Further Studies on the Raman Spectrum of Diamond.

BY

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ABSTRACT.

The Raman spectrum of an exceptionally clear and perfect diamond of 20 carats size is found to give a number of feebler lines of frequency shifts 1158, 1288, 1382, 1431, 1480 and 1585 on either side of the very intense principal line (1332) already reported. The one at 1158 is more prominent than others. There is a close correspondence between these values and some of the very weak infra-red absorption maxima of diamond given by Reinkober.

Various considerations indicate that the principal oscillation at 1332 and its components are optically inactive in ideal diamonds although in the more commonly occuring ones they may be rendered active by imperfections in crystal structure. The relatively strong absorption band at 1240 found by Robertson and Fox in some diamonds is explained on this basis. The complex band found by these authors as well as Reinkober in the region 2 to 6 μ may also be explained as due to the combinations of the principal frequency with its components and other weak active oscillations in the long-wave length region.

The results are discussed in relation to the data on specific heat of diamond. The existing theories of Debye and Born based on classical mechanics lead to results which do not agree well with the observed facts. Diamond is a homopolar crystal and a rigorous treatment based on the new mechanics appears necessary to explain the discrepancies.

The antistokes line corresponding to the principal Raman line of frequency shift 1332 has been observed and is found to be shifted from the exciting line by precisely the same amount.

The intensity of the principal Raman line is about 6 times as great as that of the 992 benzene line, an explanation for which is given from density considerations.

1. *Introduction.*

Of the various crystalline solids in which the Raman effect has been observed, diamond is probably the case of the greatest interest on account of the simplicity of its structure.[1] In a previous report[2] the author has recorded the results of the study of ten different samples of diamond. In all of them three distinct features were noticed; (1) Raman lines with frequency shift of 1332 wave numbers excited by each of the intense mercury lines, (2) a series of bands evidently in the nature of fluorescent radiation of which the most intense and best defined is at 4157 A.U., (3) a continuous spectrum extending from a fairly well defined limit at 4240 A.U. towards the red end of the spectrum. The intensity of all these features in the spectrum of diamond seemed to show remarkable variations from specimen to specimen, the Raman line being most intense and the fluorescent bands and continuous spectrum being weakest with clear white diamonds. In view of the fact that each of the carbon atoms in diamond is attached tetrahedrally to four others, it was thought that in addition to the Raman line with a frequency shift of 1332 wave-numbers there should be others which had been overlooked on account of their faintness, and a search for them was accordingly undertaken. Owing to the great kindness of the Maharajadhiraja of Darbhanga, the author had the opportunity of experimenting with two exceptionally fine diamonds, one perfectly flawless and of the purest white colour, about 20 carats size, and the other a clear but pale yellow diamond of extraordinary size (143 carats). A third smaller diamond belonging to Mr. N. C. Chunder previously used was also available for re-examination. The results described in this paper are based mainly on the spectrograms obtained with these diamonds. In all some 50 photographs,

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[1] The earliest observations were by C. Ramaswamy, Nature, 125, 704 (1930); Ind. Jour. Phys., 5, 97 (1930).

[2] S. Bhagavantam, Ind. Jour. Phys., 5, 169 (1930). See also Robertson & Fox, Nature, 125, 704 (1930) and 126, 279 (1930).

including those abtained in the earlier work, have been critically examined.

