Foreword

The objects of the Raman Research Institute include besides the promotion of scientific research and its peaceful applications, also the strengthening of international peace and goodwill through cultural exchanges, personal contacts and in other ways. With a view to promote the purposes mentioned and to enable the Institute to co-operate in the furtherence of the objects of the Gandhi Smarak Nidhi, an annual series of lectures on the subjects of "Science and human values and/or any of its aspects" has been established at the Institute with the aid of the Nidhi. The appended lecture is the third of the series and was delivered on the 2nd of October 1961.

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THE DIAMOND

BY

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1. INTRODUCTION

DIAMOND, besides being the most highly-valued of gem-stones, is a material of extraordinary interest and importance to the man of science. Both by reason of the simplicity of its structure and composition and by reason of the variety of techniques available for the investigation of its spectroscopic behaviour, the study of diamond offers a most promising approach to the elucidation of the fundamental aspects of crystal physics. Questions such as the following need an answer. What is the nature of the atomic vibration spectrum of a crystalline solid and how is it related to its structure? Why does the passage of light through a crystal result in its diffusion with a change of frequency? In what circumstances and in what manner does the absorption of infra-red radiation occur in its passage through a crystal? How are the spectroscopic properties of a crystal related to its thermal energy content? Answers to these and many other questions are furnished by the facts which emerge from a study of the spectroscopic behaviour of diamond.

A remarkable property of diamond is that even selected material of the highest quality shows an astonishing variation of behaviour in certain respects, including especially its transparency to ultra-violet light and to infra-red radiation. Specially noteworthy also are the enormous variations observed in the intensity and spectral character of the visible luminescence exhibited by diamond under ultra-violet illumination. The explanation of these and other variations and the correlations which exist between them is an important part of the field of research presented by diamond and adds greatly to the interest of the subject. But in recognising this, one should not overlook the importance of finding answers to the fundamental questions which arise in respect of all diamonds. Indeed, not unless the more general questions have been satisfactorily answered can we hope to give the correct replies to the question why particular diamonds differ amongst themselves.

The morphology, structure and properties of diamond have interested the writer and have been the subject of numerous investigations and published reports by him and his collaborators in earlier years. To enable these studies to be undertaken, specimens were acquired from time to time and the collection thus built up now includes some hundreds of diamonds of varied origins and of diverse forms and qualities. Crystals of diamonds in their natural forms as found near Panna in Central India and from the South African mines form the most attractive items in the collection. But by far the most useful specimens included in the collection are the flat polished plates, one hundred in number, which are of diverse thicknesses and sizes and exhibit varied types of behaviour. There is no more convenient form of diamond for examining its optical properties than a flat polished plate, especially if its faces have a known crystallographic orientation, as is frequently the case for the plates in the writer's collection. It is obvious that for a real understanding of the problems presented by diamond, it is necessary to study such an extensive range of material and to examine the individual diamonds in detail in respect of diverse properties, and then to compare and correlate the results thus obtained. One of the most surprising facts about diamond is the existence of the correlations which come into evidence in an extremely striking and convincing fashion in such studies. That they must be recognised and need to be explained is obvious. But more important still is the fact that they point the way to a real understanding of the nature and properties of diamond.

2. METHODS OF STUDY

It had long been the desire of the writer personally to study the infra-red behaviour of the entire collection of plates of diamond in his collection. But only recently however has the acquisition for this Institute of a Leitz recording inf a-red spectrophotometer provided with both NaCl and KBr optics enabled this project to be seriously undertaken. The region of wavelengths between 1μ and 15μ can be traversed with the NaCl optics and between 13μ and 24μ with the KBr optics. With the spectrograph properly adjusted and worked, it becomes almost a routine operation to record the percentage transmission curves in these ranges. A special point of importance which has to be attended to is the most appropriate speed of operation. To get out the records quickly, one might be tempted to tend to run the spectrograph at the maximum permissible speed. But experience shows that, especially with the plates of smaller area, this is an erroneous procedure to follow. The best records are those in which the recording apparatus is set at slow speed as the maximum of detail and the highest definition are then obtained. Merely to record the percentage transmission curves of a large number of plates can serve no useful purpose unless one also examines each individual plate by other methods of study which can throw some light on the nature of the material under investigation. Of such methods there are several. But we shall here mention only three techniques which involve the minimum of labour and at the same time are highly revealing. The first is the examination of the transparency of the material in the ultra-violet region of the spectrum. The second is the absence or presence of birefringence. The third is the visible luminescence of the diamond under ultra-violet illumination and especially the variations of the intensity and the colour of such luminescence.

