THE SCATTERING OF LIGHT IN DIAMOND AND ITS RAMAN SPECTRUM

By Dr. R. S. Krishnan

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

1. Introduction

UNLIKE many common solids, diamond cannot be had in large lumps for purposes of experimentation and one has to be satisfied with comparatively small specimens. In spite of this handicap, diamond offers such notable advantages that it is easily the best material which the physicist has at his disposal for testing theories of the spectroscopic behaviour of crystals and the scattering of light in them. In the first place, the elementary nature of diamond and the simplicity of its crystal structure make it possible to work out the consequences of any theory without excessive labour and thus obtain the data which could be compared with the experimental facts. Then again, the high refractive index of diamond and the fact that it is a valence crystal give it a large scattering power which make it possible to work with quite small specimens and yet obtain results. Further, the low atomic weight of carbon and the strength of the binding forces between the atoms result in spreading the vibration spectrum of the crystal over a wide range of frequencies. This is a feature which is highly advantageous in the critical study of Raman spectra. The frequency shifts being large, they appear widely dispersed and therefore well-resolved. Further, the greater part of the spectrum exhibiting the frequency shifts is recorded well away from the position of the exciting radiation which, unless it is completely eliminated, results with prolonged exposures in recording various spurious effects in its vicinity even with the best of instruments. Further, the fact that the vibration-frequencies are for the most part very high in the case of diamond has an important consequence namely that, except at the lowest end of the frequency range, the vibrations are not thermally excited to an appreciable extent. Secondary effects of thermal origin, *viz.*, the broadening and shifting of the Raman lines, which are of considerable importance in the case of many crystals even at ordinary temperatures, are hence negligible in the case of diamond. This has been clearly shown by the recent investigations of the author (Krishnan, 1946) on the temperature variations of the Raman frequencies of diamond. The width of the principal Raman

line with a frequency shift of 1332 cm.$^{-1}$ at room temperature is no more than that arising from instrumental and photographic factors, though at higher temperatures it broadens and has an easily measurable width.

To utilize to the fullest extent the advantages referred to above, it is necessary to work with non-luminescent diamonds. Such diamonds are also transparent in the ultra-violet and it becomes possible to employ the $\lambda\,2536 \cdot 5$ resonance radiation for exciting the Raman effect and thus take advantage of the intrinsic brightness of this radiation and its large scattering power arising from the λ^{-4} law. If the arc is effectively water-cooled and held against the wall of the tube with the aid of a magnet, the radiation is highly monochromatic and is free from any accompanying continuous spectrum. Incidentally also, by working in the ultra-violet, the larger dispersion and resolution of quartz spectrographs in that region are utilised. The importance of this in the study of Raman spectra exhibiting numerous closely spaced lines can scarcely be overstressed.

The use of an intense radiation for excitation is accompanied by certain complications, viz., a general fogging of the photographic plate due to diffuse general illumination inside the spectrograph, as also spurious lines and wings in the immediate vicinity of the exciting line arising from diffraction effects present in any optical instrument, the intensity of which is directly proportional to the brightness of the exciting radiation falling on the slit. The special advantage of using the $\lambda\,2536 \cdot 5$ resonance radiation is that these spurious effects can, with care, be completely eliminated by absorbing the exciting radiation from the scattered light by a filter of mercury vapour. The filter can be made to work so effectively that the mercury line $\lambda\,2534 \cdot 8$ the intensity of which is extremely small compared to the $\lambda\,2536 \cdot 5$ resonance radiation appears stronger than its companion in the recorded spectra. In fact, when examined under high resolution the core of the resonance radiation is found to be completely removed.

Several investigations by the author on the Raman spectrum of diamond using the $\lambda\,2536 \cdot 5$ mercury resonance radiation as exciter have already been reported in earlier publications (R. S. Krishnan, 1944, 1945 and 1946). A notable advance has, however, been made possible by reason of a recent acquisition by Sir C. V. Raman of an exceptionally colourless plate of diamond of the non-luminescent type (N.C. 174). This has enabled the author to reinvestigate the scattering of light in diamond with a large Hilger (E1) quartz spectrograph and to obtain spectra which are fully resolved and the structure of which is exhibited without any ambiguity. Preliminary reports of the results have already appeared in *Nature* (Krishnan, 1947 *a, b, c*). Further details and a full discussion are presented in this paper.

2. LIGHT-SCATTERING AND CRYSTAL DYNAMICS

The aim of the present investigation is the settlement of the fundamental question of the nature of the vibration spectra of crystals. The study of the scattering of light by the method of the Raman effect has proved its power so fully in other directions that one need scarcely doubt that it is the right method to settle also the problems of the solid state. In this connection, one may recall the pregnant remark made long ago by the late Lord Rutherford (1931) that the Raman effect " has proved, and will prove, an instrument of great power in the study of the theory of solids ". It will probably be useful before we proceed to describe the experimental results, to state the issues which need settlement and to consider them against the appropriate theoretical background.

Historically, the subject of the scattering of light in material media was first approached by theorists from two distinct points of view. The first point of view due to the late Lord Rayleigh, is that in which the individual particles of which the medium is composed, *e.g.*, the molecules of a gas, are considered to be the agents responsible for the phenomenon. The other point of view, first put forward by Einstein and later elaborated by Leon Brillouin, is that in which the medium is regarded as a continuum and the diffusion of light is ascribed to the " reflection " of the light waves by the sound waves of thermal origin assumed to be present and traversing it in all directions. Which of these two points of view is the more appropriate one clearly depends on the circumstances of the case, and is an issue to which experimental study is capable of returning a decided answer. For instance, in a gas, the Rayleigh point of view is the correct one, as is clearly shown by the fact that when we examine the light diffused by hydrogen gas with a Fabry-Perot etalon, we observe a broadening of the spectral lines which corresponds to the Maxwellian distribution of velocities of translation of the molecules (C. S. Venkateswaran, 1942 *a*). On the other hand, a similar examination of the light diffused by ethyl and methyl alcohol clearly shows a splitting of the spectral lines into two polarised components, their separation varying with the angle of observation (Sunanda Bai, 1942). Surprisingly enough, the same phenomenon is also observed in the highly viscous liquid glycerine (C. S. Venkateswaran, 1942 *b*). From these observations we shall certainly be justified in inferring that liquids exhibit a *coherent modified scattering of light* which may be regarded as a Raman effect due to pulsations of optical density occurring in phases definitely correlated with each other in adjacent volume elements of the medium. Alternatively, we may regard the spectral components as due to the Doppler shifts of frequency arising from the reflection of the light waves by moving sound waves. But

we would clearly not be justified in extending such notions to the consideration of the optical effects due to the rotations and vibrations of the molecules in a liquid. For explaining the large spectral shifts arising from such rotations and vibrations which are actually observed with liquids, we naturally go back to the Rayleigh point of view, and consider the individual particles in the medium as the responsible agents. For, the dynamics of such rotation and vibration is essentially a matter of the individual behaviour of the molecules, though indeed they may be influenced and partly modified by the interactions occurring between a molecule and its immediate neighbours.

Coming now to consider the case of crystals, it is a fact of observation that free and practically undamped propagation of elastic waves is possible in them. It is also known that in transparent crystals such waves give rise to optical effects whose strength is determined by their piezo-optic constants. There is therefore no reason to doubt that elastic waves of the three different possible kinds and of various wave-lengths, both larger and smaller than the wave-length of light, exist in crystals as the result of thermal agitation and that such waves give rise to optical stratifications of the same wave-length. But these optical stratifications cannot give rise to any observable scattering of light, unless their wave-length and orientation in relation to the direction of travel of the incident light waves is such as to give rise to a coherent reflection of the latter by the successive stratifications. The optical effects of all other stratifications would cancel out by interference. It follows *that the elastic waves of thermal origin would not give rise to any observable effect in the spectrum of light scattering*, except that which appears with small frequency shifts in the nature of Doppler effects in the immediate vicinity of the incident radiation.

