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The diamond: Its structure and properties

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ABSTRACT

A critical study of the crystal forms of diamond from various sources demonstrates that the symmetry of the structure may be either that of Class 32 or Class 31, in other words that the structure may be either centrosymmetric or non-centrosymmetric. Diamonds belonging to Class 31 may however exhibit a pseudo-octahedral symmetry of external form by reason of the interpenetration of oppositely directed structures having the lower symmetry. The existence of diamond with two differing structures provides an insight into the many remarkable properties of this material, viz., the striking differences observed in the infra-red absorption spectra, differences in transparency to ultra-violet rays, the differences in the intensity of their X-ray reflections and the variations in the intensity and colour of the luminescence exhibited by them.

The modes of atomic vibration in diamond can be completely described and their frequencies evaluated by very simple procedures. The vibration frequencies can be determined experimentally by observations of the frequency shifts in the scattering of light or by infra-red spectroscopy, the results by the two methods being fully in agreement. The heat capacity of diamond may then be computed, giving results in highly satisfactory concordance with the observational data.

The principal mode of atomic vibration having a frequency of 1332 cm^{-1} is triply degenerate. These vibrations can be excited in the lattice planes of diamond by the incidence of monochromatic X-rays if it belongs to crystal Class 31. The three-fold degeneracy of the vibration reveals itself as the three distinct spots in the resulting dynamic X-ray reflection by the octahedral lattice planes.

The complete electronic frequency spectrum of diamond has been evaluated by a very simple procedure. The results are highly successful in explaining the known optical and spectroscopic properties of diamond.

1. The crystal forms of diamond

Geometric crystallography derives its significance from the fact that the external form of a crystal discloses the symmetry characters of its internal structure and that these characters are in their turn closely related to the physical properties of the solid. The study of the crystal forms of diamond thereby becomes a highly important first step towards an understanding of its many remarkable properties. It is a characteristic feature of diamond that it is generally found as single complete crystals which are bounded on all sides by the natural faces. The extreme hardness of the material also enables it to preserve its original shape undamaged through many vicissitudes, so much so that specimens taken out of secondary geological formations usually exhibit the natural faces of the crystal with an undiminished brilliancy and lustre. These circumstances make the study of the crystal forms of diamond a highly rewarding pursuit.

As is well known, diamond belongs to the cubic system of crystals. There are five distinct classes in that system of which we are concerned here only with two, viz., those which in the usual system of numbering are referred to respectively as Class 31 and Class 32. The symmetry properties of Class 31 are the same as those exhibited by the geometric figure of a regular tetrahedron, while those of Class 32 similarly correspond to the symmetry of form of a perfect cube. Both of the classes possess six diagonal planes of symmetry, while Class 32 possesses in addition three axial planes of symmetry and a centre of symmetry. These additional features are not exhibited by Class 31.

In numerous cases, crystals of diamond of gem quality exhibit curved faces. In some diamonds one observes both plane and crystal faces in combination. There are also others which show plane faces almost exclusively. These circumstances have in the past led to much confusion and misunderstanding regarding the symmetry of the internal architecture of diamond and its relation to its external form. These difficulties however disappear if the following method of approach to the subject is adopted.

If the six diagonal planes of symmetry which are common to both Class 31 and 32 are drawn in space so that they intersect each other at some common point, and we then draw a closed surface around that point, it will be found that the surface appears divided up into 24 sectors. In the pattern thus formed on the surface, six points appear at which the diagonal planes of symmetry intersect each other in pairs, while at eight other points three of the planes intersect each other. The six points are the projections of the mid-points of the six faces of a cube, while the eight other points are the projections of the eight cube corners. If, besides the six diagonal planes of symmetry, we had also drawn the three axial planes of symmetry in their proper setting, the entire surface would have appeared divided up into 48 sectors, six of these sectors being found in each of the eight octants into which the surface would be divided up by the three mutually perpendicular axial symmetry planes.

Diamonds having only curved surfaces exhibit very varied shapes, but they all have certain features in common, namely that the exterior surface is not a single continuous sheet but is broken up into distinct areas by a pattern of sharply defined edges. This pattern exhibits the features referred to above appearing on a closed surface intersected by the six planes of diagonal symmetry of a cube. But we do not observe the features which would arise if the three axial planes of symmetry had been present. Thus, the externally observed features justify us in recognising such diamonds as crystals belonging to Class 31 and inferring from the absence of the features which distinguish Class 32 that they do not belong to Class 32.