A simple method of examination for ultra-violet transparency is to place the plate of diamond on a sheet of uranium-tinted glass which fluoresces strongly under ultra-violet illumination. A convenient source of such illumination is that commonly used for examining the luminescence of minerals, *viz* , a mercury vapour lamp in a tube of fused quartz, enclosed in a metal case one side of which is open but is covered by a filter which cuts off the visible light but allows the ultra-violet radiation of the lamp to pass through. When the lamp is held over the diamond, its transparency or lack of transparency is immediately revealed by the appearance presented by the glass plate as viewed either from above or from below. The area covered by the diamond appears dark if it is opaque and bright if it is transparent. While this simple technique suffices for a qualitative examination of the ultra-violet transparency of diamond, it is desirable to use the λ 2536.5 resonance radiation of the mercury arc isolated by a quartz monochromator for more critical studies in which it is sought to observe and photograph the variations, if any, which the plate of diamond exhibits in respect of its ultra-violet transparency over its entire area. We shall in a later part of this memoir return to the results obtained in this manner.

Examination of a diamond plate for the presence or absence of birefringence is a very simple matter. The diamond is placed on a strainfree glass plate and viewed through a pair of crossed polaroid sheets against a brilliant source of white light. Even the faintest birefringence becomes visible in these circumstances. The nature and character of the birefringence, if any, that is present can be determined by examination through a magnifier of appropriately chosen power.

The technique for observing the luminescence of the diamond is equally simple. The plate of diamond is placed on a sheet of black glass and a beam of sunlight filtered through a sheet of black glass which transmits only the ultra-violet part of the solar spectrum is focussed on it. The presence or absence of luminescence and its colour and intensity, if present, then become evident to observation. The use of filtered sunlight in the experiment ensures that the illumination of the diamond is of adequate intensity, so that a feeble luminescence is not mistakenly regarded as indicating the absence of luminescence. It is by no means generally the case that luminescence when present has the same intensity or colour over the entire area of the plate. It is possible, of course, to record the luminescence patterns of the dimond in such cases photographically on a colour film. It is sufficient, however, to photograph the luminescent diamond on ordinary film through appropriately chosen colour filters so as to exhibit these variations.

3. THE RESULTS OF THE STUDY

We now proceed to indicate in broad outline the results which have emerged from the investigations. A critical examination of the optical behaviour of all the one hundred polished plates of diamond in the writer's collection reveals that they fall into three groups. Two groups of diamonds which we shall designate here as group A and group B each form about ten per cent. of the entire number of specimens. The remaining eighty per cent. of the diamonds will here be designated as group C. The diamonds in group A exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. The diamonds in group B also exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. But the properties of the diamond in group A and the properties of the diamond in group B are so strikingly contrasted that the observer is obliged to infer that they represent fundamentally different forms of diamond. That this is actually the case and that the crystal structures of the diamonds in group A and group B are indeed dissimilar, is demonstrated by the characters exhibited by the infra-red absorption spectra of the two groups of diamond. Their spectral behaviours are completely identical in some respects and completely dissimilar in other respects. Considered in conjunction with the other differences alluded to, it is clear that the facts admit of no explanation other than that we are here concerned with basic differences in crystal architecture. What these differences are is indicated in an unmistakable fashion by the spectroscopic observations.

The remaining eighty per cent. of the diamonds which we have classed together as group C are shown by the studies to be *composite diamonds*, in other words, diamonds in which the structures characteristic of group A and the structures characteristic of group B are present side by side in the same specimen in juxtaposition. This is not an inference from theory but is a statement of actual facts of observation. The geometric patterns of various sorts which these composite diamonds exhibit are visual evidences that over the area of any one cleavage plate of diamond, there are some parts which exhibit the characteristic properties of the diamonds of group A while the other parts exhibit the characteristic properties of diamonds of group B. Moreover, these parts are distributed over the area in regular crystallographic patterns which by themselves conclusively demonstrate that the diamonds of group A and the diamonds of group B are distinct crystallographic entities different from each other.