While the continuum point of view is thus appropriate enough in considering the low frequency or elastic vibrations, dynamical principles and the observed experimental facts alike suggest that the particle point of view is the correct approach in respect of the vibrations of high frequencies appearing in the Raman spectrum. For, the high frequencies are themselves an indication that the vibrations are those of the individual atoms in the cells of the structure and not those of macroscopic volume elements in the crystal. Hence, the problem is one in particle dynamics analogous to the problem of the vibration spectra of polyatomic molecules and the results to be expected would be of a similar nature, *viz.*, a set of monochromatic frequencies, thus affording a natural explanation of the observed fact that crystals exhibit Raman spectra consisting of discrete lines. This is in fact, the approach to the subject made in the theory of the vibration spectra put forward by Sir C. V. Raman (1943), in which it is shown that a crystal containing p

atoms in each of its unit cells would have in general, $(24p-3)$ discrete frequencies of atomic vibration, though this number may be very considerably reduced by reason of the symmetry of the crystal.

On the other hand, the well-known theory of Debye, and the lattice theory of Born and Karman are both based on the belief that the ideas of continuum physics can be applied in respect of the high or infra-red frequencies of vibration of solids. In fact, the Born-Karman theory expressly assumes the existence of " optical waves " of such high frequencies. In the belief that a crystal containing N atoms necessarily possesses $3N$ *different* frequencies of vibration, the theory postulates also that the " optical wavelengths " form a triply harmonic sequence in the same way as the acoustic wave-lengths. The vast majority of the wave-lengths thus assumed to exist are comparable with the lattice spacings of the crystal and as a consequence, the vibrations postulated in the theory have a diffuse continuous spectrum of frequencies spread over a wide range and not a set of discrete lines as actually observed in the Raman effect. An escape from this obvious contradiction with the facts is sought by means of the assumption that the entire continuous spectrum is rendered inaccessible to observation by reason of optical interference except only those frequencies which possess the right wave-length to give a coherent reflection, as in the case of the acoustic vibrations. We need not here stop to discuss the validity of this suggested explanation or the validity of the basic postulates on which the Born-Karman theory rests, since, as we shall see, the experimentally observed facts in the case of diamond give the answer to both of these questions. It will suffice here to state the points at issue which have to be settled by experiment.

I. Are the vibrations in crystals which manifest themselves in the Raman spectrum, " waves " extending through the volume of the crystal, or are they the vibrations of the atoms in the individual cells of the lattice ?

II. Is the complete vibration spectrum of the crystal in the infra-red region a continuous diffuse spectrum, or is it a discrete spectrum exhibiting a finite set of monochromatic frequencies ?

3. The Scattering of Light in Diamond

We shall now briefly describe the various features observed in a fully exposed spectrum of the scattered light in diamond. Using the Hilger medium spectrograph and the diamond of the ultra-violet transparent type (N.C. 174), numerous photographs were taken with exposures varying from a couple of seconds to several hours. The spectrum of diamond recorded with 2 minutes exposure is reproduced in Fig. 1 (*b*) together with the spectrum of the mercury arc [Fig. 1 (*a*)]. A heavily exposed spectrum recorded with

6 hours' exposure is shown in Fig. 2 (b). The Raman line with a frequency shift of 1332 cm.$^{-1}$ appeared on the plate with an exposure of only five seconds. Half a minute was needed to record the Doppler-shifted Brillouin components centred about the exciting radiation, the latter itself being effectively filtered out by a mercury vapour screen. See Fig. 1 (b). The same effect could be seen more clearly in the enlarged photographs reproduced in Figs. 1 (c) and (d) and in the microphotometric records shown in Figs. 1 (e) and (f). Half an hour's exposure sufficed to record the second-order Raman spectrum, while the anti-Stokes frequency shift of 1332 cm.$^{-1}$ appeared after forty-five minutes. An exposure of 3 hours resulted in heavily overexposing the second-order Raman spectrum, but was useful in bringing out the weak terminal line having a frequency shift of 2015 cm.$^{-1}$ which was liable to be overlooked with smaller exposures (see Fig. 3). Owing to the smaller dis-
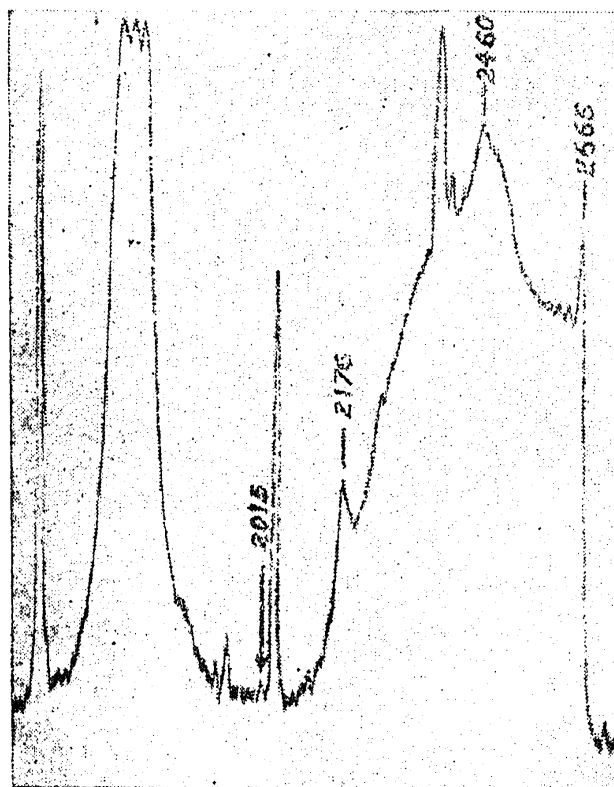

FIG. 3. Microphotometer record of the second order Raman spectrum of diamond showing the terminal line 2015 cm.^{1}

persion of the medium quartz spectrograph, the real nature of the second-order Raman spectrum of diamond is not exhibited as clearly as could be desired. The spectrum was therefore examined under the higher dispersion and resolution given by the Hilger (E1) large quartz spectrograph. Typical photographs recorded with different exposures are reproduced in Figs. 4 and 5. The principal feature noticeable in the spectra is the appearance of a whole series of sharply defined Raman lines clearly resolved from each

other. Longer exposures up to 10 hours taken with the medium quartz spectrograph revealed no new features except a couple of fainter lines in the spectrogram. These fainter lines have been identified as the 1332 Raman line excited by the feeble mercury lines. It is very significant that no hint or trace of the continuous spectrum of elastic vibrations forming the so-called " acoustic branches " of the lattice spectrum of the crystal appears on the plate even with the longest exposures. These facts will be evident from a comparison of Figs. 2 (*a*) and (*b*).

From the experimental facts stated above, it is clear that the parts of the vibration spectrum of diamond in the lower and upper ranges of frequency differ radically in their behaviour. The first part is totally inactive in light-scattering, while the second part is strongly Raman-active, giving an intense second-order spectrum. The character of the spectrum is also totally different in the two ranges of frequency. While the spectrum of the elastic vibrations is necessarily a continuous one, the discrete nature of the atomic vibration spectrum in the upper ranges of frequency is clearly manifested in the second-order Raman effect; the overtones and summations of the primary vibration frequencies appear under adequate instrumental power clearly resolved into numerous closely spaced sharp lines. These differences are fundamental and compel us to recognize that the two parts of the vibra-tion spectrum are physically of a different nature. In the lower ranges of frequency, we are concerned with elastic waves traversing the crystal from end to end and forming stationary wave-patterns, while in the upper ranges of frequency, we are concerned with the vibration of the atoms in the indi-vidual cells of the crystal lattice. The spectroscopic facts thus give a decisive answer to the theoretical issues stated at the end of the preceding section. They show that the assumptions on which the Debye and Born-Karman theories are based are unjustified and that the conclusions regarding the nature of the atomic vibration spectra to which those theories lead are altogether untenable.

4. THE DOPPLER-SHIFTED COMPONENTS

The magnitude of the frequency shifts.—As already indicated in the last section, the spectrum of the light scattered by diamond when examined with a medium quartz spectrograph using a fine slit exhibits a doubling of the λ 2536·5 line, the latter itself being completely quenched by a mercury vapour filter (see Fig. 1). The doubling is in the nature of a Doppler effect arising from the selective reflection of the monochromatic light by the approaching and receding sound waves of thermal origin in the medium. The components are called Doppler-shifted components and are sometimes

known as Brillouin components. Their frequency shift from the exciting line is given by the formula due to Brillouin

$$\Delta \nu = \pm 2\nu \frac{v}{c}\mu \sin \theta/2, \qquad (1)$$

where ν, μ, v and c are respectively the frequency of the incident radiation, refractive index of the medium, velocity of sound in the medium and the velocity of light. θ is the angle of scattering. This is the first time that the existence of sound waves of thermal origin in a solid has been demonstrated without the use of interferometers. The success is mainly due to the fact that the velocity of sound and the refractive index of diamond have high values. The resulting Doppler displacements in the frequency of the λ 2536·5 radiation scattered transversely in diamond are large enough to be recorded directly without interferometric aid using a quartz spectrograph of moderate power.