On the other hand, the octahedron is the form which distinguishes Class 32 from Class 31 of the cubic system. Hence, if a diamond exhibits the form of a regular octahedron with plane faces and sharp straight edges, we have of necessity to recognise it as belonging to Class 32 of the cubic system and not to Class 31. Diamonds exhibiting this ideal form are not unknown. In particular, the author's collection of specimens includes some small crystals of octahedral form with lustrous plane faces bounded by sharp edges. Such specimens demonstrate beyond all possible doubt that the crystal symmetry of diamond may also be that of Class 32.

The conclusion thus arrived at, viz., that some diamonds belong to Class 31 of the cubic system and that other diamonds belong to Class 32 of that system is of the highest importance. It is indeed the clue to the understanding of many remarkable properties exhibited by diamond. Before we pass on to consider the subject of the crystal structure of diamond, it will be useful here to discuss its observed crystal forms a little more fully.

It is noteworthy that crystallographers and mineralogists have in the past been unanimous in assigning diamond to the tetrahedral class of the cubic system, in other words to Class 31. They were led to make this assignment by a study of the observed crystal forms. The appearance of simple tetrahedra with plane faces and of rounded forms exhibiting the general shape of a tetrahedron clearly indicated the lower symmetry. Further, octahedra with plane faces often exhibited notches or grooves along their edges which could be interpreted as the result of the twinning of oppositely directed tetrahedral forms. A particularly interesting case of this kind is that in which the octahedral faces are not triangular in shape but have a well-defined hexagonal outline, and all the edges of the octahedron are replaced by depressions bounded by these hexagons, each depression exhibiting four faces which intersect along sharply defined edges. The author's collection of diamonds includes a specimen from South Africa showing these features. An inspection of it makes it evident that the diamond is an interpenetration twin of two hexaxis-tetrahedra.

India was the original home of the great diamonds which found their way to other parts of the world and helped to spread the fame of this gemstone. At the present time, diamonds are still forthcoming at and near Panna in Central India. Two visits to Panna made by the author many years ago gave him the opportunity of inspecting numerous specimens of the diamonds found in that area in their original form as crystals. Particular mention should be made of the magnificent set of 52 uncut diamonds ranging in size from 25 carats down to 2 carats strung together into a necklace by a predecessor of the Maharaja of Panna. The beauty of the necklace arises from the lustre and shapeliness of the gemstones. The two visits to Panna also enabled the author to acquire for his collection a set of specimens for a more detailed study.

The external features exhibited by the Panna diamonds in the collection are highly instructive. They are of very varied sizes and shapes. Two of them present a close resemblance to octahedra in their general shape. But the octahedral edges are not seen and indeed there is not the slightest indication of their presence. On the other hand, the edges along which the diagonal planes of symmetry meet the curved surface of the diamond are conspicuously visible. The six points where these planes intersect in pairs are located at the six vertices of the pseudo-octahedral form of the crystal, while the eight points at each of which three planes intersect appear at the centres of its eight curved faces. These features indicate that while the diamond has the inner symmetry of the tetrahedral class, its external form which mimics octahedral symmetry is the result of the interpenetration of oppositely directed tetrahedral forms within the diamond.

In some of the Panna diamonds, the lower or tetrahedral symmetry is much more obviously exhibited in the externally observed forms of the diamond than in others. There are also several specimens in which the external shape of the diamond resembles neither an octahedron nor a tetrahedron but is almost spherical in form. But in all cases the curved surfaces clearly exhibit the ridges where they are intersected by the six diagonal planes of symmetry of the tetrahedron.