Proceeding now to consider the result of the studies by the methods described earlier, we may first remark upon the appearance of diamonds belonging respectively to the two groups as viewed between crossed polaroids against a bright white source of light. While the edges of the ten diamonds of group A are visible by reason of the light refracted at their peripheries, the plates themselves appear quite dark. In other words, the diamonds of group A are non-birefringent, and may hence be described as *truly isotropic and optically perfect diamonds*. On the other hand, all the eight diamonds of group B exhibit a marked restoration of light as seen between crossed polaroids. The patterns of birefringence which they exhibit differ from diamond to diamond both in respect of intensity and their geometric configuration, but in none of the eight specimens is the birefringence absent. Thus, we are justified in stating that the exhibition of a visible birefringence is a general characteristic of the diamonds of group B.

The same ten diamonds of group A and eight diamonds of group B were examined for their transparency in the near ultra-violet region of the spectrum by the methods already described. They were placed on sheets of uranium-tinted glass and their transparency or opacity (as the case may be) in the near ultra-violet region of the spectrum stands immediately revealed by the luminosity of those sheets. All the diamonds of group A exhibit complete opacity, while those of group B are highly transparent to the part of the spectrum under consideration. As between themselves, the eight diamonds of group B exhibit some differences in respect of their transparency. These differences are ascribable to a slight yellowish tinge exhibited by some of the specimens, while the others are perfectly colourless.

We may next consider the behaviour of the same ten diamonds of group A and the same eight diamonds of group B in respect of the luminescence excited by the incidence of ultra-violet radiation. The two groups of diamond were placed side by side on a sheet of ordinary glass and strongly illuminated by the light of three mercury lamps enclosed in Wood's glass which cut out all the visible except some deep red. The glass sheet with the diamonds adherent to it was photographed through a cell containing an aqueous solution of sodium nitrite. This filter cuts off the scattered or reflected ultra-violet light and allows only the visible luminescence to come through. All the diamonds of group A exhibit a visible luminescence but with very different intensities in the different diamonds. The colour of the luminescence as actually observed was a clear blue in all cases. On the other hand, all the diamonds of group B are seen to be definitely non-luminescent.

We may sum up the information thus obtained as follows: The diamonds of group A are isotropic and optically perfect diamonds. They are opaque to ultra-violet radiation less than $0{\cdot}3\mu$ in wavelength, and exhibit a visible blue luminescence under ultra-violet irradiation but of varying degrees of intensity. On the other hand, the diamonds of group B exhibit a readily observable birefringence, are transparent to ultra-violet radiation of wave-lengths between $0{\cdot}3\mu$ and $0{\cdot}25\mu$, and are non-luminescent. These properties of the two groups of diamond go hand in hand with their differences in behaviour towards infra-red radiation. It will suffice here to draw attention to some of the outstanding features. In the spectral region between 2μ and 6μ, the two diamonds exhibit features which are indistinguishable from each other. On the other hand between 6μ and 12μ, the behaviour of the two diamonds is totally dissimilar. The group A diamond exhibits an absorption which goes up steeply beyond 7μ and a whole series of absorption maxima appear thereafter, while on the other hand, the group B diamond is highly transparent throughout this range. Any attempt to explain these facts should necessarily take into account the facts revealed by the studies I and should be based on sound physical reasoning and not on *ad hoc* suppositions.

4. THE COMPOSITE DIAMONDS

The many striking differences in the physical behaviour of the perfect diamonds and of the non-luminescent diamonds are a sufficient demonstration that their crystal structures are fundamentally different. Nevertheless, their structures must be closely related to each other. For, they have infra-red absorption spectra which in the second and third orders are indistinguishable, while the first order is present only for the perfect diamonds and absent for the non-luminescent ones. Spectroscopic theory considered in the light of the mechanism of infra-red absorption gives us the clue to the origin of these differences. But the differences are evidently not of such a nature as to preclude the two structures appearing in juxtaposition in one and the same diamond. Indeed, this is so frequently the case that the composite diamonds, as we shall call them, form the large majority amongst the polished plates of diamond in the writer's collection. As has already been mentioned, about ten per cent. of the specimens are perfect diamonds, another ten per cent. are non-luminescent ones, while the remaining eighty per cent. are composite diamonds.

