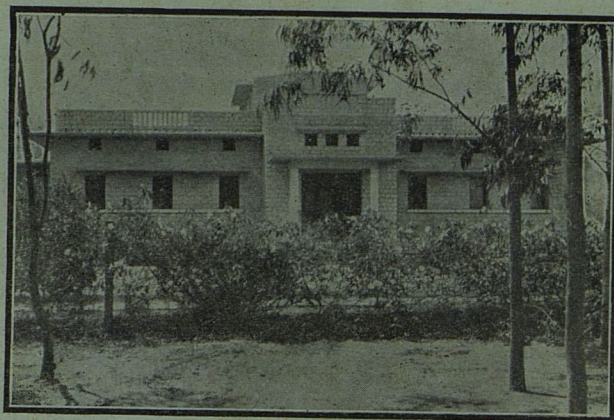


MEMOIRS
OF
THE RAMAN RESEARCH INSTITUTE

No. 86



Spectroscopic Laboratory—Front View

THE DIAMOND

BY
SIR C. V. RAMAN

BANGALORE



W. H.

CHAS. C.

...

THE DIAMOND*

BY SIR C. V. RAMAN

(Memoir No. 86 from the Raman Research Institute, Bangalore-6)

Received September 5, 1956

1. INTRODUCTION

THE many remarkable properties which diamond exhibits, taken in conjunction with the simplicity of its crystal structure and composition, make it a substance of quite exceptional interest to the physicist. In the hope that investigations made with it would result in significant contributions to knowledge, a collection of some five hundred diamonds was built up in the course of years and used by the present author and his collaborators in an extensive series of researches. It would not be possible in this lecture to survey all the topics investigated. We shall confine ourselves to the consideration of some results which have emerged from our studies and which are of fundamental significance for the physics of the solid state.

In his paper of 1907 introducing the quantum theory of specific heats, Einstein made use of the experimental data for the variation with temperature of the specific heat of diamond which had been discovered by earlier investigators to demonstrate the correctness of the basic ideas set out in his paper. The expression for the thermal energy of crystals as a function of temperature derived by Einstein in that paper was a logical deduction from his hypothesis that the structural units comprised in the crystal and capable of mechanical vibration obey the quantum rule, in other words, that their energy can only increase or diminish by quanta proportional to the frequency of vibration. Einstein did not however, deal with the question of how the modes and frequencies of vibration under consideration could be evaluated in the general case. In my address to the Lindau Conference this year, I showed how this basic problem can be handled rigorously and a solution obtained which reconciles the results of classical dynamics with the fundamental notions of the quantum theory and the principles of thermodynamics. Diamond is exceptionally well-suited for a test of the correctness of the theoretical approach set out in that address, since the necessary calculations are readily made and the experiments necessary to check the consequences of the theory are also feasible. It is the purpose of this lecture to show how perfectly the

* A lecture delivered at the Federal Polytechnic Institute in Zurich and at the Universities of Freiburg and Bonn early in July 1956, following the address on "The Physics of Crystals" given at Lindau in June, 1956. The latter address has been published in these *Proceedings* (Memoir No. 85 of the Institute), but the present memoir may be read independently of the same.

theory and the results of experiment are in accord with each other. For the sake of ready intelligibility, the subject will be dealt with from first principles.

2. THE CHARACTERISTIC VIBRATIONS OF LINEAR LATTICES

We shall commence by considering a few simple models of which the behaviour may serve to illustrate the principles underlying the general theory. The simplest of such models is a stretched string loaded by a series of equidistant particles of identical mass along its length. It is immediately obvious that a mode of oscillation is possible on such a string in which the successive particles have the same amplitude but opposite phases of vibration. Such an oscillation is pictured in Fig. 1 (a). It has all the characters of a normal mode of vibration and possesses a specific frequency which can therefore be regarded as characteristic of the system. We may next consider the case in which the particles on the string are equidistant but have alternately two different masses. It can be seen that such a system would have *three* possible modes of normal vibration with different frequencies. These modes are represented in Fig. 1 (b), (c) and (d) respectively. In Fig. 1 (b), successive particles of equal mass have identical amplitudes and oscillate in the same phase, while in Figs. 1 (c) and 1 (d), they have the same amplitudes but opposite phases, the situation thus being analogous to that pictured in Fig. 1 (a).