2. The two types of diamond

The difference between the diamonds belonging respectively to Classes 32 and 31 in respect of their symmetry properties is the same as the difference between the geometric forms of a regular octahedron and a regular tetrahedron, viz., that the former possesses a centre of symmetry whereas the latter does not. In other words, the two kinds of diamond may be described as being respectively of the centrosymmetric and non-centrosymmetric types. Two physical tests for ascertaining whether the structure of diamond does or does not possess centres of symmetry may be suggested. One is whether diamond exhibits piezo-electric or pyro-electric behaviour. The other is the study of its behaviour in respect of the absorption of infra-red radiation. In regard to the former, it may be remarked that since diamond consists of atoms all of one kind, viz., carbon, which are linked together by covalent bonds, the possibility of detecting piezo-electric or pyro-electric behaviour is exceedingly remote and may indeed be safely left out of consideration. On the other hand, the infra-red behaviour of diamond is readily tested. It is most conveniently studied with polished cleavage plates of diamond. Many such plates, including some of large size, are included in the author's collection. Studies made with these plates and a recording infra-red spectrophotometer are described and discussed in the author's Memoir No. 129 entitled "The infra-red absorption by diamond and its significance". The reader is invited to study this memoir and examine the numerous figures and photographs reproduced in it. They show clearly that the existence of centrosymmetric and non-centrosymmetric types of diamonds inferred from the study of the crystal forms is amply confirmed by the results of infra-red spectroscopy.

It is a noteworthy fact that the diamonds which exhibit an absorption of infra-red radiation in the spectral region of the fundamental atomic vibration frequencies are those which are revealed to be perfect diamonds when examined by various tests. It is thereby made evident that the absorptive power for infra-red radiation which they exhibit is an inherent property ascribable to their possessing a non-centrosymmetric structure. It is also significant that those diamonds which do not exhibit any infra-red absorption in those spectral regions and hence by inference are of the centrosymmetric class nevertheless exhibit an absorption of the second and higher orders, in other words of the overtones of the fundamental vibrational modes. In respect of this second-order absorption, the non-centrosymmetric and the centrosymmetric diamonds exhibit a precisely similar behaviour. This is a further and independent proof that the difference in behaviour of the two types of diamonds is a consequence of differences in their crystal symmetry. What exactly is the nature of the structural difference between the centosymmetric and non-centrosymmetric diamonds is a question which will be dealt with a little later. It may here be pointed out that the differences in the infra-red behaviour go hand in hand with differences of a striking nature in respect of other properties. In particular, the centrosymmetric diamonds are found to be non-luminescent under ultra-violet irradiation, whereas the non-centrosymmetric diamonds exhibit a readily observable luminescence. The centrosymmetric diamonds exhibit a high degree of transparency to the near ultra-violet region of the spectrum, whereas the non-centrosymmetric diamonds show a strong absorption in the same region. These relationships have been demonstrated by appropriate methods and illustrated in the Memoir No. 129 already mentioned.

3. Normal vibrations of crystal structures

A fundamental theorem in dynamics due to Lagrange states that the small vibrations of a system of connected particles may be expressed as a summation of a set of normal modes with precisely defined frequencies in each of which the particles of the system all move in the same or opposite phases and that the number of such modes is equal to the number of degrees of freedom of movement in the system. The theorem sets no limit to the number of particles contained in the system and it is obvious that it provides the correct approach to the subject of the dynamics of crystal lattices in its relation to the theory of the specific heats of crystals and of their spectroscopic behaviour. The simplicity of the crystal structure of diamond enables us on the basis of this definition of the normal modes of vibration of its structure to describe them fully and proceed to the evaluation of their frequencies. These topics are dealt with fully in parts VI, VII and VIII of Memoir No. 129 and the frequencies as computed and as observed in the records of infra-red absorption have been compared with each other.

It will suffice briefly to recall the findings. It emerges that the diamond has nine normal modes of atomic vibration, the principal mode of highest frequency being that in which the two interpenetrating lattices of carbon atoms of which the diamond is composed oscillate as units against each other. The other eight modes may be described as oscillations of the layers of carbon atoms present in the octahedral and cubic planes respectively, either normally or tangentially to themselves, and the adjacent layers being either in the same or in the opposite phases.

4. Spectral shifts in light scattering

The discovery made by the author in February 1928 that monochromatic light diffused in a crystal is accompanied by additional radiations of altered frequency provides an extremely simple and precise method of identifying the modes of atomic vibration in crystals. On the basis of this earliest observations, the author in his address to the Faraday Society at its Bristol meeting in September 1929 suggested that the more perfectly ordered is the atomic space-grouping in a crystal, the sharper would be the lines recorded as frequency shifts in its spectrum of light-scattering. A striking confirmation of this emerged from the observation made soon afterwards that even with a very small diamond, a very sharp and intense line with a frequency shift of 1332 wave-numbers per second is recorded. This frequency shift arises from the mode of vibration of the diamond structure with the highest frequency.