It is well known that for any given direction in a crystal, there are in general three distinct sound velocities, one longitudinal and two transverse. One should therefore expect to observe six Doppler-shifted components three on either side of the exciting radiation. The spectrogram taken with diamond N.C. 174 and the medium quartz spectrograph, and reproduced in Fig. 1 (b) exhibited only two Brillouin components. This might be due to the small dispersion of the spectrograph. Moreover, diamond N.C. 174 had curved edges and as such, it was not quite suited for making a quantitative verification of equation (1) and also for investigating the directional variation of the velocity of sound in diamond. Another specimen of diamond of the non-luminescent ultra-violet transparent type, namely N.C. 60, was therefore chosen for the present investigation. It was in the form of a rectangular plate (10 × 6 × 1·5 mm.) with faces and edges well polished. X-ray diffraction studies (Ramachandran, 1946) indicated that the length, breadth and thickness of the diamond N.C. 60 were parallel to $01\bar{1}$, 111 and $\bar{2}11$ directions. As the specimen was slightly yellowish in colour, its transparency to the λ 2536·5 radiation was definitely less than that of N.C. 174.

Diamond N.C. 60 was clamped with its faces vertical and facing a vertical quartz mercury arc of special design. The light scattered in the transverse horizontal direction and emerging out of the smaller edge was focussed on the slit of a Hilger E1 large quartz spectrograph. The spectrum was photographed with exposures of the order of six hours using a slit width of 0·02 mm. A typical spectrogram together with a comparison spectrum of the mercury arc is reproduced in Fig. 6. In the spectrum of the direct arc the λ 2536·5 line has been completely absorbed. In the

scattered spectrum, on the other hand, one observes four displaced components which are more clearly seen in the enlarged photograph and the microphotometer record reproduced in Figs. 7 (*a*) and 8 (*a*) respectively. The
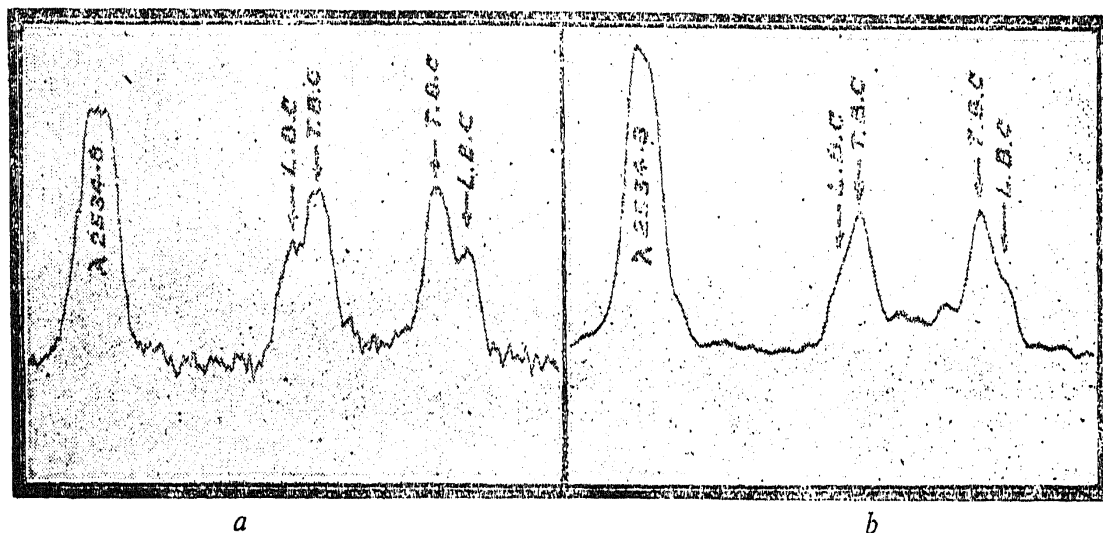

a   *b*

FIG. 8. Microphotometer records of thermal scattering in diamond for two different orientations : L.B.C. = longitudinal Brillouin components ; T.B.C. = transverse Brillouin components.

frequency shifts of the two pairs of Brillouin components are $\pm 8 \cdot 8$ cm.$^{-1}$ and $\pm 5 \cdot 4$ cm.$^{-1}$ and the corresponding values of the velocity of sound calculated from equation (1) are 18,080 and 11,000 metres per second. μ is taken as $2 \cdot 61$ for $\lambda 2536 \cdot 5$. It follows therefore that the outer pair of components arise from the longitudinal sound waves in diamond, while the inner brighter ones are due to the transverse sound waves. Unlike in many other crystals, the transverse components in diamond are brighter than the longitudinal components. The Doppler-shifted components have a finite width which might be attributed to the fact that the light incident on the plate of diamond was a convergent beam with a semi-angle of convergence of the order of 15°. The angle of scattering, θ, had a mean value of 90°.

Determination of the sound velocities in diamond.—For a cubic crystal, the squares of the three possible velocities for a sound wave travelling in a direction whose direction cosines are *l*, *m* and *n* are given by the three roots of v^2 in the following determinantal equation:—

$$\begin{vmatrix} c_{11}l^2 + c_{44}(m^2 + n^2) - \rho v^2 & (c_{12}+c_{44})\,lm & (c_{12} + c_{44})\,ln \\ (c_{12} + c_{44})\,ml & c_{11}m^2 + c_{44}(l^2 + n^2) - \rho v^2 & (c_{12} + c_{44})\,mn \\ (c_{12} + c_{44})\,nl & (c_{12}+ c_{44})\,nm & c_{11}n^2 + c_{44}(l^2 + m^2) - \rho v^2 \end{vmatrix} = 0 \quad (2)$$

where c_{11}, c_{12} and c_{44} are the three elastic constants and ρ the density. Using the values of the elastic constants of diamond obtained by Bhagavantam and Bhimasenachar (1946) by the ultra-sonic method, namely $c_{11} = 9 \cdot 5 \times 10^{12}$