2. *New Raman frequencies of diamond.*

There is no difficulty at all in photographing the 1332 principal Raman line, its intensity being so great that even with tiny diamonds an hour's exposure is usually enough. With diamonds of larger size such as those used in the present investigation, this line can be visually observed. The situation is quite different with regard to other fainter lines and experimentation is rendered difficult by several disturbing factors. Most of the diamonds examined have a pale yellow colour and the violet radiation of the mercury arc lamp is sensibly weakened in passing through them. Thus except with unusually clear and colourless diamonds, the only mercury line which fully serves the purpose of exciting feeble lines is 4358 A.U. The cut of the diamond is such that all the facets send out the maximum of internally reflected light which carries with it a certain amount of continuous radiation of the mercury arc and presents an unfavourable background for the detection of feeble lines. In view of the long exposures involved and the extreme feebleness of the new lines, all attempts to use filters of various kinds in the path of the incident light proved unsuccessful. This difficulty is partly avoided by carefully adjusting the well focussed image of the diamond on the slit of the spectrograph in such a way that a minimum of the reflected light falls on it. A more serious difficulty is the presence of the continuous fluorescent radiation characteristic of the diamond which is superposed on the Raman lines. This feature cannot be got rid off as part of it is still excited by 4358 A.U. even after the elimination of 4046 A.U. In view of these difficulties it is found that an optimum exposure with the full mercury arc just enough to bring out the feeble lines on as light a background as possible is necessary to yield the best results.

On a spectrogram obtained after an exposure of about 6 hours with Mr. Chunder's diamond, a feeble line could be seen clearly at 4590·1 A.U., the intensity of which is only a few hundredths of that of the principal line. This is shifted by 1158 wave numbers from the 4358 mercury line. The corresponding line from 4046 falls at about 4245 A.U. which is in the region where the fluorescent continuous spectrum starts. Examination of the spectrograms obtained with this diamond indicated the existence of some feeble lines accompanying the principal line and rather close to it.* A well exposed spectrogram obtained with the white Darbhanga diamond showed these companion lines clearly. The exceptional clearness of this sample is a great advantage as it transmits the 4046 radiation quite freely. Besides the principal Raman line, a line corresponding to 1158 wave numbers excited by 4046 could be seen clearly on the plate. Various component lines accompanying the principal line, particularly on the long wave-length side have been observed. The frequency shifts of these lines are as follows : 1288, 1332 (principal line), 1382, 1431, 1480, 1585. The intensity of all the lines except 1332 is extremely low.

3. *Relation to Reinkober's absorption data.*

Reinkober [3] has investigated the infra-red reflection and absorption of diamond with notable results. His reflection measurements which were made with an exceptionally clear diamond showed that there was no detectable variation of the reflecting power throughout the infra-red region. Taking the observed refractive index of diamond for the red λ 7600 line as 2·402 and extrapolating the values up to 20 μ on the basis of the usual dispersion formula involving a characteristic absorption in the ultra-violet at 1246 A.U., its reflecting

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* The author has recorded such a result in his previous paper with one of the diamonds. In subsequent investigations, these companion lines have appeared in almost every well exposed photograph.

[3] Ann. d. Phys., 34, 343 (1911).

power may be calculated from Fresnel's formula. The following Table shows the calculated values :

TABLE I

Reflecting power of diamond.

Wave-length in μ	·76	2	10	20
Refractive index	2·402	2·391	2·381	2·380
Reflecting power %	17·02	16·83	16·68	16·67

The values for the long wave-lengths are in close agreement with 16·5% as found by Reinkober throughout the region lying between 2 and 19μ. This suggests that there are no optically active frequencies in the infra-red region which could sensibly affect the refractivity of diamond. Such a view is in agreement with the fact that diamond is composed of neutral atoms linked by homopolar bonds in a crystal lattice possessing a high degree of symmetry.