None of the other fundamental modes of vibration of the diamond structure can manifest itself as a frequency shift for the reason that the alternation of phase of the movement as we pass from each cell of the structure to the next would cancel out the effects to be expected. It would be possible, however, for the modes to manifest themselves as overtones with doubled frequency shifts or also as summational frequency shifts. The effects thus arising would naturally be extremely feeble. In practice, they would be overpowered by the spectrum of the luminescence of diamond which is simultaneously recorded. The efforts made to record the second-order spectrum of diamond in the scattering of light proved successful only when non-luminescent diamonds were available and use was made of the intense excitation provided by the λ 2537 resonance-radiation of a water cooled magnet-controlled mercury lamp. The second-order spectrum of diamond as actually recorded in this manner exhibits features in excellent agreement with what is to be expected on the basis of the dynamic theory and other relevant considerations.

A very sharp line which is recorded at one end of the spectrum with a frequency shift of 2666 wave-numbers is clearly identifiable as the octave of the highest fundamental frequency of 1332 wave-numbers. Another line which stands out clearly near the other end of the spectrum with the frequency shift of 2176 is clearly the octave of the frequency 1087 which is that of the oscillation of the cubic layers in the crystal normally to themselves. A strong band covers the range of frequency shifts from 2540 to 2450 and has a peak intensity at 2460. This arises from the superposition of the octaves and summation of the two frequencies 1273 and 1219, these being respectively the eight-fold and the six-fold degenerate oscillations tangential to themselves of the octahedral and cubic layers of atoms. The frequencies of 1176, 1010, 746 and 624 respectively are not recorded in the second-order spectrum of light-scattering.

The non-appearance of some of the vibrational modes and the observed relative strength of those which are actually recorded as octaves or summations in the second-order spectrum can be fully explained on the basis of the nature of the respective modes. It should be stated here that the spectrum of light-scattering and the spectrum of infra-red absorption do not differ noticeably in respect of the frequencies of the modes of vibration manifested therein. But the intensity relationships are altogether different in the two cases, as is indeed to be expected in view of the wholly different mechanisms involved.

5. The dynamic reflection of X-rays

Under the title "A new X-ray effect", the author with his assistant Nilakantan announced in the issue of *Current Science* for April 1940, the discovery of a highly remarkable phenomenon exhibited by diamond when a pencil of X-rays emitted by a copper target passes through it and the diffracted X-rays are recorded on a photographic plate. The specimen employed was a cleavage plate normal to the octahedral planes of the crystal. The diamond itself was of the type described earlier in this article as non-centrosymmetric, in other words, a diamond which does not give any sensible restoration of light when examined between crossed polaroids and displays infra-red activity both of the first and the second orders. The original publication of April 1940 was followed by several others in the *Proceedings of the Indian Academy of Sciences* in the years 1940 and 1941. Owing to unavoidable reasons, the subject was then laid aside and could be resumed only after many years when more powerful X-ray equipment became available. The results and conclusions then arrived at are set out in the author's Memoir No. 109 entitled "The diffraction of X-rays by diamond". Numerous illustrations of the phenomenon as observed in various settings of the crystal are reproduced in it.

Studies on the crystal perfection of the diamonds actually used in the work described in Memoir No. 109 were made by single crystal and double crystal X-ray spectroscopic methods. The results of the examination proved that they were absolutely perfect or ideal diamonds as is shown by their spectra which have been reproduced with the same memoir. It was further demonstrated by photographs appearing in the memoir that the X-ray diffraction effects observed exhibit the same type of symmetry as the diamond itself; for example, the different sets of octahedral planes give identically similar results. Using a diamond which was a triangular twin, its two components show precisely similar effects turned round through 60°. It was thus firmly established that the effects under study were truly characteristic of the diamond crystal.

The importance of the studies described in Memoir No. 109 is that they demonstrate the effect discovered in the year 1940 to be a reflection of monochromatic X-rays by the lattice planes of the crystal with a small but quite definite change of frequency and that this X-ray effect is exactly analogous to the optical effect observed in the scattering of monochromatic light by diamond, with the difference that it is only exhibited by diamonds which are infra-red active in respect of the fundamental vibration of the frequency of 1332 wave-numbers, whereas the optical effect can be observed with all diamonds. The dynamical theory shows that this mode of vibration of the crystal structure of diamond is triply degenerate; in other words, it occurs along any of the three cubic axes of the crystal. This is beautifully confirmed by the fact that in appropriate settings of the diamond, the dynamic X-ray reflection by each octahedral plane appears as three well-separated spots: the reflections by other lattice planes show analogous effects in accord with the theoretical considerations developed in the memoir.

