontally across the page against the layers B_1 and A_2 moving together in the opposite direction.

TABLE I

Descending order of Frequency	Degeneracy	Description of Mode
I ··	3	Oscillation of the two lattices
II ··	8	Tangential antisymmetric oscillation of the octahedral planes
III ··	6	Tangential symmetric oscillation of the cubic planes
IV ··	4	Normal symmetric oscillation of the octahedral planes
V* ··	3	Normal antisymmetric oscillation of the cubic planes*
VI* ··	3	Normal symmetric oscillation of the cubic planes*
VII ··	4	Normal antisymmetric oscillation of the octahedral planes
VIII ··	6	Tangential antisymmetric oscillation of the cubic planes
IX ··	8	Tangential symmetric oscillation of the octahedral planes

* *Note.*—Modes V and VI have the same frequency.

3. THE VALENCE FORCES

The forces coming into play when the atoms in diamond oscillate are principally of two kinds, *viz.*, those due to changes of bond-lengths and those due to changes of bond-angles. The forces of the first kind are predominantly of greater strength, and this fact taken together with the geometry of the modes enables us readily to arrange them in a descending sequence of frequency as shown in Table I. We shall, to begin with, consider only the forces due to the changes of bond-lengths. It is immediately evident that they are absent in the tangential symmetric oscillation of the octahedral planes, as also in the tangential antisymmetric oscillation of the cubic planes described in the preceding paragraph. These two modes have therefore the lowest frequencies and are accordingly placed at the bottom of the table. On the other hand, the tangential antisymmetric oscillation of the octahedral planes, and the tangential symmetric oscillation of the cubic planes both involve large variations of bond-length. By reference to Figs. 1 and 2, it is seen that the changes of bond-length in each case are exactly the same as in the analogous movements of the two lattices against each other in mode I. Accordingly, these three modes have the highest frequency and are placed at the top of the table. The four modes in which the atomic layers move normally to themselves remain to be considered. It is readily seen that the symmetric and antisymmetric normal vibrations of the cubic planes would

have identical frequencies owing to the disposition of the valence bonds and of the atoms in equidistant layers. On the other hand, the symmetric and antisymmetric normal oscillations of the octahedral planes are obviously different. A simple calculation based on the inclination of the valence bonds to the direction of movement shows that the symmetric oscillation would have a higher frequency than the antisymmetrical, while the normal oscillation of the cubic planes would have an intermediate frequency.

In the final ordering of the modes, we have also to consider the forces due to the variations of the bond-angles. These differ notably in the modes VIII and IX in which bond-length variations are totally absent, as also in the modes I, II and III in which they are of equal magnitude, and hence enable us to arrange them in the proper sequence of frequency. The tangential symmetric oscillation of the octahedral planes (mode IX) obviously involves variations of fewer bond-angles than the tangential antisymmetric oscillation of the cubic planes (mode VIII). It therefore now appears at the bottom of the table, with the latter immediately above it. The principal lattice oscillation (mode I) involves variations of all six bond-angles and is therefore placed at the top of the table, followed in order by the tangential antisymmetric oscillation of the octahedral planes (mode II) and the tangential symmetric oscillation of cubic planes (mode III) in which only three bond-angles and one bond-angle respectively vary sensibly. The nine eigenvibrations as thus finally arranged are shown in Table I.

4. NUMERICAL EVALUATION OF THE EIGENFREQUENCIES

The descending sequence of frequency shown in Table I is sufficient to enable the modes of vibration manifesting themselves in the spectrum of diamond to be individually identified. It is possible, however, to go further and make a numerical estimate of the frequency of each of the modes, thereby confirming the assignment of the observed spectral frequencies to the different modes and placing their identification on a secure basis. We shall proceed to show how this may be done.

In any eigenvibration, equivalent atoms have the same amplitude of motion, and since the masses of the two sets of equivalent atoms in diamond are the same, it follows that the atomic displacements are also the same. It is sufficient therefore to find the forces acting on any one atom in a given mode of vibration to ascertain its frequency. The principal forces acting on each atom are (1) the force proportional to its own displacement, and (2) the forces proportional to the displacements of the four atoms with which it is linked by valence bonds. The displacements of the more distant neighbours would also give rise to forces, but these would be smaller, and owing

to the alternation of phase in successive layers would tend to cancel each other out. We may accordingly limit ourselves to the forces specified above.