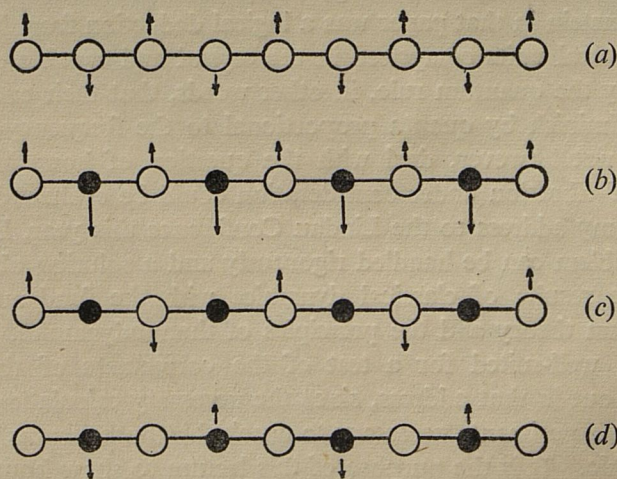


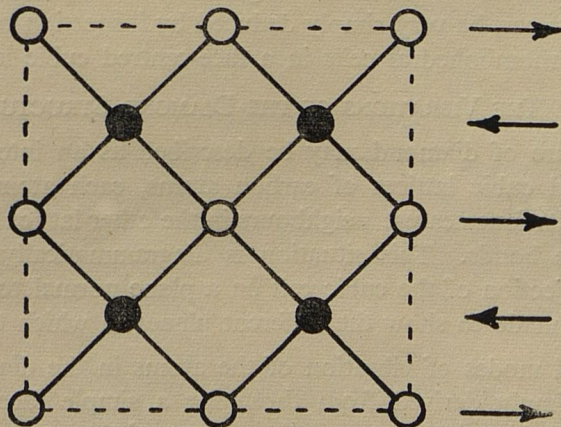
FIG. 1. The characteristic vibrations of linear lattices.

The foregoing results can readily be generalized. It can be proved that a periodic linear lattice with p particles in each unit of its structure would have $(2p-1)$ normal modes and frequencies of vibration; in $(p-1)$ of these

modes, the amplitudes and phases of vibration of the corresponding particles in the successive units are the same, while in the p other modes, they have the same amplitudes but opposite phases. It can also be shown analytically that any initial disturbance set up locally on such a linear lattice would resolve itself quickly into a summation of the $(2p-1)$ characteristic modes of oscillation with their respective frequencies.

3. THE NORMAL VIBRATIONS OF CRYSTAL STRUCTURES

The basic principle of crystal architecture is that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes in two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following an unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed. Since these two alternatives are possible for a unit translation



Mode I.

FIG. 2. Diamond: the principal mode of oscillation.

along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. In each of these situations, the equations of motion of the p atoms contained in the unit cell of the structure can be written down and completely solved, giving us $3p$ solutions. Thus in all we have $24p$ solutions. $(3p-3)$ of these solutions represent normal modes of vibration of the first kind, $21p$ solutions represent normal modes of the second kind and the 3

remaining solutions represent the simple translations of the unit cell of the structure.

The general principles set forth above enable us to describe in simple geometric terms, the normal modes of vibration of the atoms located at the points of a Bravais lattice for each of the known fourteen species. In the general case when $p = 1$, we have 21 distinct normal modes and frequencies of vibration, besides the three translations. But, if the lattice possesses some elements of symmetry, the number of distinct frequencies would be notably reduced. We shall consider here the case of the face-centred cubic lattice. The primitive translations in such a lattice may be taken as the lines joining a cube corner with the centres of the three cube faces meeting at that corner. Applying the symmetry operations of the point group O_h to which the lattice belongs and considering the 8 possible combinations of the phases of atomic vibration, the 21 modes of vibration which thereby result can be grouped together and described as follows: I: a vibration of the alternate octahedral planes of atoms with opposite phases normally to themselves (degeneracy 4); II: the same but transversely to the planes (degeneracy 8); III: the vibrations of the cubic planes of atoms normally to themselves (degeneracy 3); IV: the same but with the vibrations tangentially to the planes (degeneracy 6). The same results can be very simply deduced by inspection of a model exhibiting the unit rhombohedral cells in a face-centred cubic lattice.