The possibility of observing the dynamic X-ray reflections by diamond arises because the mode of vibration of the structure which gives rise to them is highly monochromatic and repeats itself in the same fashion as we pass from cell to cell in the structure. Thus, the appearance of these reflections is itself a demonstration of the correctness of the approach to the dynamical theory of the atomic vibrations in diamond set out in Memoir No. 129.

6. The tetrahedral carbon atom

As has been described earlier, the study of the crystal forms of diamond leads us to conclude that there are two types of diamond of which the inner structures are respectively centrosymmetric and non-centrosymmetric. Actual observation shows that the diamonds of the centrosymmetric type exhibit the infra-red absorption of the second-order only, whereas diamonds of the non-centrosymmetric type exhibit both the first and second-order infra-red absorptions. Observation also shows that these same two types of diamond exhibit noteworthy differences in respect of their transmitting power for light appearing in the near ultra-violet part of the spectrum. Finally, we have the remarkable differences in the X-ray diffraction phenomena which they exhibit. Taking these facts into consideration, we are obliged to infer that we are here concerned with a fundamental difference in the symmetry characters of the binding of the carbon atoms within the crystal with each other.

Diamond may be very simply described as the result of two sets of carbon atoms holding each other in place, each atom of one set being surrounded by four others in a tetrahedral setting. The local symmetry at the centre of each carbon atom is only tetrahedral. What the symmetry of the structure is which results from the linking together of each carbon atom with four others depends on the nature of the linking. This question is fully discussed in the author's Memoir No. 104 entitled "The tetrahedral carbon atom and the structure of diamond". It has been shown that there are indeed alternative possibilities for the nature of the binding between the carbon atoms which do not involve any difference in the charges of the atoms, nor any difference in the energy of their binding.

The approach to the problem indicated in Memoir No. 104 enables us to understand why diamonds whose symmetry of structure is only tetrahedral may nevertheless succeed in exhibiting a pseudo-octahedral symmetry of form. The oppositely directed tetrahedral forms of the structure are indistinguishable from each other except in their geometric setting. Hence, they can freely intermingle with each other and the aggregate thus formed would tend to mimic octahedral symmetry to a greater or less extent. The aggregate would only be approximately but not absolutely homogeneous. The way is thus opened to a deeper understanding of various recondite properties of diamond, as we shall presently see.

7. The luminescence spectra of diamond

For a diamond to exhibit luminescence under ultra-violet irradiation, it is clearly necessary that it should be capable of absorbing the incident radiation. Diamonds of the non-centrosymmetric type exhibit a blue luminescence of which the intensity varies enormously with the specimen under study. Spectroscopic examination reveals that these diamonds exhibit an absorption band located near the violet end of the spectrum. Further, at exactly the same wavelength, an emission band appears in the spectrum of luminescence. A lowering of the temperature of diamond to $-180°$ C results in a spectral sharpening of both the absorption and the emission with a shift towards shorter wavelengths. *Per contra*, raising the temperature of the diamond results in a great increase in their spectral widths. With the diamond held at $-180°$ C, the sharpened line appears at $\lambda 4153$. This is accompanied in emission towards greater wavelengths and in absorption towards smaller wavelengths by a system of bands exhibiting an observable discrete structure. Measurements show that these bands owe their origin to the vibrations of the diamond structure accompanying the change in the electronic energy levels which manifests itself as the emission or absorption at $\lambda 4153$.

The enormous variations in the strength of the blue luminescence as between different diamonds is readily understood in terms of the non-homogeneity of structure due to the intermingling of the positive and negative tetrahedral forms in the substance of the diamond. The greater the number of the discrete blocks in the aggregate, in other words, the greater is the mosaicity of the structure of the diamond, the more intense would be its luminescence and the stronger would be the associated absorption of light. This explanation is confirmed by the experimental result that the intensity of the ordinary X-ray reflections by the lattice planes increases *pari passu* with the intensity of its luminescence. The angular width of the reflection of monochromatic X-rays also increases in the same circumstances.