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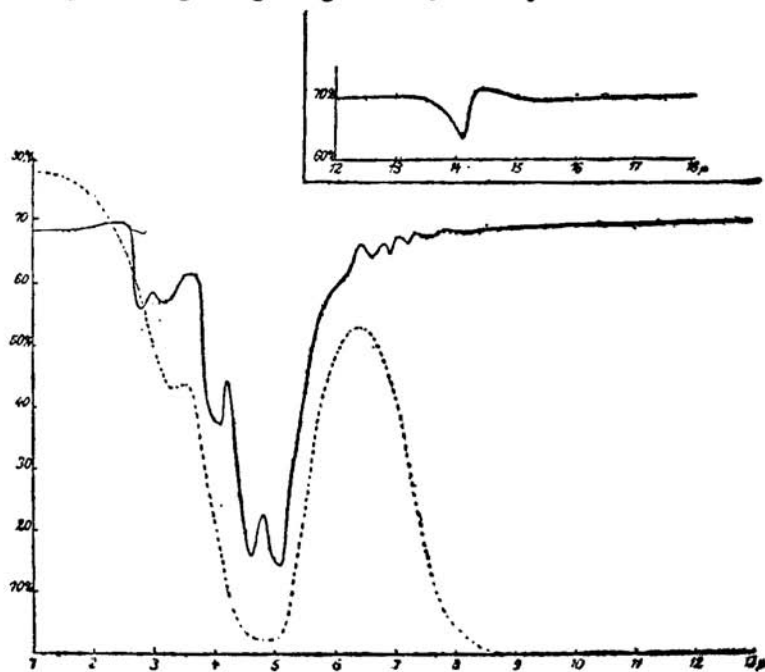
The absorption measurements were made by Reinkober with another piece of diamond, 1·26 m.m. thick. His curve is reproduced above. He found a region of intense absorption showing pronounced maxima and minima between 3900 and about 1500 wave numbers, the prominent absorption maxima as read off from his curve corresponding to 3586, 3132, 2430, 2179 and 1962. At longer wave lengths, there is only a weak absorption ; but this fluctuates markedly, a series of maxima and minima being observed. Maxima of absorption are obtained at 1600, 1516, 1450, 1387, 1330 and 1235 wave numbers. Beyond this up to the remotest infra-red region investigated by him, he observed complete transparency except for a weak absorption at 710 wave numbers. It is very interesting that the principal Raman line at 1332 coincides very definitely with a point of maximum absorption in Reinkober's curves, and further, that the feeble companions to it observed in the spectrum of the white Darbhanga diamond are also represented in it. This is clear from Reinkober's curve enlarged and reproduced below. The dotted lines proceeding downwards indicate the absorption maxima, and their relation to the full lines representing the Raman spectrum on the same scale of frequencies is obvious from the figure.
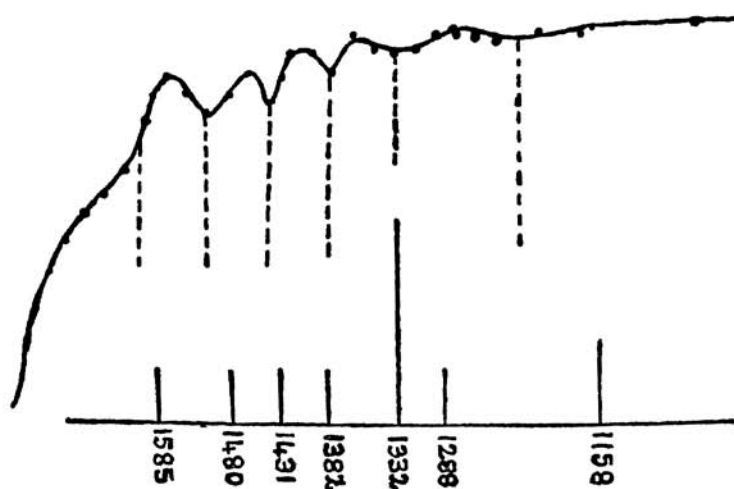
We have now to consider the explanation of the fact that the Raman line 1332 which appears with great intensity in the scattered light with white diamonds is present only as an extremely feeble absorption in Reinkober's curve. There is no doubt that it corresponds to the principal mode of oscillation of the diamond lattice, for various properties such as its specific heat, thermal and elastic constants calculated theoretically assuming it to be the characteristic frequency agree reasonably with observation. The high intensity with which it appears in the spectrum of the scattered light with clear white diamonds, on the one hand, and the extreme feebleness with which it appears in the infra-red absorption on the other both suggest that it corresponds to an oscillation which is optically inactive, or at least would be inactive in an ideal diamond. Its feeble appearance in absorption would on this view be attributable to slight deviations of the crystal structure from complete perfection.