4. THE VIBRATIONS OF THE DIAMOND STRUCTURE

The structure of diamond may be described as an interpenetration of two face-centred cubic lattices of carbon atoms, each atom in one lattice being linked to its four nearest neighbours in the other lattice by tetrahedrally directed valence bonds. This situation is diagrammatically represented in Fig. 2 by a projection of the cubic cell on a plane normal to the cubic axis. (No attempt is made to show the different planes in which the atoms lie.)

The normal modes of vibration of the atoms in the diamond structure may be very simply derived from those for a simple face-centred lattice listed above by taking into account the phases of the motion of the atoms in the two lattices which may be either the same or opposite. The nine possible modes of vibration thus derived are depicted in Figs. 2, 3 and 4. The principal mode which is depicted in Fig. 2 is a translatory movement of the two lattices in opposite phases. This is triply degenerate and can occur along anyone of the three cubic axes, as indicated by the arrows in the figure. Fig. 3 shows the diamond structure viewed in a direction normal to a trigonal axis of symmetry and exhibits the octahedral layers of atoms. The normal and tangential movements of these planes in the two possible relative phases

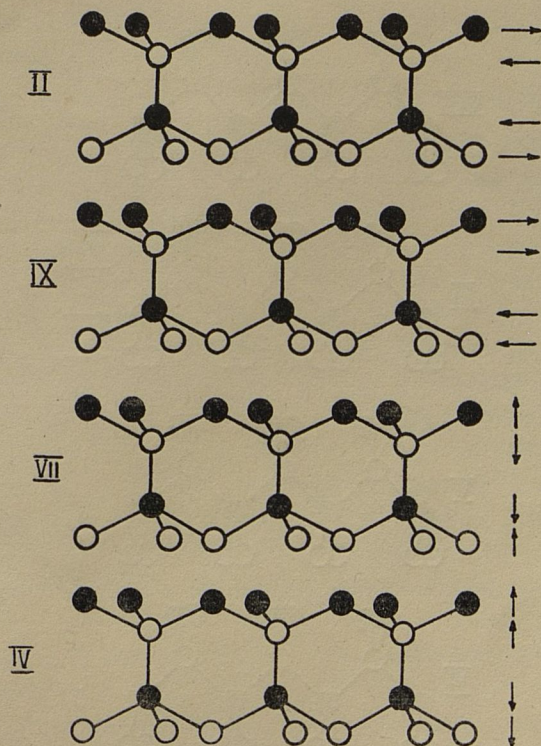


FIG. 3. Diamond: normal and tangential oscillations of the octahedral layers.

give us four modes of vibration; the directions of movement of the atomic planes are indicated by arrows in the figures. Fig. 4 shows the structure of diamond as viewed in a direction slightly inclined to a face diagonal and exhibits the cubic layers of atoms. The directions of movement of these layers in the four possible modes are likewise indicated by arrows in the figure.

Very simple considerations enable us to arrange the nine normal modes of vibration of the diamond structure in the descending order of their frequencies as indicated by the Roman numerals entered against them in Figs. 2, 3 and 4. The triply degenerate oscillation of the two interpenetrating lattices against each other shown in Fig. 2 would evidently have the highest frequency of all, since the movement involves variation of all the four bond lengths and all the six bond angles at each carbon atom; the restoring forces brought into play would therefore be the maximum possible. It is likewise evident that the mode marked IX in Fig. 3 would have the lowest frequency of all and the mode marked VIII in Fig. 4 would be the next lowest. For, in neither of these modes is there any variation of the bond lengths; in mode