The easiest and also the most convincing demonstration that any particular specimen is a composite diamond is furnished by observations of its ultra-violet transparency. The technique of such observations has already been described. The λ 2536·5 radiation of a mercury arc lamp passes through the diamond and is then incident on a fluorescent plate in close contact with it. The luminescence of the plate then immediately reveals the variations in the transparency of the diamond over the different parts of its area.

Another very instructive demonstration of the composite nature of a diamond is furnished by observations of the luminiscence excited by ultra-violet radiation. Such luminescence may be observed either through a filter which transmits only the blue end of the spectrum or through a yellow filter which cuts out the blue and green altogether and transmits only the yellow, orange and red. The characters of the luminescence are found to be totally different as observed through the two filters and these differences are very revealing in respect of the structure of the diamond.

Still another method of observation is to view the diamond between crossed polaroids against a bright source of light. A perfect diamond would, of course, exhibit no birefringence. A non-luminescent diamond, on the other hand, would exhibit a birefringence of the kind described in the fourth part of this memoir, but no trace of the structure thus revealed would appear in its ultra-violet transparency. Composite diamonds, on the other hand, exhibit birefringence patterns of which the features can be recognised both in the ultra-violet transparency patterns and in the patterns of luminescence, and especially in the latter as seen through a yellow filter.

We shall now briefly consider what these facts of observation signify. It is well known that diamonds are usually found in nature as complete single crystals which are ordinarily not of any great size. In these circumstances, the composition and properties of any one crystal may be expected to be uniform within its interior. The actual position is rather different, as we have seen. In about ten per cent. of the cases, we find diamond to exhibit a definite set of properties and in another ten per cent. of the cases a different set of properties. Moreover, in a large majority of cases the crystal exhibits regions in its interior where one kind of diamond appears and other regions where the other kind appears. Further, the regions where the two kinds appear are bounded by crystallographic planes of importance, *viz.*, the octahedral or the dodecahedral planes. The only reasonable explanation that can be put forward for this situation is that the crystal structure of diamond may assume one or another of certain alternative forms which are different but nevertheless resemble each other sufficiently to appear in juxtaposition in the same crystal. All the phenomena with which we have been confronted in our studies have to be explained on this basis.

5. THE STRUCTURE OF DIAMOND

Diamond exhibits in its structure the most perfect demonstration of the validity of the concept of the tetrahedral carbon atom. Each carbon nucleus is held to four other nuclei grouped around it in an exactly tetrahedral configuration, these four other nuclei again being connected to others grouped around them in the same fashion. The structure thus built up is continued in all directions throughout the volume of the crystal. How and why this tetrahedral configuration is set up and maintained with the perfection actually observed are questions which we shall not here enter into. What we are here concerned with is the ordering of the atomic nuclei within the volume of the crystal. The structure of diamond may be described compendiously as composed of two interpenetrating face-centred cubic lattices. For our present purpose, it is more usefully regarded as composed of two interpenetrating rhombohedral lattices, eight nuclei situated at the points of each of which delineate the unit rhombohedral cell. Thus, two sets of eight nuclei, in other words, 16 nuclei taken together form the unit with the dynamical behaviour of which we are concerned in our studies. The nuclei appear in the crystal in equidistant layers parallel to its cubic planes, while in the octahedral layers the nuclei appear in layers which are alternately nearer together and further apart in the ratio of one to three.