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dynes/cm.^{2}, $c_{12} = 3 \cdot 9 \times 10^{12}$ dynes/cm.^{2} and $c_{44} = 4 \cdot 3 \times 10^{12}$ dynes/cm.^{2}, the values of the three possible sound velocities along specific directions perpendicular to the cubic axis, the dodecahedral axis and the octahedral axis in diamond have been evaluated. The variation of sound velocity with direction along the three sections has been graphically represented in Figs. 9, 10 and 11. A comparative study of these curves shows that the
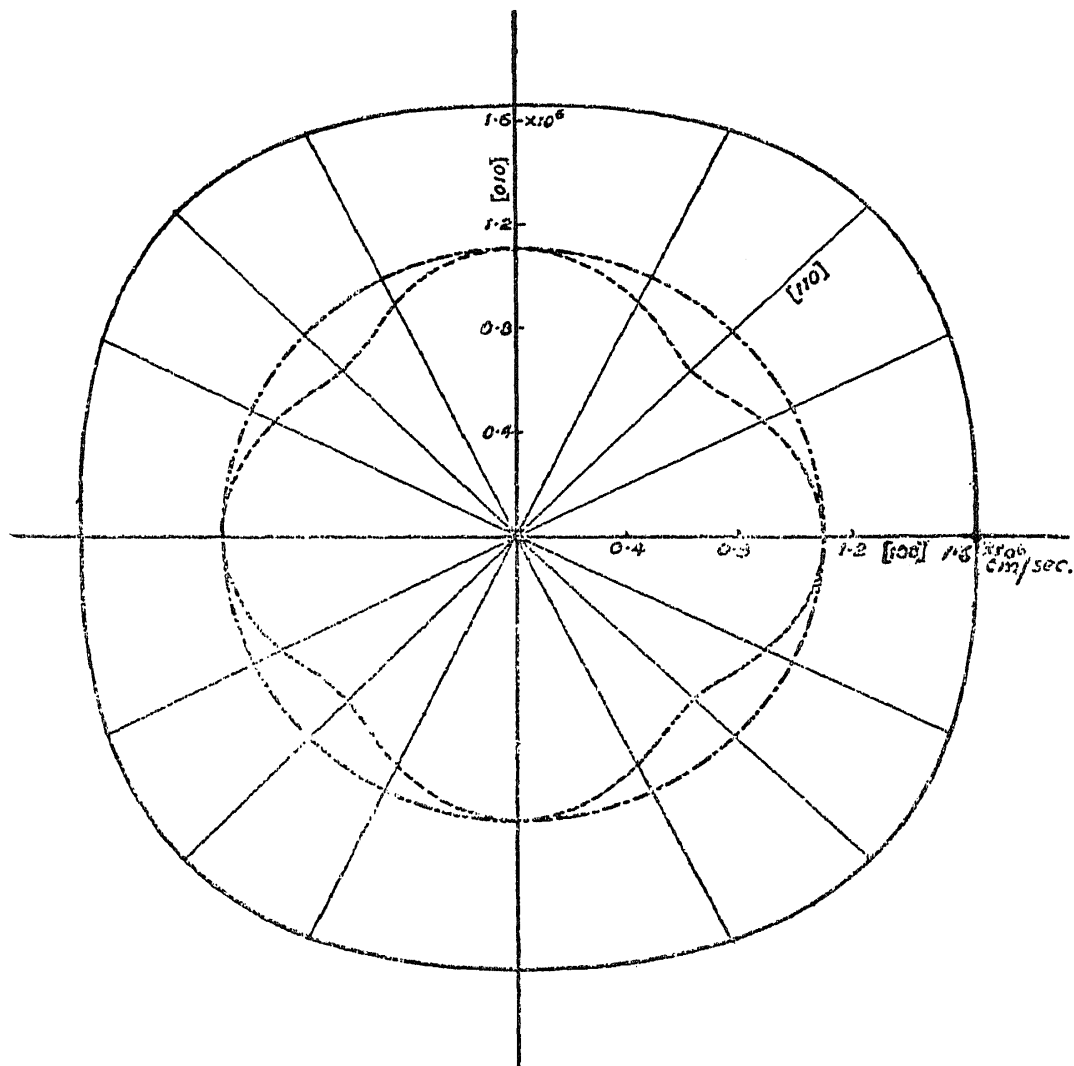

FIG. 9. Directional variation of sound velocities in diamond ; section perpendicular to the cubic axis. Continuous curve refers to longitudinal sound waves and broken curves to transverse sound waves.

two sets of transverse sound waves in diamond have very nearly the same velocity in all the directions. The maximum difference is along the dodeca-hedral axis, the velocities for the transverse waves being equal to 11,080 and 8,950 metres per second. This is why only one pair of transverse Brillouin components is recorded in the scattered spectrum of diamond. The longi-tudinal sound waves have the maximum velocity of 18,120 metres per second along the octahedral axis and the minimum velocity of 16,500 metres per second along the cubic axis.

In order to study the directional variation of sound velocity in diamond, the transversely scattered light was photographed using the large quartz spectrograph for different orientations of diamond (N.C. 60) with reference to the directions of illumination and observation. Enlarged photographs showing the Doppler shifted components corresponding to three different settings of the diamond are reproduced in Fig. 7 and two microphotometric
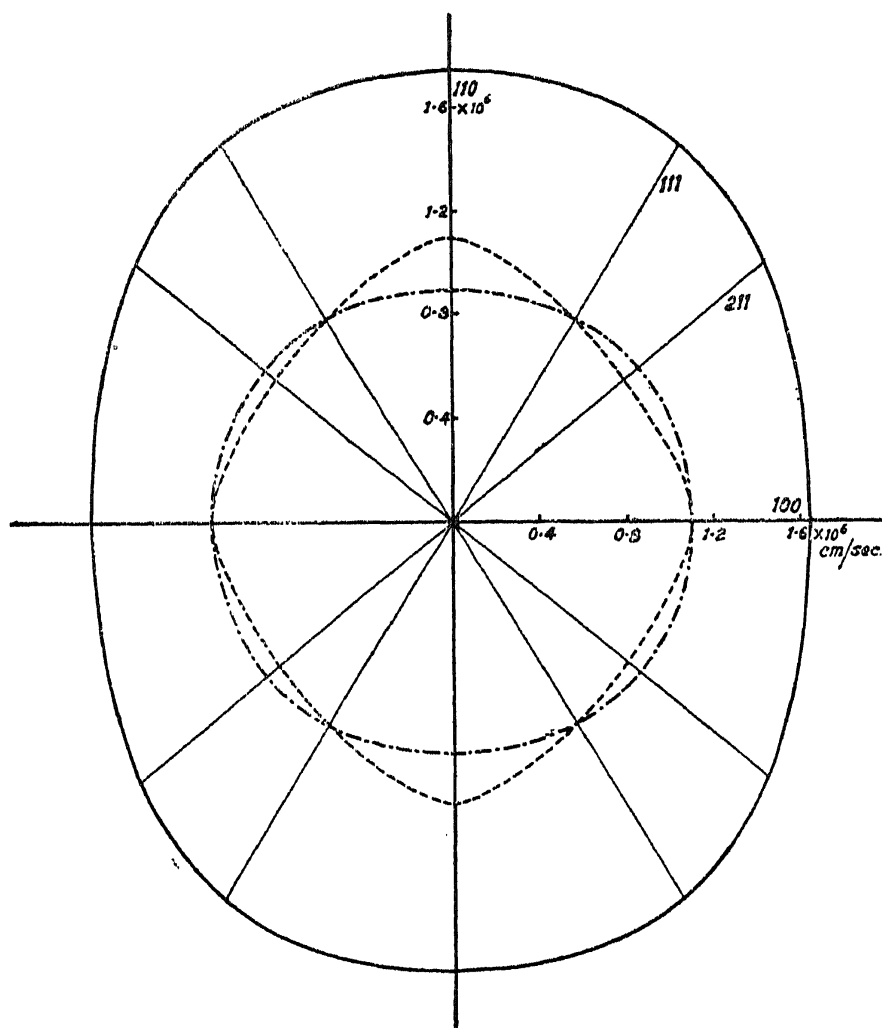

Fig. 10. Directional variation of sound velocities in diamond; section perpendicular t the dodecahedral axis.

records are included in Fig. 8. As is evident from the reproduced photographs, one observes only four Doppler-shifted components in light-scattering in diamond, one pair each due to longitudinal and transverse sound waves. The pair due to transverse sound waves is always brighter than the longitudinal components.

From a comparative study of the photographs reproduced in Fig. 7 and the microphotometric records in Fig. 8, it becomes evident that the velocity of sound waves varies with direction inside the diamond. For example, for the second setting, the inner and outer components are les