Reinkober's curve does not show any absorption corresponding to the Raman frequency of 1158 wave numbers. The reason for this is not clear. It is possibly also an inactive frequency but a more likely explanation is that it is a very weak and only feebly active frequency and as such is likely to have been missed in absorption. It is also to be noted that we do not find in the Raman spectrum, any line corresponding to the feeble absorption at 710 found by Reinkober. This does not however disprove its real existence as a feeble active oscillation frequency.

4. *Other infra-red absorption data.*

It is a very remarkable fact that the absorption of diamond seems to depend on the sample under examination. For instance the early observations of Julius indicated a strong absorption from about 3000 to 1500 wave numbers followed by a narrow region of transmission up to 1200. This result is similar to that obtained by Reinkober. On the other hand all wave-lengths beyond this region are found by Julius to be totally absorbed whereas Reinkober reports that they are very

freely transmitted. More recent observations by Robertson and Fox indicate four absorption bands at 3353, 2438, 2086 and 1246 wave numbers. Although the three high frequency bands roughly agree with absorptions found by Reinkober, the absorption at 1246 is of a totally different character from the one found by him in this region. These authors find that such a result persists in seven different diamonds although they refer to one, which they call abnormal, showing absorption like that of Reinkober's diamond. Such remarkable variations are very significant and are perhaps closely connected with the already observed variations of the intensity of the principal Raman line in different specimens.

Some special characters of diamond which are of interest to us may now be mentioned. Different samples seem to show different values for their dielectric constants.[4] Pirani found in one case the very high value of 16·47, whereas other authors have reported values ranging from 5·5 to 8, while the value derived from the optical refractive index is 5·67. Under the action of light, diamonds become electrically conducting. This phenomenon is known as photoconductivity and was investigated by Gudden and Pohl.[5] According to Walter the absorption spectrum of diamond has bands at 4155A. U., the effect being marked in some crystals and feebler in others. The fluorescent band observed by the author at 4157 A.U. shows similar variations in that it is strong with blue diamonds but weak with colourless ones. All these facts suggest that under certain conditions the electrons of the diamond lattice pass into a mobile state and thus become active. The structural variations consequent on such a change will naturally result in the alteration of all or some physical properties of the substance ; in particular those that have their origin in the optical electrons such as absorption, refractivity, conduction etc. It is reasonable to suppose that the infra-red oscillation corresponding to 1332 which is inactive under ideal conditions, ceases to be so in a great majority of the commonly

[4] See Treatise on Inorganic Chemistry, J. W. Mellor, 5,781 (1924).
[5] Zeit. f. Phys., 17, 331 (1923).

occuring diamonds and begins to appear in absorption. The band observed by Robertson and Fox at 1246 is a broad one which covers within its' width, the observed Raman line at 1332 and its two companions on the long wave-length side at 1288 and 1158. The mean of the two latter frequencies is 1223, and can be reasonably identified with the absorption maximum observed by Robertson and Fox. It appears that the complex absorption observed by Reinkober as well as by Robertson and Fox in the region between 3500 and 1900 is the result of combinations between the various characteristic frequencies observed in the Raman spectrum and others in the long wave-length region beyond 1600. For example the three bands at 3353, 2438 and 2086 observed by the latter authors may be explained as $2 \times 1332 + 710$, $1332 + 1158$, $1332 + 710$. Better agreement can also be obtained by considering the other Raman frequencies lying in the neighbourhood of the principal line. That these combinational frequencies should give rise to the high intensities of absorption observed in this region is a difficulty which becomes less acute if we remember that the 1332 oscillation, although inactive, is intrinsically a very powerful one as a result of which it may give rise to prominent absorption when it combines with other weaker active frequencies. That the strong absorptions observed in diamond correspond to combinational frequencies rather than to fundamental vibrations of the lattice is seen to be a reasonable hypothesis when we recall Reinkober's observation that the reflecting power of diamond shows no increase whatsoever in the region of such strong absorption.