A crystal is an extended system which is a three-dimensionally periodic array in space of structural units, each of which contains a finite number, which we shall denote by p, of non-equivalent mass-particles. The interaction of the structural units with each other has, of necessity, to be considered in considering the possible modes of vibration of these structural units. By writing down the equations of motion of the p non-equivalent particles in any one structural unit and proceeding to solve them to find their normal modes of vibration, it is readily established that there are really eight species of normal modes, all of which are comprised in the following statement: *in any one normal mode, equivalent atoms in the successive cells of the structure situated along its axes have the same amplitude of vibration and a phase which is either the same or else alternates in successive cells of the structure along one, two or all three axes of the lattice.* The alternatives for the three axes of the lattice being independent, we have 2×2×2 or 8 distinct possibilities, in other words, 8 distinct species of normal modes. The same result may also be very simply derived from the consideration that the structure of the crystal is brought into coincidence with itself by a unit translation along any one axis, and hence a normal mode of vibration which is a property of the structure must also conform to the principle of translational symmetry. This is possible only if, following a unit translation, the amplitudes of vibration of equivalent atoms remain unaltered and the phases all remain unaltered or else are all reversed. This way of regarding the matter is instructive since it indicates that what we have referred to as the normal modes of vibration of the structural units may equally well be described as the stationary modes of vibration of the extended system of particles forming a periodic structure which constitutes the crystal.

The geometric characters of the free vibrations of the structure may be deduced in the following manner. Considering a simple rhombohedral lattice, the eight possible situations regarding the phase of thc movements at its lattice points give us firstly, a simple translation of the whole lattice, four movements in which the nuclei in the alternate octahedral planes move in opposite phases and three others which are movements of the cubic planes alternately in opposite phases. There are two rhombohedral lattices to be considered and their phases may be either the same or opposed to each other. The directions in which the movements occur are determined by the symmetry of the structure. They would evidently be either normal or tangential to the layers concerned, the tangential movements being twice as numerous as the normal ones. The translation of the two lattices if in opposite phases yield a triply degenerate mode of vibration, and if in the same phase only a simple translation. Thus, in all, we have nine species of normal modes, but only eight distinct frequencies since the fifth and sixth modes are indistinguishable. The mode of highest frequency is an oscillation of the two interpenetrating lattices of carbon nuclei with respect to each other. The other frequencies represent the oscillations of the octahedral or cubic layers in the crystal either normally or tangentially to themselves.

6. THE INFRARED BEHAVIOUR OF DIAMOND

Various questions arise which need an answer. Why is there any absorption of infra-red radiation in its passage through diamond? What part do the nuclei and the electrons in its structure respectively play in this phenomenon? Why do some diamonds exhibit infra-red absorption both of the first order and of the second order, and why do others exhibit only the second-order absorption? Why do the different normal modes exhibit very different infra-red activities and why do such activities differ respectively in the first order and second-order absorption? Why is the explanation of the relationships actually observed between the infra-red behavior of diamond and such other properties as ultra-violet transparency and luminescence? We shall now endeavour to answer these questions.

The absorption of infra-red radiation in its passage through a crystal involves the conversion of the energy of the electromagnetic field into vibrational energy in the solid, in other words, its degradation into heat. The spectrographic records show that the absorption is preferential with respect to certain modes or frequencies of vibration. We naturally, therefore, turn our attention first to the movements of the atomic nuclei in the crystal and consider the action of the electric field of the incident radiation on the positive charges of these massive particles. Here, however, we find in all the normal modes of vibration, that for every nucleus which is in oscillation, there is another nucleus which is a near neighour and oscillates with the same amplitude but in an opposite phase. Hence, considering them together, the net transference of energy from the field to the nuclei would be a vanishing quantity. In other words, the atomic nuclei do not play the primary role in infra-red absorption, and we have to recognise the electrons or negative charges in the crystal as the active agents in that process. The field of the radiation disturbs the electrons and their movements result in the nuclei being disturbed from their positions of equilibrium and set into vibration. But it is the electronic movements associated with such vibrations and not the movements of the nuclei themselves which react with the field and result in the absorption of the incident radiation.