clearly separated from each other than for the other two settings, showing thereby that the velocities of longitudinal and transverse waves are nearer to each other in the second case than in the other two cases. Interchanging the directions of illumination and observation for a given setting of the plate of diamond did not change the nature of the pattern obtained.
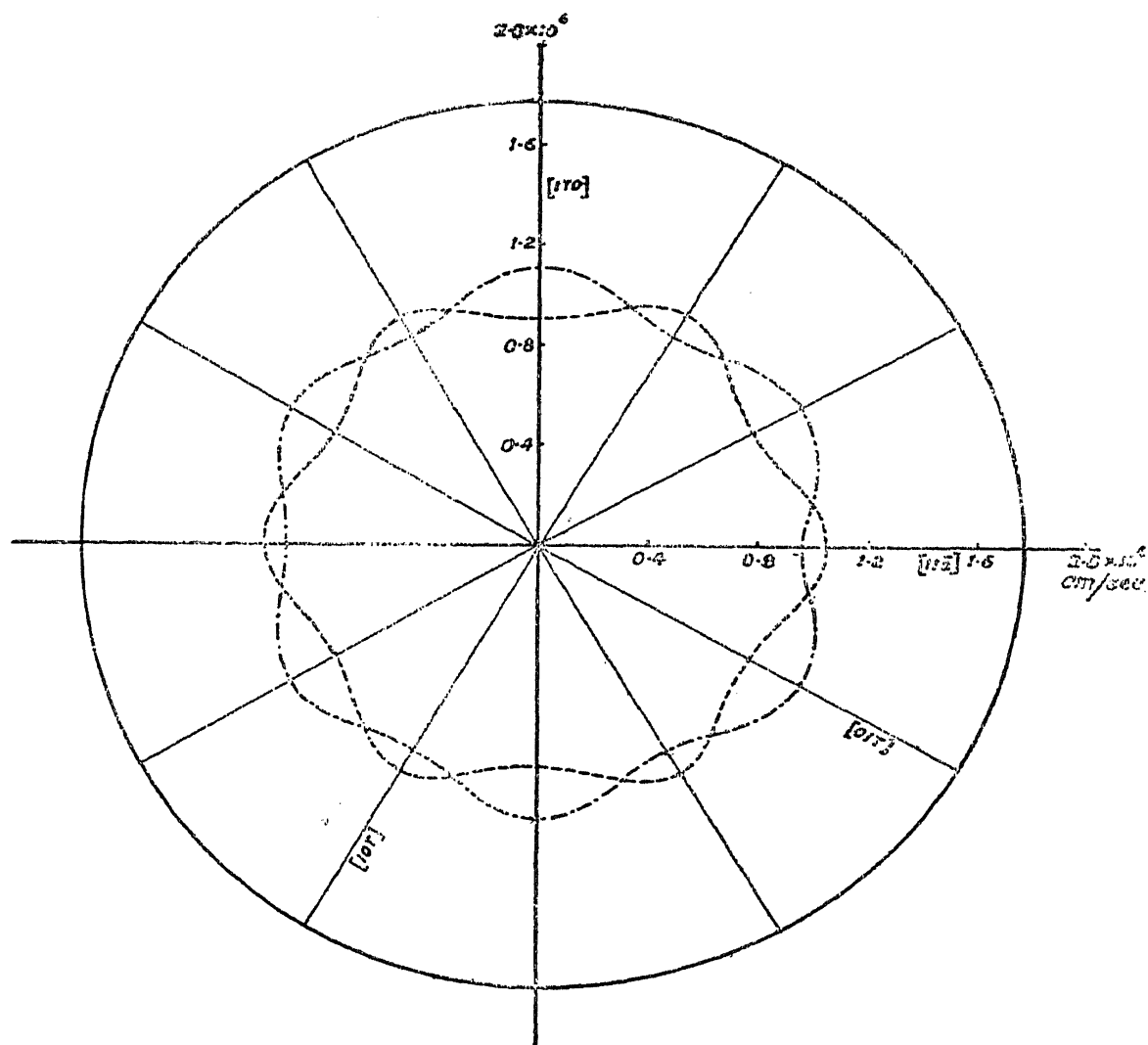

Fig. 11. Directional variation of sound velocities in diamond ; section perpendicular to the octahedral axis.

The frequency shifts of the longitudinal and transverse Brillouin components for the three different orientations of the diamond have been measured and the corresponding sound velocities have been evaluated. The values are entered in Table I. The theoretical values of the velocities of longitudinal and transverse sound waves corresponding to the first two settings of the diamond could be read off from the curves reproduced in Figs. 11 and 10. For the third setting the values were calculated directly from the known elastic constants of diamond. The agreement between the experimental and theoretical values of the velocity of sound in diamond is fairly satisfactory.

TABLE I

Setting	Incident beam parallel to	Direction of observation parallel to	Plane of Scattering parallel to	Nature of the Brillouin component	Frequency shift in cm.$^{-1}$	Velocity of sound in metres/sec.	
						Observed	Calculated
1	$\bar{2}11$	$01\bar{1}$	(111)	Longitudinal	$\pm 8\cdot 8$	18,080	17,800
	$\bar{2}11$	$01\bar{1}$	(111)	Transverse	$\pm 5\cdot 4$	11,000	$\begin{cases} 10,300 \\ 9,800 \end{cases}$
2	$\bar{2}11$	111	$(0\bar{1}1)$	Longitudinal	$\pm 8\cdot 0$	16,400	16,500
	$\bar{2}11$	111	$(01\bar{1})$	Transverse	$\pm 5\cdot 6$	11,500	$\begin{cases} 11,000 \\ 10,600 \end{cases}$
3	$01\bar{1}$	111	$(\bar{2}11)$	Longitudinal	$\pm 8\cdot 5$	17,500	17,300
	$01\bar{1}$	111	$(\bar{2}11)$	Transverse	$\pm 5\cdot 5$	11,200	10,500

Intensity of the Brillouin components.—Leontowitsch and Mandelstamm (1932) derived a formula for the intensity of the light reflected or transversely scattered by sound waves of thermal origin in the medium

$$I = \frac{\pi^2}{2\lambda^4} \, kT\mu^8 \left\{ \frac{2\,(p_{12}^2 + p_{44}^2)}{c_{11} + c_{12} + 2c_{44}} + \frac{p_{44}^2}{c_{44}} \right\} \tag{3}$$

where I is the intensity of light sattered by 1 cm.^{3} of the substance for natural light of unit intensity, λ the wave-length of light, μ the refractive index, c_{ik} elastic constants, p_{ik} Pockels' elasto-optical constants and T the temperature of the scattering substance. According to Hans Mueller's analysis (1938), the first term inside the double brackets is the contribution due to longitudinal sound waves, while the second term represents the contribution due to the transverse sound waves. The values of the elasto-optical constants for diamond as determined by G. N. Ramachandran (1947) are $p_{11} = 0\cdot 125$, $p_{12} = -0\cdot 325$ and $p_{44} = 0\cdot 11$. Putting these values of p_{ik} and the values of c_{ik} as determined by Bhagavantam and Bhimasenachar (1946) in equation (3), the contributions due to the longitudinal and transverse sound waves to the intensity of thermal scattering in diamond have been evaluated. The intensities of the longitudinal and transverse Brillouin components are respectively $1\cdot 14 \times 10^{-5}$ and $0\cdot 31 \times 10^{-5}$ for incident light of unit intensity. Thus according to the formula of Leontowitsch and Mandelstamm, the longitudinal components should be about four times more intense than the sum of the transverse components. This is in complete contradiction with the experimental observation, namely that the transverse Brillouin components are much brighter than the longitudinal components (see Figs. 7 and 8). The subject therefore requires further investigation.

Temperature dependence of intensity.—According to Leontowitsch and Mandelstamm's formula, the intensity of thermal scattering is directly proportional to the absolute temperature. In order to verify this result in the case of diamond the following procedure was adopted. For work above room temperature, a specially designed heater similar to the one described by the author in one of the earlier publications (Krishnan, 1946) was used. With the aid of a quartz medium spectrograph and diamond N.C. 174 two photographs of the scattered spectrum were taken on the same negative, one with the crystal maintained at room temperature, *i.e.*, 305° T. and the other at 570° T. For work below room temperature, a demountable Dewar flask with quartz windows was used. A mixture of solid carbon dioxide and alcohol formed the refrigerant for one observation below the room temperature, and liquid air for a second observation. Using the above arrangement the scattered light was photographed with the diamond maintained successively at 175° T. and 85° T.