It may also be noted here that Robertson and Fox report that they have not been able to locate the absorption at 710 observed by Reinkober.

5. Specific heat of diamond.

The case of diamond is of special interest as it is a classical example in which the heat content falls off very rapidly with decreasing temperature. From a very complete investigation

of its specific heat at low temperatures Nernst[6] has shown that the value is not even a thousandth part of that predicted by Dulong and Petit's law. Many investigators have attempted to explain these remarkable variations on a theoretical basis. Einstein[7] was the first to formulate the quantum theory of specific heat on the assumption that the atoms are independent planck oscillators. He assumed that the important oscillation of the diamond lattice lies at about 900 wave numbers and successfully explained the observed phenomena at moderately high temperatures. The theory does not however account for the values at low temperatures. Subsequent attempts by Nernst and Lindemann[8], Simon[9], Schrödinger[10] and others are primarily based on the assumption of an empirical characteristic frequency of the lattice which yields the best agreement and have only met with partial success. The situation now is however slightly different as the Raman spectrum provides us with a precise knowledge of the fundamental frequency of oscillation viz., 1332. Taking this as the limiting frequency of the Debye spectrum, the specific heat may be calculated: values are compared with the observed data in Table II. The values of the Debye function are taken from his original paper. [11] For intermediate temperatures they are obtained by interpolation. Experimental values are taken from the work of Nernst, Lindemann and Weber.

TABLE II: Specific heat of diamond.

Temperature	48	86·5	92	205	209	220	283	306	331	358	413	479	879
C, calculated	0·007	0·053	0·056	0·55	0·59	0·68	1·24	1·45	1·67	1·92	2·47	3·0	4·76
C, observed	0·00	0·03	0·03	0·62	0·66	0·72	1·35	1·58	1·84	2·12	2·66	3·28	5·29

[6]   Ann. d. Phys., 86, 395 (1911)
[7]   ,,   , 22, 180 (1907)
[8]   Zeit. f. Elektrochemie, 817 (1911)
[9]   Sitz. der Preuss. Akad. Wiss., 83, 477 (1926)
[10] Handbuch der Phys., 10, 275 (1926)
[11] Ann. d. Phys., 39, 789 (1912)
[12] See M. Born, Dynamik der Kristall Gitter (1923)

It will be seen that the agreement is not quite satis-
factory. In the low temperature region the observed specific
heats are only about half the calculated values. It is
interesting to note that the discrepancies are very systematic
in that the observed specific heat is too low at low temperatures
and too high at high temperatures and are therefore probably
not due to experimental errors. The failure of the Debye
theory noticed here is not surprising if we remember that the
observed infra-red spectrum of diamond is not that presup-
posed by the theory. Whereas the Debye theory assumes a
long and practically continuous series of oscillations ranging
from zero to a limiting value where they all crowd up, the
experimental results show that there are a certain number of
discrete frequencies of which the one at 1332 is the most
important but not the highest as the latter is also accompanied
by weaker lines of still higher frequencies. Such remarkable
phenomena which cannot satisfactorily be explained on the
basis of the old quantum theory of specific heat show that we
have in diamond a case where the classical mechanics com-
pletely breaks down.

6. *Interpretation of the new frequencies.*

A natural question that arises out of the foregoing con-
siderations is regarding the origin of the new frequencies.
The general theory of lattice oscillations developed by Born
indicates 3N oscillations for a crystal containing N individual
particles which divide up into 3S series. Three of these
comprise the acoustic waves and are in the long wave-length
region. Of the rest 3S—3 series which are known as the optical
series, a certain number may fall in the ultra-violet and the
rest in the infra-red region of the spectrum according as how
many of the particles are electrons and how many are atoms.
S is the number of particles in each basis group of the lattice.
In crystals possessing elements of symmetry, some of the
series may overlap, the actual number being reduced according-
ly. The question now arises as to whether the observed
Raman frequencies represent merely the heads of various