We denote the three force-constants with which we are concerned by P, Q and R. P is the restoring force on the atom under consideration arising from a unit displacement of itself along a cubic axis. Q and R are the forces on the atom arising from a similar displacement of one of the atoms linked with it, Q being parallel to the displacement, and R perpendicular to it. P being taken as a positive quantity, it is evident that Q would be negative and that P/4 would be the order of magnitude of its numerical value or rather an upper limit for the same. For, the restoring force P may be regarded as due to the displacement of an atom relatively to its four nearest neighbours, though the more distant atoms may also sensibly contribute. Further, owing to the tetrahedral disposition of the valence bonds, R and Q would be nearly equal to each other. More definitely, it can be said that $Q > R > Q/2$. The upper limit Q for R would be reached if the forces arise solely from the variation of bond-length, but we know that this is not the case and that the variation of bond-angles has also to be considered. The lower limit for R, namely Q/2, is set by the consideration that the forces due to variation of bond-angles would then be so large that modes IV, V, VI and VII in Table I would no longer form a descending sequence of frequency. The ratios $P : Q : R$ are thus known *a priori*, at least approximately, from considerations based on the structure of diamond.

TABLE II
Calculated and Observed Eigenfrequencies of Diamond

Mode	F (Operative Force-constant)	$Q=-P/4$ $R=2Q/3$	$Q=-P/5$ $R=2Q/3$	$Q=-P/6$ $R=2Q/3$	Observed Frequency
		cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
I	P−4Q	1332	1332	1332	1332
II	P−2Q−2R	1276	1282	1287	1250
III	P−4R	1216	1230	1240	1232
IV	P+2Q−4R	1018	1057	1087	1149
V & VI	P	942	993	1031	1088
VII	P−2Q+4R	860	925	973	1008
VIII	P+4R	544	678	770	752
IX	P+2Q+2R	385	573	688	620
	P =	6·28	6·975	7·536	×10⁵ dynes per cm.
	Q =	−1·57	−1·395	−1·256	do
	R =	−1·047	−0·93	−0·837	do

Denoting the mass of the carbon atom by *m*, the frequency in wave-numbers by *ν* and the velocity of light by *c*, we write

$$4\pi^2\nu^2c^2m = F,$$ (1)

where F is the operative force-constant, *viz.*, the magnitude of the force acting on the atom per unit displacement. This is shown for each of the different modes in the second column of Table II. The formulæ are readily derived by reference to the modes as described in Table I. We remark that P necessarily appears in each case. Q appears with a factor equal to the number of linked atoms which move in the same phase as the atom under consideration, less the number moving in the opposite phase; the factor is -4, -2, 0, $+2$, 0, -2, 0 and $+2$ respectively for the modes as listed. The force-component R is perpendicular to a cubic axis and does not therefore appear in the frequency expressions for modes I, V and VI, the motion being along a cubic axis. In the remaining modes, the movement is along a body-diagonal or a face-diagonal of the cube, and R therefore appears in the formulæ with a multiplying factor equal to the number of atoms effective in each case. A check on the formulæ is obtained by putting $Q = -P/4$ and $Q = R$, when the frequency comes out as the same for the first three modes, as zero for the last two and as a descending sequence for those between.

Table II makes a comparison of the observed frequencies with those calculated on the basis of the P:Q:R ratios shown at the head of each column, the corresponding numerical values of P, Q and R which give the frequency of the first mode as 1332 cm.$^{-1}$ being shown below. It will be seen that there is good agreement between the figures appearing in the last two columns, thus supporting the identification of the modes with the observed spectral frequencies, as well as the theoretical approach on which the calculations are based. The agreement is, of course, not perfect, but this is only to be expected, since the forces have been ignored which arise from the more distant atoms. The fact that Q comes out as $-$ P/6 and not as $-$ P/4 is a clear indication that such forces are small, but are not negligible. This interpretation of the discrepancies between the figures shown in the last two columns of Table II is completely confirmed by an investigation of K. G. Ramanathan (1947) appearing elsewhere in these *Proceedings*. The dynamics of the problem has been very fully worked out by him, taking account of no fewer than 28 atoms in the equations of motion.