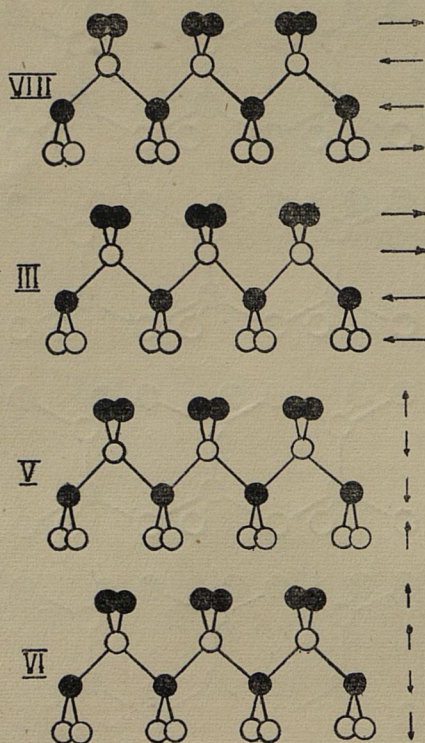


FIG. 4. Diamond: normal and tangential oscillations of the cubic layers.

IX, only two bond angles vary and in mode VII only four bond angles, the rest of them remaining unaltered. *Per contra*, the same modes but with the relative phases of motion of the adjacent layers reversed, *viz.*, mode II shown in Fig. 3 and mode III shown in Fig. 4 may be expected to have high frequencies which follow that of mode I in the order indicated. It remains to determine the sequence of the frequencies of the four remaining modes. It is obvious that the modes marked V and VI in Fig. 4 would have identical frequencies; for in these modes, the cubic layers which move normally to themselves, in other words along the cubic axis, are equidistant. Finally, we remark that the modes marked IV and VII in Fig. 3 may be expected to have frequencies respectively higher and lower than the common frequency of modes V and VI, though the differences would not be large. In mode IV, the oscillation involves the maximum stretching of one bond out of the four in the successive layers of the structure, the three others remaining invariable, while the mode VII, the bond along which the motion takes place remains of invariable length, while the three other bonds inclined at a large angle to the direction of movement are tilted periodically. The restoring forces

acting in the direction of movement may be expected to be distinctly greater in the former case than in the latter.

5. NUMERICAL EVALUATION OF THE FREQUENCIES

Exact formulæ are readily derived for the eight distinct frequencies of vibration in terms of the force constants expressing the interactions between each carbon atom and the surrounding ones. The equations of motion from which these formulæ are derived take a very simple form by reason of the fact that the relative displacements of the atoms are either zero or else are twice the value of the absolute displacement of each atom. The force-constants are most conveniently defined in terms of the components of the relative displacements and the forces of interaction resolved along the three cubic axes and considering their ratios. The symmetry of the structure results in a very considerable diminution in the number of distinct force-constants: it is found that two constants express the interactions with the four nearest neighbours, five others the interactions with the twelve next nearest neighbours, and five more the interactions with the twelve more distant neighbours. However, on writing down the equations of motion, it emerges that only three of the five force-constants for the next nearest neighbours actually appear in them and that the five force-constants for the twelve more distant neighbours also appear in the equations as sums of which there are only two. Accordingly, if we restrict ourselves to the interactions with the twenty-eight nearest neighbours of any given atom, we have only seven force-constants to deal with.

The seven force-constants referred to above will be denoted by α , β for the first four atoms; θ , ϕ , ψ for the next twelve and k and χ for the twelve atoms still further out. By way of explanation, it may be stated that the force-constant α refers to the case in which the force and displacement are both along the same cubic axis, while β refers to the case in which they are mutually perpendicular. The constant θ refers to the case in which the force and displacement are parallel to each other but are both perpendicular to the line joining the atoms which is a face-diagonal of the cube; ϕ and ψ refers to the cases in which the component forces and displacements both lie in the same plane as this diagonal, but the force and displacement are parallel to each other for ϕ and perpendicular for ψ . The constant k refers to the cases in which the components of force and displacement are parallel to each other while χ refers to the cases in which they are mutually perpendicular. k and χ both represent the joint effect of a whole set of twelve atoms.