From what has been stated, it follows that in seeking for an explanation of infra-red activity, we have to fix our attention on the movements of the electronic charge-clouds in the crystal. It is the symmetry of the distribution of the negative electric charge in its undisturbed state as well as when it is modified by the nuclear movements which determines the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

Since all diamonds exhibit the absorption spectrum of the second order, it is appropriate that we first consider how such absorption arises. We may, for the present, leave out of consideration the mode of highest frequency and discuss the infra-red activity of the other modes of vibration of lower frequencies. It is a specific feature of all these modes that the alternate layers of nuclei located at the points of the same lattice oscillate in opposite phases. Hence the electrons attached to the nuclei in those layers would also oscillate in opposite phases. Hence, it might be thought that the displacements of electric charge when summed up would vanish and hence that these vibrational modes would fail to exhibit any infra-red activity. But this conclusion is subject to an important qualification, *viz.*, the movements considered are of infinitesimally small amplitude. When this is no longer the case, the approach of any two layers towards each other and the recession of the next two layers from each other would not necessarily produce equal displacements of electric charge. Their difference would represent the resultant displacement of charge and this would evidently be periodic with *twice the frequency* of the vibrational mode. It follows that there could, in favourable circumstances, be an absorption of radiation having *double the frequency* of each of the vibrational modes under consideration. This, to put it briefly, is the explanation of the absorption spectrum of the second order exhibited by all diamonds.

Infra-red activity of the second order demands that the normal mode under reference should result in the negative charges suffering displacements of substantial magnitude. Whether this is actually the case would depend upon the nature of the vibration. When we compare the different normal modes with each other from this point of view, it becomes evident that their infra-red activity would be very different in the different cases. Indeed, we could without difficulty group the modes in the order of the strength of the infra-red activity which they might be expected to display.

We shall now consider the activity of the principal mode of vibration having the highest frequency which is manifested by the perfect diamonds. Expressed in wave-numbers, this frequency is shown by studies on the scattering of light to be 1332 cm.$^{-1}$ This is also the value exhibited in the first-order absorption spectrum. The feature which distinguishes this mode from the several others of lower frequencies is that the vibrations appear in the same phase in the successive cells of the structure along its axes and not alternately in opposite phases as in these other modes. As a consequence, the effects arising from the individual cells of the structure are coherent and cumulative and the observable result attains large values.

Diamond, does not exhibit any enhanced reflecting power in the region of wavelengths between 7.5μ and 10μ, and the fact that we can use plate thicknesses of a millimetre or more in studying its absorption spectrum in this range of wavelengths is a clear indication that the first-order absorption is extremely weak. That it is, however, not a spurious effect due to defects of structure or extraneous impurities is made abundantly clear by the facts set forth earlier. In particular, it should be mentioned that though the first-order is weak, it is not weaker than the second-order absorption. The constancy of the relative strength or the first and second-order absorption spectra in numerous specimens of perfect diamond, and the fact that the same vibrational modes which are manifested in the first order appear with doubled frequencies in the second order, is a clear indication that the first order absorption exhibited by the perfect diamonds is a fundamental property of such diamonds.

As has already been remarked, what we are here concerned with are the symmetry properties of the distribution of negative electric charge in the crystal. As the two latticcs are constituted of nuclei carrying the same positive charge, any suggestion that one of the lattices carries a large share of the electronic charge-cloud than the other can be ruled out immediately. Not only is such a situation inherently improbable, but it would also have consequences which are disproved by the facts of the case. Any lack of symmetry in the density of the charge distribution as between the two lattices would result in an enormously more powerful first-order absorption than that actually observed. All that we can legitimately infer from the observed infra-red behaviour is that in the structure of the diamonds which exhibit the first-order absorption, the electronic configuration, meaning thereby the variables which specify the state of the electrons in the crystal, including especially the orientations of their spins, do not conform to the requirements of octahedral symmetry, whereas in the diamonds in which the first-order absorption is absent, these requirements are satisfied.

The foregoing may be summed up by the statement that the electronic states in perfect diamonds possess only the lower or tetrahedral symmetry of the cubic class, while in the non-luminescent class of diamond that have the higher or octahedral symmetry. The situation here recognised enables us to understand the very significant relationship which is observed between the spectroscopic behaviour of diamond in regions of the spectrum which are so far apart as the infra-red between 7μ and 12μ and the ultra-violet between 0.2μ and 0.3μ. If the differences in Infra-red behaviour are ascribable to differences in the electronic configuration, corresponding differences are necessarily expected in the ultra-violet absorption spectra. It also becomes intelligible why the diamonds of group A and group B exhibit contrasting behaviours in respect of luminescence. Absorption of the incident radiation is a *sine qua non* for its re-emission in a modified form which is termed luminescence. Whereas diamonds of group A do absorb radiation in the near ultra-violet, group B diamonds are transparent to such radiations. It is, therefore, not surprising that group A diamonds exhibit luminescence whereas group B diamonds do not.