A second type of luminescence having a greenish-yellow colour is exhibited by many diamonds. Spectroscopic examination of this luminescence with the diamond held at a temperature of − 180° C reveals that it arises from an emission band at λ 5032 accompanied by a vibrational band system at greater wavelengths. Likewise and in the same circumstances, these diamonds exhibit an absorption band at λ 5032 accompanied towards lesser wavelengths by vibrational bands. This type of luminescence is found to be exhibited by diamonds of the composite type, in other words, by diamonds in which both the centrosymmetric and the non-centrosymmetric are located in juxtaposition. In such cases, the luminescence is exhibited by the diamond as a set of parallel streaks over its area and not as continuously distributed within its volume. Photographs exhibiting these features have been reproduced in Memoir No. 129.

8. The electronic spectrum of diamond

Each of the carbon atoms in diamond has a shell of four electrons surrounding the nucleus. These electrons play the principal role in holding the atoms together in the ordered structure of the crystal. The atomic vibration frequencies are determined by the strength of such binding and by the masses of the atomic nuclei and they appear in the infra-red range of the spectrum. If, on the other hand, we assume the nuclei to be at rest and only the electrons to be disturbed from their positions of equilibrium, their oscillations would appear in the ultra-violet region. To evaluate the modes and frequencies of electronic vibration, we may proceed on the assumption that all four electrons in the shell behave as a single unit of which the mass is four times that of an electron, and that these shells oscillate around their positions of equilibrium in the same manner as the atomic nuclei in the vibrations of infra-red frequencies. The evaluation of the electronic spectrum of diamond then becomes a simple matter. We have only to multiply the infra-red frequencies by the square root of the ratio between the mass of a carbon atom and the mass of the four electrons taken together. The results of thus evaluating the electronic spectrum of diamond are shown in table 1.

The following results emerge from table 1. The electronic spectrum of diamond consists of a set of eight monochromatic frequencies which lie in the ultra-violet range. The highest frequency corresponds to the wavelength λ 1010 and the lowest frequency to the wavelength λ 2157. That this evaluation is highly

Table 1. Evaluation of electronic frequencies.

Mode	Degeneracy	Atomic vibration frequency (wave-numbers) cm^{-1}	Electronic spectrum (wavelengths) Å
I	3	1332	1010
II	8	1273	1057
III	6	1219	1104
IV	4	1176	1144
V & VI	3 + 3	1087	1238
VII	4	1010	1332
VIII	6	746	1804
IX	8	624	2157

successful in describing the actual behaviour of diamond is evident. The cut-off wavelength for diamond in the ultra-violet is $\lambda\,2240$, which is close to the greatest wavelength of $\lambda\,2157$ appearing in table 1. The highest frequency represented by the wavelength $\lambda\,1010$ would be that principally responsible for the optical dispersion of diamond, while the others of greater wavelengths would play only minor roles. This follows from the fact that only the mode of highest frequency repeats itself from cell to cell of the structure, while the others alternate in phase and their first-order effects would therefore cancel out. The refractive index of diamond in the spectral range extending from the red in the visible to the limit of transmission in the ultra-violet has been determined with great care by Peters. It is accurately represented by the formula given by him

$$(n^2 - 1) = \frac{\varepsilon_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{\varepsilon_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

where $\varepsilon_1 = 4{\cdot}3356$, $\varepsilon_2 = 0{\cdot}3306$, $\lambda_1 = 1060$ Angstroms and $\lambda_2 = 1750$ Angstroms. It will be seen that ε_1 is far larger than ε_2 and that the wavelength λ_1 is reasonably close to the smallest wavelength $\lambda\,1010$ appearing in table 1. The difference between this wavelength and the wavelength $\lambda\,1060$ which appears in the two-term dispersion formula of Peters may be explained as arising from the small contributions made by the adjoining modes of lower frequency listed in table 1. The formula fits the observed data of dispersion for both types of diamond in a very satisfactory manner.

9. The ultra-violet absorption spectra

The electronic spectrum of diamond as shown in table 1 consists of eight monochromatic wavelengths in the ultra-violet. But when the transmission of ultra-violet radiation through a plate of diamond of the centrosymmetric type is examined, what is observed is a complete cut-off of the spectrum over the entire range of wavelengths covered by table 1. How is this discrepancy to be explained? We are assisted in finding the answer to this question by the fact that the wavelength at which the cut-off appears shifts with the temperature at which the diamond is held, altering from λ 2393 at 314° C to λ 2240 at − 174° C. It is thereby made evident that the thermal agitation strongly influences the strength of the absorption by diamond. We have also to take note of the fact that the excitation of electronic vibrations by the incident radiation would be accompanied by the excitation of vibrations of the infra-red frequencies and of their overtones. In consequence, the frequencies at which absorption could occur would be very numerous and not eight only. Even at the temperature of liquid air, the thermal broadening of the electronic lines would not be negligible. Inevitably, therefore, the final result would be in the nature of a complete cut-off for any moderate thickness of the absorbing plate.