Table I shows the eight frequencies of vibration arranged in the sequence already explained which will be found entered in the first column. The

TABLE I
Evaluation of Frequencies

Mode No.	Degeneracy	Complete formula $4\pi^2\nu^2c^2m =$	a, β only	$a, \beta, \theta,$ ϕ, ψ only	$a, \beta, \theta,$ $\phi, \psi,$ k, χ
I	3	$4a + 12k$	1332	1332	1332
II	8	$3a + \beta + 2\theta + 4\phi - 2\psi + 3k - 3\chi$	1250	1285	1250
III	6	$2a + 2\beta + 4\theta + 4\phi + 6k + 6\chi$	1162	1232	1239
IV	4	$a + 2\beta + 2\theta + 4\phi + 4\psi + 9k - 6\chi$	952	1099	1149
V & VI	3+3	$2a + 8\phi + 6k$	942	1088	1088
VII	4	$3a - 2\beta + 2\theta + 4\phi + 4\psi + 3k + 6\chi$	931	1068	1008
VIII	6	$2a - 2\beta + 4\theta + 4\phi + 6k - 6\chi$	651	752	740
IX	8	$a - \beta + 2\theta + 4\phi - 2\psi + 9k + 3\chi$	460	538	621

second column shows the degeneracy of each of these modes. The total of the figures shown in this column amounts to forty-five as is to be expected. The third column shows the operative force-constants in each case in terms of the seven force-constants, viz., a, β for the first group; θ, ϕ, ψ for the second group; k and χ for the third group. In the fourth, fifth and sixth columns are given respectively the values of the frequencies calculated with only the first two constants, then with only five and finally with all the seven. The values of the constants in each case have been so chosen as to give the same frequency for the principal mode. They are given in Table II.

It will be remarked from Tables I and II that even with only two force-constants we obtain a rough approximation to all the frequencies and that with five constants we get a fair approximation to the values calculated with all seven constants shown in the last column of Table I. It will also be seen from Table II that the force-constants fall off rapidly in magnitude as we proceed to the more distant neighbours. The magnitudes of the force-constants in each group are also related to each other in the manner that could have been expected *a priori* from their respective definitions as given above.

TABLE II
Values of Force-Constants Used

Force-constants	Table I, Column 4	Table I, Column 5	Table I, Column 6
a	3.135×10^5 dynes/cm.	3.135×10^5 dynes/cm.	2.78×10^5 dynes/cm.
β	$1.637 \times$..	$1.682 \times$..	$1.746 \times$..
θ	..	$0.012 \times$..	$0.010 \times$..
ϕ	..	$0.262 \times$..	$0.262 \times$..
ψ	..	$0.240 \times$..	$0.228 \times$..
k	$0.12 \times$..
χ	$0.00 \times$..

6. THE SCATTERING OF LIGHT IN DIAMOND

Spectrograms of the light scattered by diamond when illuminated by the light of a mercury arc lamp exhibit, for each of the monochromatic radiations of the incident light, a single sharp line with a frequency shift of 1332 cm.^{-1} which may be identified with the highest of the frequencies listed in Table I. But no lines appear with frequency shifts other than that mentioned. This is readily understood, since in all the modes except that of the highest frequency, the atomic oscillations have opposite phases in the successive layers, and hence the effects arising at these layers cancel each other out. Overtones and combinations of the frequencies of all the normal modes are, however, permitted to appear as frequency shifts in light scattering, thereby making the existence of these modes open to observation. That diamond would exhibit this type of light-scattering was theoretically predicted, following which experimental studies undertaken by Dr. R. S. Krishnan confirmed the expectations.

The second-order spectrum of light scattering is of extremely low intensity, and one has necessarily to use diamonds of small size for the experiments. Further, it is necessary to record the spectrum under high dispersion to enable its features to be adequately exhibited. These difficulties are successfully overcome by the aid of the extremely intense $\lambda 2537$ radiations

emitted by a quartz water-cooled mercury arc when it is set between the poles of an electro-magnet. It is necessary, of course, to employ diamonds which are transparent to the ultra-violet region of the spectrum. In these circumstances, it is also essential to use mercury vapour as a filter inside the spectrograph to absorb the intense $\lambda 2537$ radiations before they reach the photographic plate, and thus prevent its fogging.