5. ACTIVITY IN LIGHT-SCATTERING

We shall now consider the activity of the various modes of vibration in light-scattering. Equivalent atoms in the structure have the same phase in mode I, while they are alternately in opposite phases in successive layers in the other modes. The changes of optical polarisability therefore add up for mode I, while they cancel out (*to a first approximation*) in the other modes. Mode I is therefore active in light-scattering, while the others are not.

TABLE III

Theoretical Activity of the Eigenvibrations

(For explanation see text)

Serial order	Frequency cm.$^{-1}$	Light Scattering		Infra-red Absorption	
		1st Order	2nd Order	1st Order*	2nd Order
I ..	1332	Active	Strong	Inactive	Inactive
II ..	1250	Inactive	Strong	Inactive	Very Weak
III ..	1232	Inactive	Very Strong	Inactive	Very Weak
IV ..	1149	Inactive	Strong	Inactive	Weak
V & VI ..	1088	Inactive	Weak	Inactive	Strong
VII ..	1008	Inactive	Very Weak	Inactive	Strong
VIII ..	752	Inactive	Inactive	Inactive	Inactive
IX ..	620	Inactive	Inactive	Inactive	Inactive

* *Note.*—The entries in the fifth column of the table assume that the electronic structure of diamond has octahedral symmetry. For a discussion of the infra-red activity of the first order arising when this is not the case, see Section 7 below.

In the second approximation, the non-linear dependence of the optical polarisability on the atomic displacements has to be considered. It is evident that if the *increase* in optical polarisability due to the approach of two atoms is different from the *decrease* due to their recession by an equal amount, the effects of the successive layers would not cancel out completely, leaving a residue which passes through a complete cycle of changes twice during each oscillation and has therefore twice its frequency. Superposition of two modes with different frequencies would, in addition, yield a residual effect with a summational frequency. In considering the magnitude of such effects, it is useful to regard the valence bonds themselves as the units which are optically polarisable. We represent each bond as having an ellipsoid of polarisability of its own. The tetrahedral grouping of the ellipsoids in the crystal secures its optical isotropy in the non-oscillating state. Alterations of bond-lengths during a vibration produce changes in the axial dimensions of the ellipsoids, while variations of bond-angle would alter their orientations. Only major changes could be expected to give observable second-order effects. Accordingly, we are justified in assuming that only changes of bond-length would give such effects. The strength of the effects would be determined principally by the absolute magnitude of the variations of bond-length, and only to a lesser extent by the number of bonds so varying.

The activity of the various eigenvibrations has been assessed and shown in the fourth column of Table III on the basis of the foregoing considerations.

Modes VIII and IX do not involve changes of bond-length and should therefore be inactive. Mode VII is a normal oscillation of the octahedral layers involving changes of three bond-lengths out of every four, but these changes are very small. Accordingly, this mode should exhibit only a very weak second-order activity. Modes V and VI are normal oscillations of the cubic planes in which two out of every four bonds vary in length, but the changes are definitely larger than in mode VII. Their activity should therefore be greater than that of mode VII. In mode IV, only one bond out of every four varies, but the entire motion is along this bond, and the change in its length is therefore considerable. Accordingly, this mode should be strongly active. In the three remaining modes of highest frequency in the table, the bond-length variations are large, but the number of bonds varying is different, being four in mode I, three in mode II, and two in mode III. The *individual* variations in bond-length are greatest in mode III, less in mode II and least in mode I. Accordingly the second-order activity in light-scattering should be strongest 'in mode III, less in mode II, and least in mode I, though very considerable in all three cases.

The second-order activity is essentially dependent on the absolute magnitude of the atomic displacements and unless these are large, their results would be of negligible intensity. The atomic displacements are determined by the consideration that the energy of vibration is $h\nu$ for a single excitation and $2h\nu$ for a double excitation. The amplitudes of vibration would be very small and the second-order effects, therefore wholly unobservable if this energy be distributed over the entire volume of the crystal or even over a large number of lattice cells. We may remark further, that since the *elastic vibrations* of a crystal extend over its whole volume, they cannot exhibit any second-order activity in light-scattering. The first order activity is also cancelled out completely by optical interference except in the very special case of a coherent reflection.