It may also be remarked that the inference from the infra-red data that group A diamonds possess only tetrahedral symmetry of the electronic configuration whereas group B diamonds exhibit the full octahedral symmetry receives massive support from the well-established facts regarding the crystal morphology of diamond, as well as from the phenomena of X-ray diffraction in diamond. But it would take us too far from our present theme to enter into these matters in detail. We therefore now return to a discussion of the details of the first-order absorption spectrum.

One of the remarkable features of the first-order absorption is the sudden change from a high degree of transparency to complete or nearly complete opacity occurring at the characteristic frequency of $1332.^{-1}$ or wavelength 7.5μ. At lower frequencies or longer wavelengths, the absorption shows a progressive diminution and ceases to be significant beyond 12μ. The curve of the percentage transmission between these wavelengths represents the effect of the movements of the electronic charge-clouds in the crystal excited by the incident radiation. The changes in its course at various points indicate the influence of the nuclear vibrations of lower frequencies. The activity of these modes in the first-order absorption rapidly decreases as the difference between their frequencies and the frequency of the active fundamental of highest frequency increases. This indicates that the electronic linkages in the crystal result in a coupling between the various possible modes of vibration of the nuclei. A striking illustration of such coupling is furnished by the astonishing intensity and sharpness of the absorption peak at 7.3μ or 1370 cm.$^{-1}$, which appears separated in the records from the steep increase in absorption at 7.5μ or 1332 cm.$^{-1}$ The absorption at 1370 cm.$^{-1}$ is clearly the result of the summation of the two lowest frequencies (746 cm.$^{-1}$ + 624 cm.$^{-1}$) of the diamond structure. That it shows up in such a remarkable fashion is a consequence of its close approximation in frequency to the major absorption at 1332 cm.$^{-1}$ It is also an impressive demonstration that the vibrational modes which manifest themselves in the infra-red absorption of diamond have sharply-defined monochromatic frequencies.

7. EVALUATION OF THE SPECIFIC HEAT

Einstein in his classic paper of 1907 introducing the quantum theory of specific heats showed that the thermal energy content of all material bodies depends in a fundamental way on the vibration frequencies of their atomic constituents in the region of the infra-red. Crystalline solids were included within the scope of his theory and the case of diamond was specially considered by him in the paper. The very striking changes which appear in the specific heat of diamond with alterations in temperature had been discovered by H. F. Weber in the year 1875 and Einstein made use of Weber's data to illustrate and support his theory. Assuming that the atoms in diamond had a single characteristic frequency of vibration corresponding to an infra-red wavelength of 11μ, Einstein showed that the general trend of the specific heat changes observed by Weber could be accounted for.

Earlier, it has been remarked that the structure of diamond has eight specific frequencies of free vibration lying in the wavelength range between 7.5μ and 16μ. The spectrographic record of infra-red absorption by diamond enables us to recognise these frequencies and determine them with the necessary precision. On the basis of the spectroscopically determined frequencies, and without introducing any other data or any arbitrary constants, the entire course of the variation of the specific heat of diamond over the temperature range from the absolute zero upwards to 1000° K. can be computed.

We may usefully here sketch the theory of the specific heats of crystals as envisaged by Einstein. He begins by showing that the acceptance of Planck's radiation formula leads to the consequence, that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency could only increase of diminish by quanta proportional to that frequency. A procedure which enables this principle to be used for the evaluation of the thermal energy of crystals is then outlined. The thermal energy is identified with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over the volume of the crystal. The total number of these oscillators is assumed to be the same as thrice the number of atoms comprised in the crystal. It is further assumed that the oscillators can be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets in then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets. Einstein obtained an explicit formula for the thermal energy of the crystal as a function of the temperature.

It is evident that there is adequate justification for the various steps in the foregoing argument. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may therefore be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. The argument implies that the atomic vibration spectrum of a crystal would exhibit a set of frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater, the higher the frequency of the oscillators under consideration.

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