Spectrograms obtained in the manner explained are reproduced as Fig. 1 in Plates II and III respectively. The spectrum in Plate II was recorded with a medium-sized spectrograph and that in Plate III with a larger instrument of higher resolving power. A microphotometer record of the spectrum obtained with the smaller instrument is reproduced in juxtaposition with the spectrum itself as Fig. 2 in Plate II, below which has been placed the spectrum of the mercury arc alone as a comparison. Fig. 2 in Plate III reproduces the microphotometer record of the second-order spectrum obtained with the larger instrument and below it the spectrum itself to admit of ready comparison with the features seen in it.

The features visually observed in the spectra and confirmed by inspection of their microphotometric records are diagrammatically represented in Fig. 5 below, the measured frequency shift being indicated against each feature.

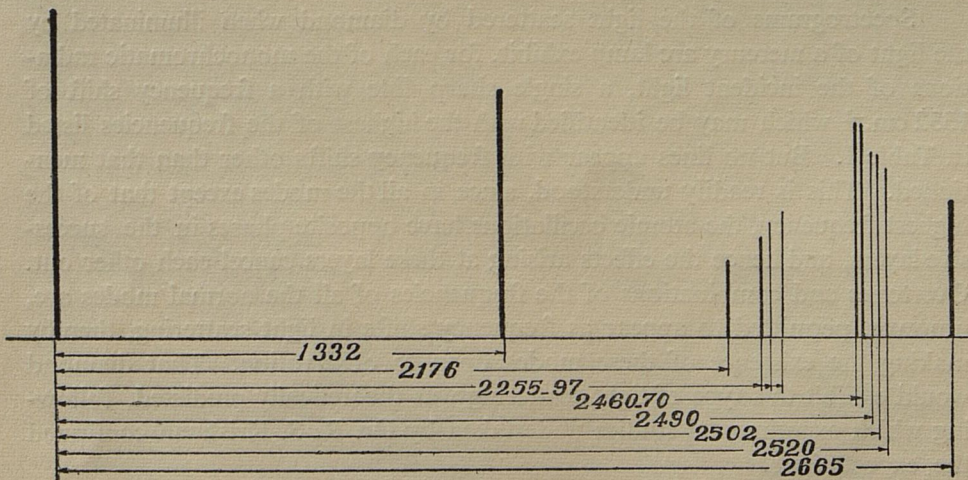


FIG. 5. Frequency shifts in light scattering.

Very conspicuous is the sharply defined peak of intensity terminating the second-order spectrum and exhibiting a frequency shift of 2665 cm.^{-1} . This is clearly to be identified as the octave of the principal mode of vibration having a frequency shift of 1332 cm.^{-1} : its measured spectral width of

8 wave numbers is also approximately double the spectral width of that frequency shift at room temperature.

Very conspicuous also in the microphotometer records is the sharply defined peak of intensity with a frequency shift of 2176 cm^{-1} . This is clearly the octave of the common frequency 1088 cm^{-1} of modes V and VI listed in Table I.

Of much greater intensity than either of the peaks mentioned above is that which can be recognised both in the spectra and in the microphotometer records as a clearly resolved pair of lines whose frequency shifts are 2460 and 2470 cm^{-1} respectively. The calculated frequency of the octave of mode III in Table I is 2478 cm^{-1} and this is sufficiently close to the position of the doublet to justify our identifying the latter with it.

Close to the doublet but clearly separated from it appear a group of rather diffuse lines whose frequency shifts are 2490, 2502 and 2520 respectively. The mean of these three shifts is 2504 and we may therefore identify the triplet of lines as being the octave of mode III in Table I whose calculated value is 2500 cm^{-1} .

Finally, we have a group of rather inconspicuous maxima, of which the most evident is one with frequency shift of 2255 cm^{-1} followed by a series of others with larger frequency shifts. The octave of mode IV the frequency of which is 2298 cm^{-1} lies within this range.

7. SOME CONCLUDING REMARKS

Spectroscopic investigation of the scattering of light in diamond thus decisively confirms the theoretical result that its structure possesses a discrete set of normal modes of vibration with well-defined frequencies forming a sequence as indicated in Table I. Various details revealed by the study, viz., the great differences in the relative intensities with which the various modes appear and the spectral splitting which some of them exhibit are also readily explicable.