6. ACTIVITY IN INFRA-RED ABSORPTION

To simplify the discussion of the activity of the modes in infra-red absorption, we shall here restrict ourselves to the case in which the electronic structure of diamond can be assumed to possess octahedral symmetry. The distribution of electron density has then a centre of symmetry at the point midway between every pair of linked carbon atoms. Since, further, the carbon atoms have equal masses, these points would continue to be centres of symmetry of the electron distribution in mode I, which would therefore be inactive to all orders of approximation. The remaining modes (II to IX) would also be inactive but for a different reason, *viz.*, that the phase of

the vibration is reversed at each successive layer of atoms and the effects of successive layers would therefore cancel each other out in *the first approximation*.

We have now to consider whether the oscillations of the atomic layers in the modes II to IX would give rise to electric moments in the individual layers large enough to give an *observable second-order effect of double frequency*. The tetrahedral symmetry of diamond ensures that the atomic nuclei are also the centres of distribution of the negative electric charges surrounding them. But when the layers of atoms oscillate *normally* to themselves and the neighbours on either side of each layer do not move *symmetrically* with respect to it, the tetrahedral symmetry of distribution of charge would evidently be disturbed. As a result, each atomic plane would become an oscillating electric double layer, thereby giving rise to an observable second-order infra-red activity. A *tangential* oscillation of the atomic layers would, however, not be effective in the same manner or to the same extent. If, further, as in modes VIII and IX, the valence bonds only tilt but do not stretch, no appreciable dipole moments could develop. The relative activities of the various modes can be assessed on the basis of these considerations and are shown in the last column of Table III. We may remark that modes V and VI are normal oscillations of the cubic planes, while modes IV and VII are those of the octahedral planes. In mode VII, the closely adjacent atomic layers approach and recede from each other, while the more distant ones remain at the same distance. In mode IV, the situation is reversed, *viz.*, the closely adjacent layers remain at the same distance apart from each other, while the more distant one recedes and approaches. In these circumstances, it is clear that mode VII should exhibit greater infra-red activity than mode IV, as shown in the table.

7. THE SPECTROSCOPIC FACTS

The spectroscopic behaviour of diamond has been very thoroughly investigated at Bangalore with the result that we have a wealth of experimental results at our disposal. The data for the spectral frequencies obtained by different methods have been set together in parallel columns and represented in the form of a chart below (Fig. 3). For lack of space, the chart omits reference to the infra-red *emission* spectra. These, however, closely follow the corresponding *absorption* spectra.

The Scattering of Light.—Spectroscopic studies made prior to 1943 had revealed that diamond exhibits in light-scattering a frequency shift of 1332 cm.$^{-1}$, evidently representing our mode I. Following on the publication of his theory (Raman, 1943), the present writer confidently ventured to
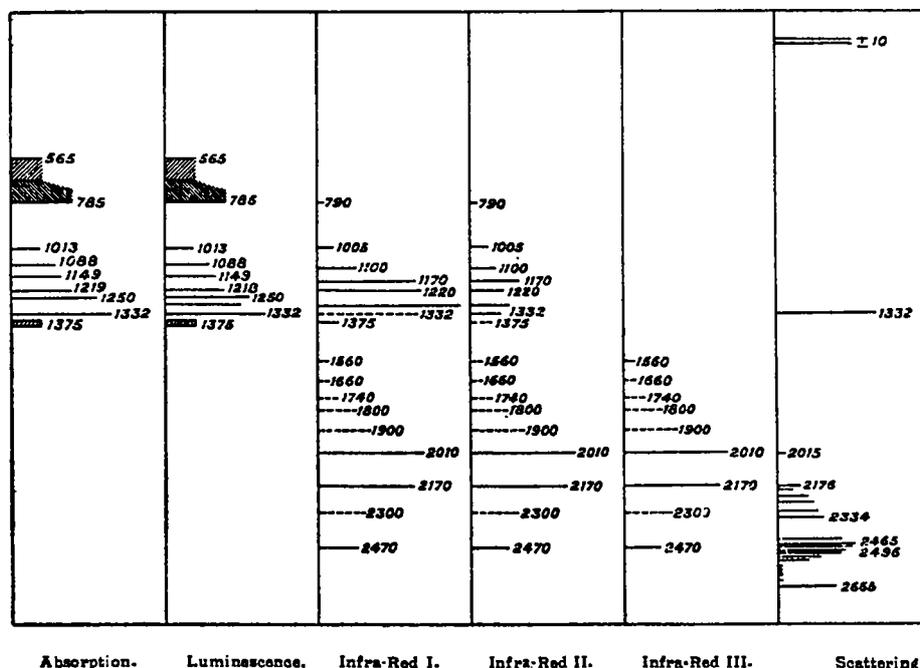
Absorption.   Luminescence.   Infra-Red I.   Infra-Red II.   Infra-Red III.   Scattering.