The intensities of the Doppler-shifted components are markedly influenced by temperature. This is beautifully illustrated by the series of photographs reproduced in Fig. 12 (*a*) to (*d*). They represent the spectra of the scattered light taken with the diamond maintained successively at 570°, 305°, 175° and 85° T. The corresponding enlargements showing the Doppler shifted components and the companion mercury line $\lambda\,2534\cdot8$ are reproduced in Figs. 12 (*e*) to (*h*). It will be noticed from the reproductions that in contrast with the 1332 Raman line the intensity of which is practically unaffected by the change of temperature of the diamond, the Doppler-components become rapidly weaker with falling temperature. This is to be expected on theoretical grounds, since for the Doppler-shifted components $h\nu_s \ll kT$ while for the Raman line $h\nu_r \gg kT$. At room temperature, *i.e.*, at 305° T. the aggregate intensity of all the Doppler shifted components is less than one fourth the intensity of the Raman line.
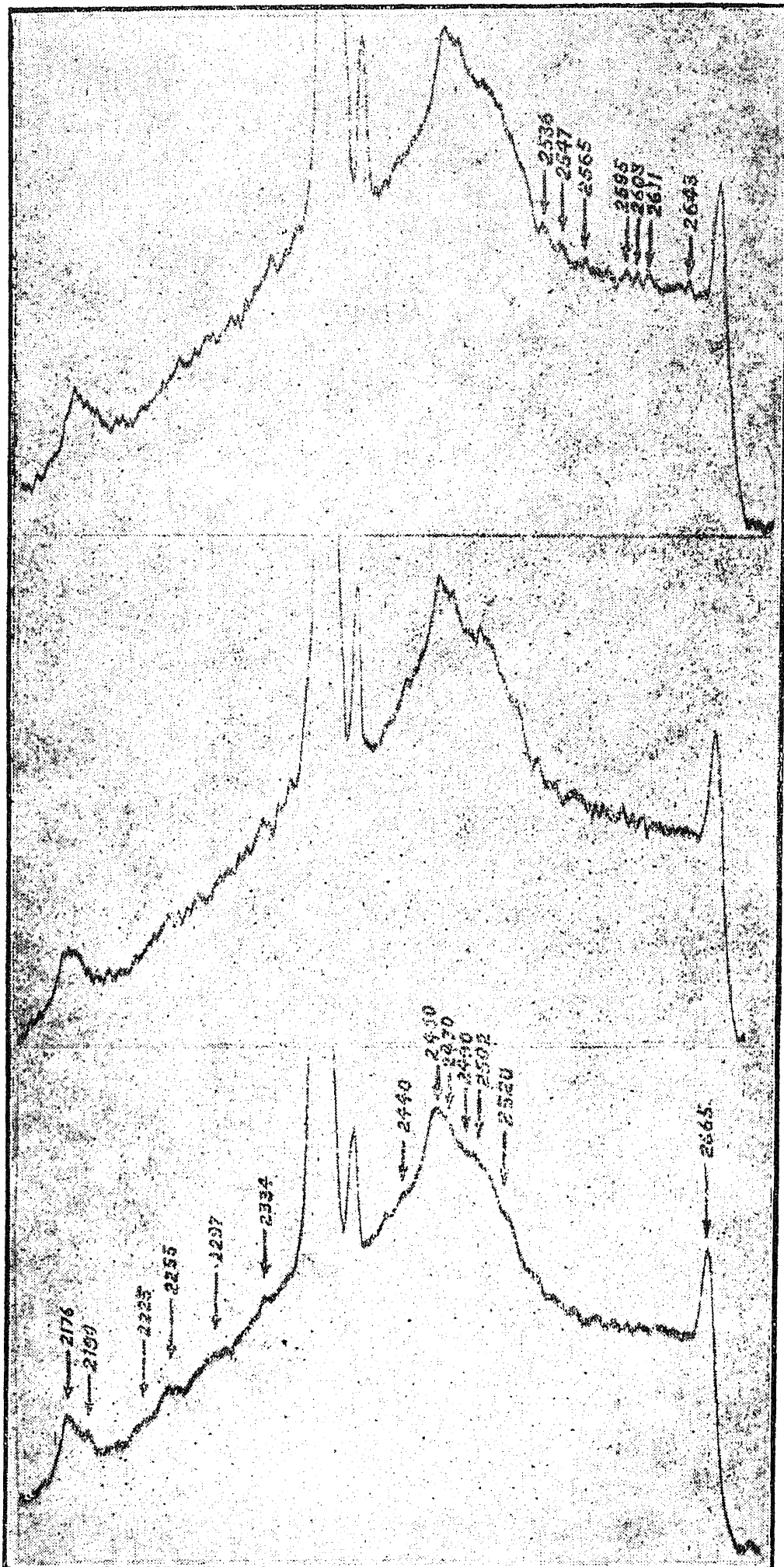
5. First-order Raman Spectrum

Only a single Raman line with frequency shift of $1332\cdot0$ cm.$^{-1}$ appears in the first order spectrum of diamond. This frequency represents the fundamental vibration of the diamond structure, *viz.*, the triply degenerate mode in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other. Longer exposures did not exhibit any Raman line having a frequency shift less than 1332 cm.$^{-1}$ except a couple of fainter lines which appeared in the region of low frequency shifts and were identified as the 1332 Raman line excited by the feeble mercury lines on the shorter wavelength side of $\lambda\,2536\cdot5$. The appearance of a single Raman line in the first

order spectrum of diamond is a direct consequence of the high symmetry of its crystal structure. It is found that there is no measurable difference in the frequency shifts of the principal Raman line in the spectra of the ultraviolet transparent and opaque types of diamond.

6. THE SECOND-ORDER RAMAN SPECTRUM

The true nature of the second-order spectrum of diamond is exhibited unambiguously in the series of photographs reproduced in Figs. 4 and 5. These represent the prints enlarged from different spectrograms taken with a Hilger E1 large quartz spectrograph and diamond N.C. 174. The exposures used varied from 12 hours to a maximum of 4 days. The greater dispersion and resolution of the large quartz spectrograph have enabled the author to bring out the salient features of the second-order spectrum more clearly than was possible in the previous investigations. The most striking feature noticeable in the spectra is the appearance of a whole series of sharply defined Raman lines clearly resolved from one another. The prominent ones have been marked in Figs. 4 and 5 with their respective frequency shifts in wave numbers from the exciting line. The terminal line with a frequency 2015 cm.$^{-1}$ is more clearly seen in the microphotometer record reproduced in Fig. 3. The width of the individual Raman lines, as is evident from a comparison with the lines of the mercury arc, is no greater than that arising from the instrumental and photographic factors. Besides the Raman lines whose positions are marked in Figs. 4 and 5, there are other fainter lines just discernible in the spectrogram against a fainter unresolved background of apparently continuous spectrum. These faint lines are more clearly seen as small kinks in the microphotometer records reproduced in Fig. 13. That they are genuine Raman lines and are not due to chance fluctuations has been verified by comparing the microphotometer records taken at different regions on the same negative and with different spectrograms. Three typical records are reproduced in Fig. 13. The positions of the fainter lines are marked in the figure.

The second-order Raman lines of diamond are listed in Table II together with their frequency shifts in wavenumbers from the exciting line and their widths in wavenumbers. Taking the intensity of the most intense line as 15 arbitrary units, the intensities of the remaining lines have been estimated and the values are included in Table II. Excluding the two terminal Raman lines with frequency shifts $2665 \cdot 4$ cm.$^{-1}$ and 2015 cm.$^{-1}$, the Raman lines in the second-order spectrum of diamond can be classified into three groups.

FIG. 13. Microphotometer records of the second order Raman spectrum of diamond taken with the Hilger E 1 large quartz spectrograph.

TABLE II

No.	Frequency shift in cm. (Observed)	Width in cm.$^{-1}$	Relative intensity	Assignment	Frequency shift in cm.$^{-1}$ (Calculated)
1	2015	3	1	Octave, $2\nu_6$	
2	2176	4	5	Octave, $2\nu_5$	
3	2190		3		
4	2225	3	3	Combination, $\nu_4+\nu_5$	2237
5	2255	5	6	Combination, $\nu_2+\nu_6$	2258
6	2297	4	7	Octave, $2\nu_4$	
7	2334	4	8	Combination, $\nu_2+\nu_5$	2338
8	2440	4	10	Octave, $2\nu_3$	
9	2460	3	15		
10	2470	3	15		
11	2490	4	12	Octave, $2\nu_2$	
12	2502	4	12		
13	2520	4	9		
14	2536	3	4		
15	2547				
16	2565			Combination, $\nu_1+\nu_3$	2564
17	2593				
18	2603				
19	2611				
20	2643				
21	2665·4	4	10	Octave, $2\nu_1$	

The first group which lies on the longer wavelength side of the mercury line λ 2698·9, consists of six very sharp, intense and closely spaced lines with frequency shifts ranging from 2440 cm.$^{-1}$ to 2520 cm.$^{-1}$. It is interesting to note that most of the lines of this group are more intense than the 2665·4 line. The second group consists of six Raman lines of moderate intensity and sharpness with frequency shifts ranging from 2176 to 2334 cm.$^{-1}$ lying on the shorter wavelength side of λ 2698·9. The third group comprises half a dozen feeble lines imperfectly resolved and appearing in the region of frequency shifts bounded by the 2520 and 2665·4 Raman lines.