The non-appearance of modes VIII and IX as frequency shifts even in the second-order scattering is not surprising. In these modes of vibration, neighbouring atoms of carbon do not approach or recede from each other but move laterally. Hence, no very sensible variations in the optical polarisability of the structural units are to be expected. *Per contra*, the approach and recession of neighbouring carbon atoms is very conspicuous in modes I, II and III and the appearance of the octaves of these modes with notable intensities is therefore in accord with expectation. That modes II and III

appear even more strongly than mode I is clearly a consequence of their degeneracies being 8 and 6 respectively as compared with the degeneracy 3 of mode I. The strength with which the peak at 2176 cm.^{-1} is recorded is likewise explicable as due to the superposition of the effect of six modes having a common frequency.

That a second-order spectrum of light-scattering is at all observable becomes intelligible when it is recalled that the oscillators which are set in vibration and diffuse the incident radiation with a diminished frequency are the structural elements in the crystal. These are of extremely small dimensions and contain relatively few atoms. Hence, the absorption by them of a quantum of energy would result in vibrations of which the amplitude cannot be considered as infinitesimally small in relation to the interatomic distances. It follows that the periodic variation of optical properties resulting from the vibration would exhibit anharmonicity. Frequency shifts corresponding to overtones and combinations of the frequencies of the normal modes can therefore appear in the scattered light. The mechanical anharmonicity associated with vibrations of finite amplitude may likewise result in the splitting up of energy levels which in the harmonic oscillator approximation can be considered as identical.