FIG. 3. Spectral Frequencies in cm.$^{-1}$ as observed by various methods

predict that diamond should also exhibit a second-order spectrum with other frequency shifts explicable as octaves and combinations of its eight fundamental frequencies. An experimental investigation undertaken by Dr. R. S. Krishnan soon afterwards confirmed this prediction. A detailed report on his latest findings appears in a paper by Dr. R. S. Krishnan (1947) appearing in these *Proceedings*. His earlier papers (1944, 1946) on the subject also contain valuable experimental material to which the reader is referred. It will suffice here to remark that these publications clearly establish the discrete character of the vibration spectrum of diamond indicated by the present theory. *Of particular significance is the notable intensity of the second-order spectrum in relation to that of the first order, which clearly demonstrates that the energy of the high-frequency vibrations in the crystal is not diffused through it in the form of a " wave ", but is concentrated in extremely small regions comparable in volume with its lattice cells.* The interesting fact that the octave of the 1332 line is not the most intense one in the second-order spectrum,—being, in fact, the third in order of intensity—finds its explanation in the theoretical considerations set out in Section 5 of the present paper. Dr. R. S. Krishnan's earlier spectrograms did not reveal the octave of mode VII. The theoretical prediction that it should appear in the second-order spectrum though only with a very small intensity has, however, been confirmed in his most recent investigations.

Infra-Red Absorption.—All diamonds without exception exhibit an infra-red absorption in the region of frequencies between 1560 cm.$^{-1}$ and 2470 cm.$^{-1}$, the strength of which shows no appreciable variation from specimen to specimen. It is therefore clearly a fundamental property of diamond. The existence of such absorption and its spectral characters are explained by the theoretical considerations set out in Section 6 of the present paper. The two prominent peaks in infra-red absorption appearing at 2010 cm.$^{-1}$ and 2170 cm.$^{-1}$ are clearly the octaves of the fundamental frequencies 1008 and 1088.

A study of the crystal forms of diamond from a new point of view (Raman and Ramaseshan, 1946) has shown clearly that the crystal symmetry of diamond is, in general, only tetrahedral, though some diamonds undoubtedly possess the higher or octahedral symmetry of structure. The fact that the great majority of diamonds exhibit infra-red activity of the first order ceases to be surprising in the light of this finding. The striking variations in the strength of such activity in different specimens also find their natural explanation in the interpenetration of the positive and negative tetrahedral structures which is also clearly indicated by the crystallographic evidence. From our present point of view, these facts are chiefly interesting since infra-red activity of the first-order makes the fundamental frequencies themselves accessible to observation. The three columns marked (I), (II), (III) in Fig. 3 represent results typical of those observed with different diamonds.

A full report on the infra-red absorption spectra of numerous diamonds is made by K. G. Ramanathan (1947) in a paper appearing in these *Proceedings*. It will suffice here to make a few remarks supplementing those contained in Section 6 of the present paper on the theoretical aspects of the subject. The small difference in structure which gives rise to the first-order activity in most diamonds would not make any difference in respect of the second-order activity. Hence no changes are necessary in respect of the entries in the last column of our Table III. If there were no interactions between the different normal modes, tetrahedral symmetry would result in making mode I active, the other modes remaining inactive in the first approximation. Actually, however, the differences between mode I and the other modes are due only to the differences in the phases of movement of the atomic layers. In view of this geometric similarity of the movements and the anharmonicity of the forces arising from the atomic displacements, a strong interaction between the different " normal " vibrations is inevitable. Such interaction would be the more powerful, the smaller the difference of frequency between mode I and the other mode under consideration. We need not therefore be surprised to find, as is actually the case, that the infra-red

activity of mode I results in the modes with frequencies not very remote from it also showing an observable activity of the first-order.