As already pointed out in section 4, the discrete character of the second-order Raman spectrum is a contradiction of the conclusions regarding the nature of the atomic vibration spectra of crystals to which the theories of Debye and Born lead. The appearance of several discrete frequencies in the second order spectrum of diamond, on the other hand, finds a natural explanation in the new theory of lattice dynamics put forward by Sir C. V. Raman. According to the Raman theory, diamond has nine fundamental modes of oscillation of which two have identical frequencies. The vibration spectrum of diamond has therefore eight numerically different vibration frequencies. If $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6, \nu_7$ and ν_8 are the frequencies arranged in the descending order of magnitude, their degeneracies are respectively 3, 8, 6, 4, 3 + 3, 4, 6 and 8. Of these, the highest frequency corresponds

to the triply degenerate vibrations of the two interpenetrating Bravais lattices of carbon atoms and is active in the Raman effect. It has a value of 1332 cm.$^{-1}$ The other seven frequencies represent the oscillations of the layers of carbon atoms parallel to the faces of the octahedron or cube occurring normal or tangential to these planes with the phases reversed at each successive equivalent layer. All these seven modes are inactive in the Raman effect as fundamentals. They may, however, appear in the second-order Raman spectrum as octaves and combinations.

Coming now to the identification of the Raman lines appearing in the second-order spectrum, the terminal line with a frequency shift of 2665 cm.$^{-1}$ is obviously the octave of the principal mode of oscillation. It is important to note that the frequency shift of this line is very nearly double that of the 1332 Raman line. This fact suggests that the mechanical anharmonicity factor for this particular mode of vibration is small. From theoretical considerations based on the intensities of the Raman lines, it is possible to identify the lines with frequency shifts 2502, 2460, 2297, 2176 and 2105 cm.$^{-1}$ as octaves of the modes of vibration ν_2, ν_3, ν_4, ν_5 and ν_6 respectively. See the papers by Sir C. V. Raman (1947) and by K. G. Ramanathan (1947) appearing in this Symposium. The remaining two modes, namely ν_7 and ν_8 have low frequencies and their octaves are not observed in the second-order spectrum. The frequencies in wavenumbers of the first six modes are as follows:—$\nu_1 = 1332$, $\nu_2 = 1250$, $\nu_3 = 1232$, $\nu_4 = 1149$, $\nu_5 = 1088$ and $\nu_6 = 1008$ cm.$^{-1}$ On the basis of the above identification, the Raman lines with frequency shifts 2225, 2255, 2334 and 2565 cm.$^{-1}$ can be satisfactorily explained as combinations and the calculated values of their frequency shifts are entered in column 6 of Table II. There remain only five more prominent lines with frequency shifts 2190, 2440, 2470, 2490 and 2520 for the appearance of which a satisfactory explanation has to be found. From an examination of the second-order spectrum reproduced in Fig. 4, it will be seen that the first one falls in the vicinity of the 2176 line ($2\nu_5$), the next two fall on either side of the 2460 line ($2\nu_3$) and the last two fall on either side of the 2502 line ($2\nu_2$), forming in all three sets of which the second and the third almost run into each other. The only rational explanation appears to be that since ν_2, ν_3 and ν_5 are highly degenerate oscillations, the degeneracy is partly removed by the anharmonicity resulting in the splitting of the octaves into two or more components. Similar effects have been observed in the case of polyatomic molecules. Certain energy levels that coincide in the harmonic oscillator approximation split into a number of levels when anharmonicity is taken into consideration. In other words, when second-order effects are taken into account, the high degeneracy of the fundamental vibration does

not remain, but a splitting occurs due to anharmonicity. Splitting of the octaves of ν_2 and ν_3 may in part be attributed to resonance effect arising from the fact that these two vibrations have very nearly the same frequency and that combinations $\nu_1 + \nu_4$ and $\nu_2 + \nu_3$ fall roughly in the region of the octaves.

The author is grateful to Professor Sir C. V. Raman, F.R.S., for the loan of the diamonds used in the present investigation and also for suggestions and encouragement.

7. SUMMARY

A detailed study of the scattering of light in diamond and its Raman spectrum has been made using the $\lambda 2536 \cdot 5$ mercury resonance radiation as exciter. The scattered spectrum exhibits two pairs of Doppler-shifted components, one pair due to the longitudinal sound waves, and the other due to the two sets of transverse sound waves which have very nearly the same velocity. The velocities of the longitudinal and transverse sound waves estimated from the observed frequency shifts of the displaced components are in agreement with those calculated from the elastic constants of diamond. The directional dependence of sound velocity in diamond has been quantitatively verified. Contrary to expectation, the longitudinal Doppler components are found to be less intense than the transverse Doppler components.

The second-order spectrum of diamond has been examined with a quartz spectrograph of high dispersion and resolution. It exhibits a whole series of sharply defined Raman lines the frequency shifts of which have been tabulated. The prominent ones which are 15 in number have been satisfactorily explained as octaves or combinations of six of the eight fundamental frequencies of vibration of the diamond lattice to be expected on the basis of the Raman theory, some of which are split due to the removal of degeneracy by anharmonicity and due to resonance effect.

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DESCRIPTION OF PLATES

PLATE IX

FIG. 1. (*a*) Filtered mercury spectrum taken with a medium quartz spectrograph.

   (*c*) and (*e*) Enlargement and microphotometer record respectively showing λ 2534·8 and the wings of λ 2536·5.

   (*b*) Raman spectrum of diamond showing the Brillouin components (B.C.) and the 1332 Raman line.

   (*d*) and (*f*) enlargement and microphotometer record of the Brillouin components.

PLATE X

FIG. 2. (*a*) Filtered mercury spectrum taken with a medium quartz spectrograph.

   (*b*) Heavily exposed Raman spectrum of diamond.

FIG. 6. Raman spectrum of diamond showing the Brillouin components and the 1332 Raman line taken with a large quartz spectrograph (E1) together with a comparison spectrum of the mercury arc.

PLATE XI

FIGS. 4–5. Second-order Raman spectrum of diamond taken with E1 quartz spectrograph. Enlarged from different negatives.

PLATE XII

FIG. 7. Enlargements showing the Doppler-shifted components and the companion mercury line λ 2534·8, L.B.C. and T.B.C. are respectively components due to longitudinal and transverse sound waves. (*a*), (*b*) and (*c*) correspond to three different settings of the plate of diamond.
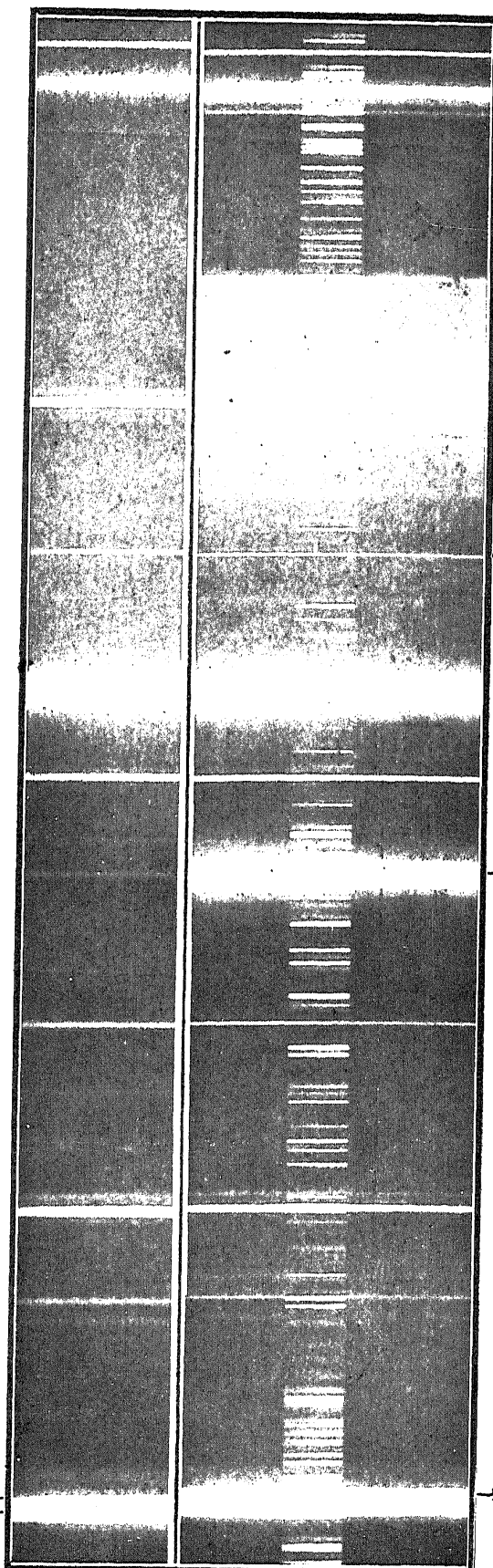
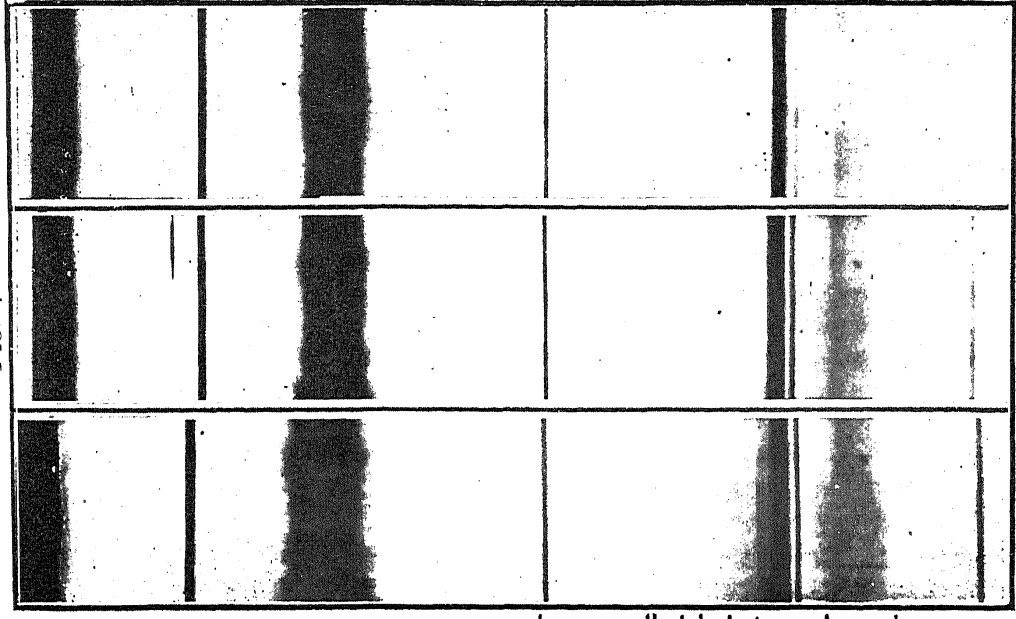FIG. 12. Scattering of light in diamond at different temperatures.