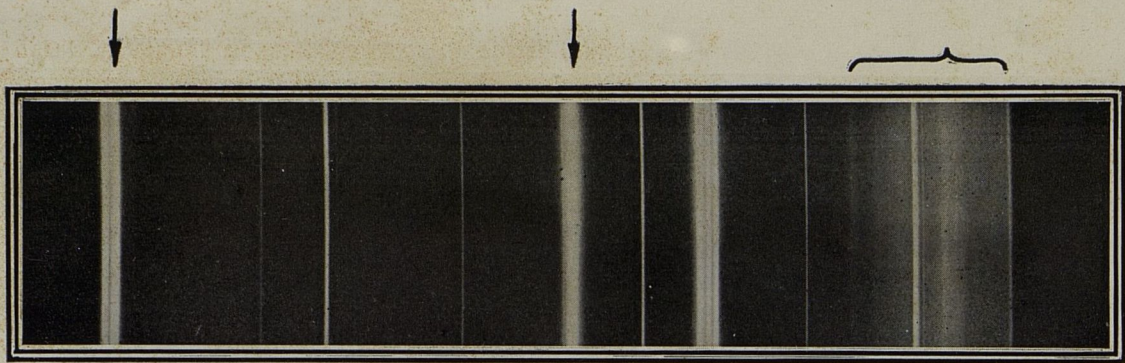


FIG. 1

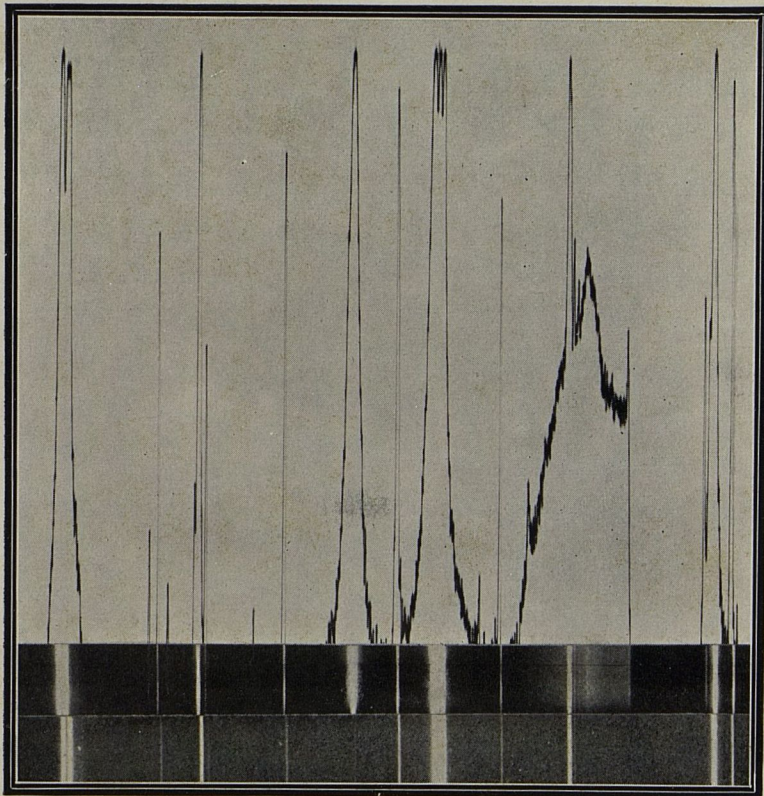


FIG. 2

Scattering of light in diamond: medium spectrograph.

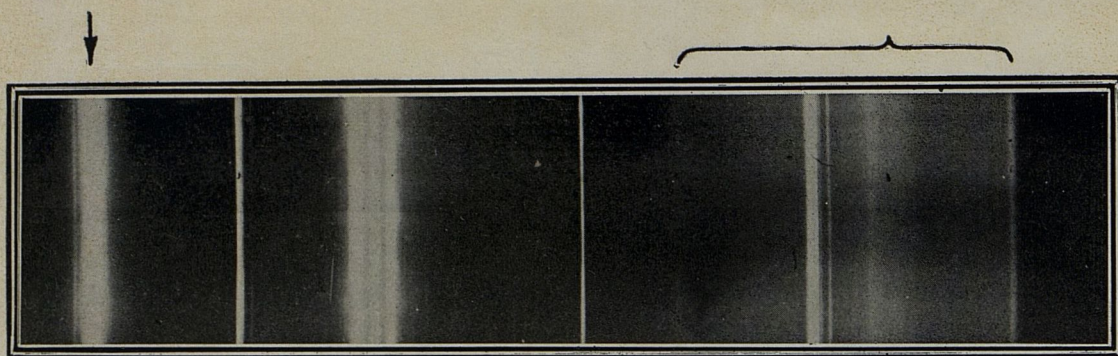


FIG. 1

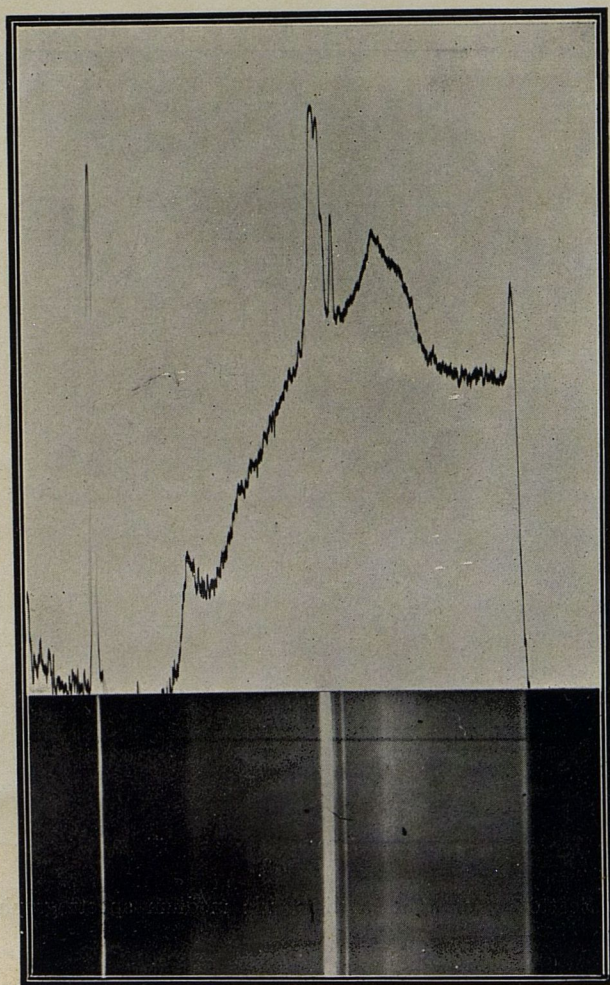


FIG. 2

Scattering of light in diamond: large spectrograph.