Emission and Absorption by Luminescent Diamonds.—The emission spectra of luminescent diamonds are of two different kinds, *viz.*, "blue luminescence" and "yellow luminescence", and there are also two corresponding types of absorption spectra. These have their origin in electronic transitions which appear at λ 4152 and λ 5032 respectively and combine with vibrational transitions in the crystal, giving a spectrum stretching respectively towards longer wave-lengths in emission and towards shorter wavelengths in absorption. The spectra are best studied with the diamond held at liquid air temperatures, the features observed in the spectra being then most sharply defined. The vibrational frequencies as determined from the emission and absorption spectra are practically identical. Indeed, these spectra exhibit a remarkable mirror-image symmetry about the electronic transition (λ 4152 or λ 5032 as the case may be), in respect of both position and distribution of intensity, thereby affording a clear demonstration that they arise from the combination of the electronic and vibrational frequencies of the crystal.

The spectroscopic behaviour of no fewer than 28 diamonds in luminescence and absorption has been investigated in detail by Miss Anna Mani (1944). Her paper may be consulted for a full report on the subject including further details. One of her most interesting findings is that the vibration spectra accompanying the λ 4152 and λ 5032 electronic transitions are strikingly different in respect of the distribution of intensity. The vibrational transitions accompanying the λ 4152 transition are principally those lying in the upper or infra-red range of frequency and their overtones, while those accompanying the λ 5032 electronic transitions are principally the "elastic" vibrations of lower frequency. Hence, the "blue" luminescence and corresponding absorption spectra are those which are important from our present point of view. Miss Mani has shown that the λ 4152 transition is really a doublet, the width of the components as well as their separation varying with the specimen under study. Even at liquid air temperature, the total width covered by the electronic transition is never less than 20 cm.$^{-1}$ and may be as such as 50 cm.$^{-1}$. This width necessarily appears in the spectra when the electronic frequency combines with the vibrational frequencies and hence obscures to some extent the monochromatic character of the latter. Even so, the discrete nature of the vibrational spectrum in the upper ranges of frequency is clearly manifest in the emission and absorption by "blue" luminescent diamonds when held at liquid air temperatures. The observed frequency differences are shown in our chart (Fig. 3).

8. SUMMARY

Considerations based on the crystal structure of diamond enable its nine eigenvibrations to be arranged on a descending scale of frequency. The magnitude of the force-constants involved can also be defined within narrow limits. The numerical values of the frequencies evaluated on the basis of the theoretical formulæ show a close agreement with the observed values. The geometry of the modes determines the changes in bond-polarisabilities and electron distributions produced by them, from which their activities in light-scattering and in infra-red absorption can be ascertained both in the first and in the second approximation. A comparison of the results with the experimental facts shows a striking agreement. The observed intensity of the second-order effects in relation to those of the first order indicates that the eigenvibrations are localised in volume elements comparable in size with the lattice cells of the crystal.

REFERENCES

Krishnan, R. S.	.. *Proc. Ind. Acad. Sci.,* A, 1947, **26.**
————————	.. *Ibid.,* 1944, **19,** 216.
————————	.. *Ibid.,* 1944, **19,** 298.
————————	.. *Ibid.,* 1946, **24,** 25.
————————	.. *Ibid.,* 1946, **24,** 45.
Mani, Miss Anna	.. *Ibid.,* 1944, **19,** 231.
Raman, C. V.	.. *Ibid.,* 1943, **18,** 237.
——— and Ramaseshan, S.	.. *Ibid.,* 1946, **24,** 1.
Ramanathan, K. G.	.. *Ibid.,* 1947, **26,** 481.
————————	.. *Ibid.,* 1947, **26,** 469.