When the diamond is of the non-centrosymmetric type, there is a sensible absorption of wavelengths greater than λ 2240 instead of free transmission as in the case of the centrosymmetric diamonds. Much depends on the actual thickness of the plate of diamond with which the observations are made. A plate which has a thickness of only a tenth of a millimetre exhibits a sensible transmission for wavelengths less than λ 3000, the cut-off then being located at λ 2240 as in the case of diamonds of the other kind. But if the thickness is a few millimetres, there is practically complete extinction up to λ 3000. A noteworthy feature is manifested by these diamonds, viz., the appearance of a series of absorption maxima in the spectrum. By cooling the diamond to − 180° C and by using diamonds of appropriate thickness, and a spectrograph of adequate resolving power and suitably regulating the exposures, it is possible to record and measure exactly the positions of as many as 25 distinct lines in the wavelength range between λ 3347 and λ 3015. Some of these lines are of considerable intensity, and others are less conspicuous. Further out in the ultra-violet between λ 2240 and λ 3015, it is possible to record and measure other absorption minima, the most conspicuous of them being the sharp doublet λ 2356–2360 and the doublet λ 2296–2298.

Two questions here arise calling for an answer. What is the origin of the absorption observed in the region of wavelengths greater than λ 2240, and why does its spectrum exhibit a series of sharply-defined lines? Further, why is this absorption exhibited only by diamonds having a non-centrosymmetric structure? In considering these questions, it should be remarked that there are no measurable differences in refractivity between the two types of diamond. It may be inferred from this that the electronic spectrum exhibited in table 1 is identical for both types of diamond and that the absorption frequencies manifested in the region under consideration make no sensible contribution to refractivity. A possible explanation of this situation is that these absorptions arise from the same set of electronic frequencies as those listed in table 1, but *diminished* by the subtraction therefrom of the overtones of various orders of the infra-red frequencies. The subtractions would yield a series of discrete frequencies, the strength with which they are manifested decreasing rapidly in the higher orders. If the process of such absorption is regarded as involving a kind of infra-red activity, their non-appearance with centrosymmetric diamonds and their manifestation with diamonds of the other type becomes intelligible.

Before leaving this topic, we may remark that the manifestation of a whole series of sharp lines in the absorption spectrum of diamond is a convincing demonstration that the electronic spectrum of diamond is not continuous but exhibits a discrete and enumerable set of sharply-defined frequencies, capable of manifesting themselves as such in appropriate circumstances.

10. Thermal and thermo-optic behaviour of diamond

Utilizing the spectroscopically determined frequencies of atomic vibration with their respective degeneracies as listed in table 1, it is a simple matter to evaluate the heat-capacity of diamond over the entire range of temperatures from 0° to 1000° absolute. The Einstein functions multiplied by the respective degeneracies for each of the atomic vibration frequencies may be added up. We then add the contribution to the thermal energy made by the three omitted degrees of frequencies representing the translations of the atoms. The total is divided by 48. We thereby obtain a representation of the variation of specific heat with temperature which exhibits a very satisfactory agreement with the facts of observation. The calculations are fully set out in part X of the author's Memoir No. 129. It is, therefore, unnecessary to traverse the same ground here.

A remarkable property of diamond is that its refractive index increases with the temperature, indeed more and more rapidly as we proceed to higher temperatures. Studies of this phenomenon have shown it to be a consequence of the progressive fall with temperature of the characteristic dispersion frequencies of diamond. The characteristic frequencies in the infra-red also exhibit a similar fall which is also proportionately the same. This can readily be understood in view of the electronic and infra-red frequencies being related to each other as shown in table 1.

As an illustrative example, it may be mentioned that the principal vibration frequency which is 1333 cm^{-1} at −180° C falls to 1332 at 30° C, to 1327 at 320° C, to 1321 at 630° C, and to 1316 at 850° C. The corresponding frequency shift as observed in the spectrum of light scattering remains remarkably sharp over the whole of this temperature range.