$1332\,cm^{-1}$

2nd order
Raman
Spectrum
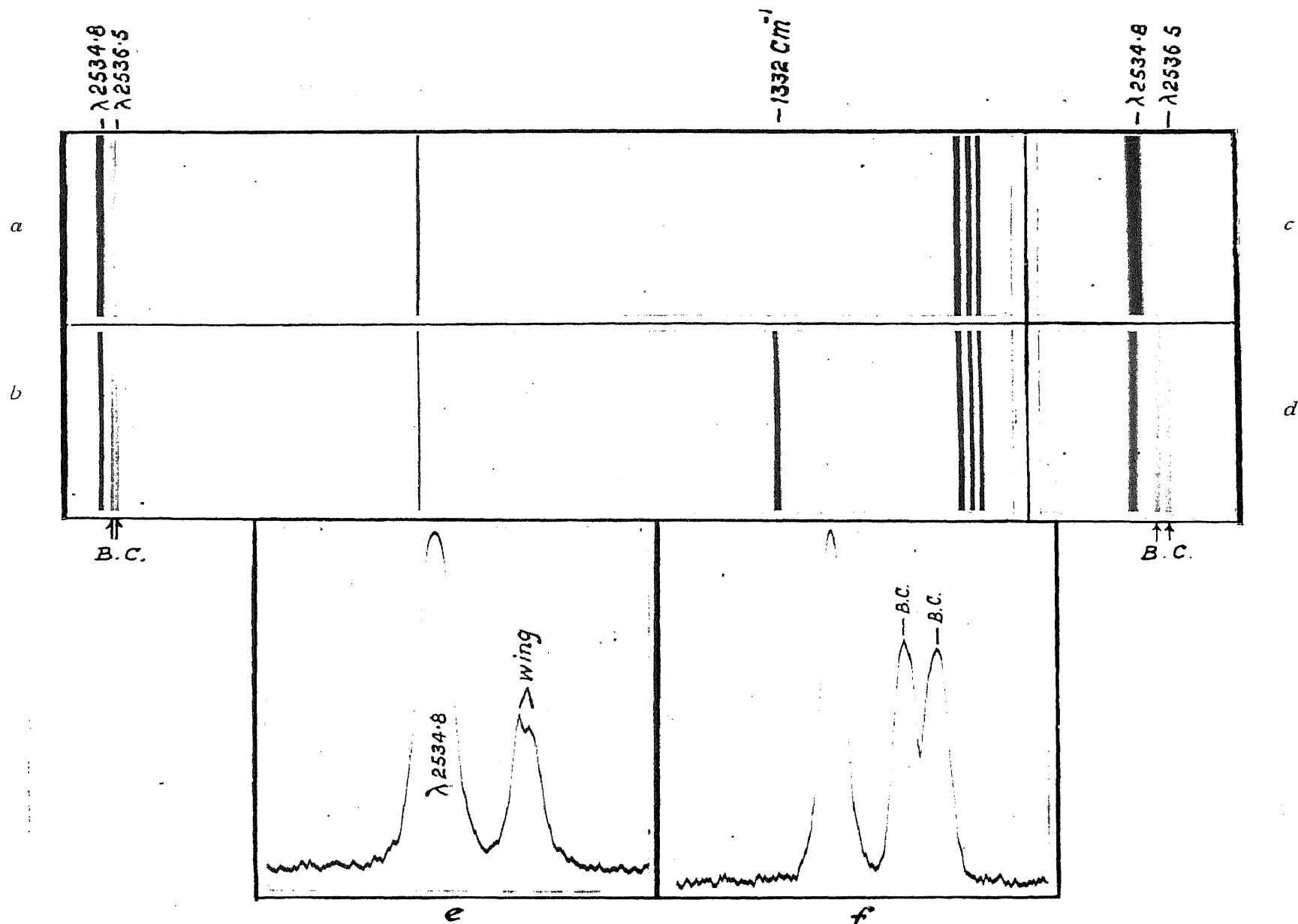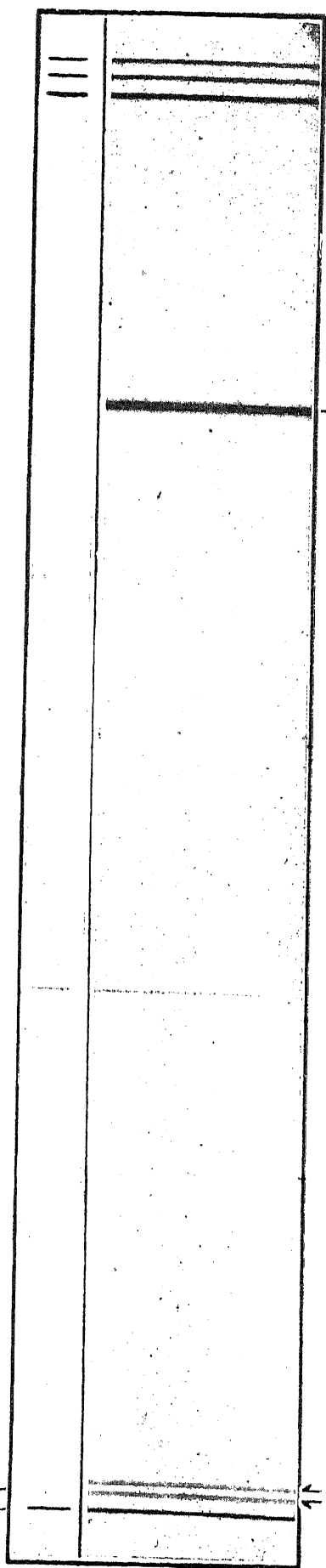
$-1332\,cm^{-1}$

BRILLOUIN
COMPONENTS

536.5
534.8

$\lambda 2536.5$
$\lambda 2534.8$

→ Brillouin
Components

Fig. 4

1332 Cm⁻¹

λ 2698·9

2460
2470
2490
2502
2520

2665·4

a

b

c

2015

2176
2190
2225
2255
2297
2334

2440

2536

Fig. 5

1332 Cm⁻¹

2460
2470
2490
2502
2520

2665·4

a

b

c

2176
2190
2225
2255
2297
2334

2440

2536

FIG. 7

FIG. 12