different optical series or only the fine structure components of any one particular series. It seems difficult to accept either of these explanations as the number seems to be one too many in the former case whereas in the latter, although the more or less constant spacing of the various lines suggests such an explanation, they appear to be too far apart to constitute one series. On the whole it appears reasonable to suppose that the absorption extending from about 1100 to 1600 is in reality one fundamental oscillation and perhaps the only important and most powerful one associated with the diamond lattice. Its fine structure is due to some cause which is at present very obscure. It is however very significant that diamond is a homopolar crystal, and many of the curious phenomena observed above may receive an explanation based the modern theories of homopolar binding as developed by Heitler and London.

7. Intensity, polarisation and other results.

In the previous paper three components of the fluorescent band system were reported. In the present investigation, besides these which were found to occur in precisely the same positions, two others are observed making up five components in all. The wave-lengths of these bands are 4131, 4157, 4175, 4186 and 4196 A. U. The one at 4157 A. U. is the strongest and extends over 10 A. U. The fact that the fluorescent bands are observed in the clearest white diamond makes it clear that it does not arise from any extraneous impurities in the diamond.

The antistokes Raman line corresponding to the principal frequency has also been observed in two plates and is shifted by 1332 wave numbers from the exciting line, in absolute agreement with the shift of the stokes line. The intensity of the stokes line, on the basis of Boltzmann distribution law, should be 544 times that of the antistokes one at the room temperature ; the observed intensities are of the right order of magnitude.

The large Darbhanga diamond which was about 3 cms. in its linear dimensions afforded an opportunity of studying the absolute intensity and the state of polarisation of the principal Raman line. There is no doubt that the great intensity of this line is in part due to repeated internal reflections which enhance the total scattering of light within the diamond. To eliminate this source of error as far as possible, the diamond was immersed in distilled benzene contained in a cubical glass vessel. When this was done, it was noticed that the light yellow colour disappeared and the diamond seemed colourless, apparently as the result of the weakening of the internal reflections. The diamond fluoresced with a brilliant blue light when the image of the mercury arc was focussed on it by a glass condenser.

An aperture was placed in front of the diamond and the spectrum of the scattered light exposed for a known time. The diamond was removed and a series of graded exposures of the spectrum of the light scattered by benzene illuminated with the same aperture were given on the same plate. A visual comparison of the brightness of the lines on the plate showed that the diamond line is at least 6 times as strong as the principal 992 Raman line of benzene for equal exposures.

Such an extraordinary intensity of the principal diamond line is of interest, especially if we remember that the oscillations that are being compared have their origin in the forces that bind the carbon atoms in both cases. A simple explanation can however be given in terms of the densities of the scattering material. The density of diamond (3.51) is much greater than that of benzene (0.88) which means that the number of oscillators per unit volume is nearly four times larger in diamond than in benzene. Further in the spectrum of benzene, there are other lines besides the 992 which appear and need to be taken into account to consider the total energy of vibration of the carbon atoms. Taking these facts into consideration the intensity of the line obtained with diamond is not altogether surprising.

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With a nicol interposed in the path of the scattered light, two photographs corresponding to the vertical and horizontal components are taken side by side on a plate with a view to estimate the state of polarisation of the line. * The results indicate that there is a considerable imperfection of polarisation, contrary to the observation of Ramaswamy who finds that the line is well polarised. It must be noted however that the work is rendered unreliable by the presence of internal reflections and repeated scattering, and more detailed investigations with diamonds of suitable shape are necessary to decide the state of polarisation with certainty and the variations it might show in different samples analogous to the variations in intensity.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman who kindly suggested the problem and gave many valuable suggestions and helpful criticism in the course of the work. Grateful acknowledgements are also due to His Highness the Maharajadhiraja Bahadur of Darbhanga whose kindness in loaning valuable diamonds made this research possible.

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* Correction due to the instrument is introduced in the times of exposures. See S. Bhagavantam, Ind. Jour. Phys., 5, 59 (1930)