QUANTUM THEORY OF X-RAY REFLECTION: EXPERIMENTAL CONFIRMATION

By Sir C. V. Raman and Dr. P. Nilakantan

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

CONTENTS

1. Introduction

THE fundamental discovery that the lattice planes in a crystal give rise to monochromatic X-ray reflections of a second kind involving a change of frequency was made in the laboratories of this Institute and announced at the Easter meeting of the scientific societies of Bangalore held on the 22nd March 1940. It was an essential part of the discovery that the experimental characters of the phenomenon as actually observed were such as to place it entirely outside the range of the accepted theories in X-ray optics. The explanation of the newly discovered phenomena, in fact, demanded the introduction of radically new ideas regarding the nature of the vibrations possible in crystal lattices and also regarding the nature of the interactions which occur when X-rays traverse a crystal. These new ideas were indicated simultaneously with the new experimental facts in an article in *Current Science* for April 1940. Though new to X-ray physics, the ideas set out in that article had already emerged more or less clearly from the spectroscopic investigations on the scattering of light in crystals which had previously been engaging the attention of the laboratory.* The application of these ideas in the field of

---

* A brief summary of these investigations and the ideas emerging therefrom will be found in the Franklin Medal Day lecture to be published in the *Franklin Institute Journal* for September 1941.

X-ray research was thus almost inevitable. The further investigations which have since been continued systematically at this Institute have not merely confirmed the statements made in the first publication, but have also shown that the new X-ray results taken together with the earlier spectroscopic studies compel revolutionary changes in our concepts of the solid state. In fact, the X-rays directly demonstrate what had been previously only inferred from the optical evidence, namely, that the lattice vibrations appearing as monochromatic lines in the spectrum of a crystal possess a degree of orderliness and coherence which is astonishing and truly as remarkable as the orderliness of the static arrangement of the atoms characteristic of a crystal. The optical and X-ray methods of investigating the lattice vibrations in crystals thus stand in the closest relation, supplementing each other. The optical methods enable us to analyse the infra-red vibrations into their frequency spectrum and only indirectly to infer their geometric character. The X-rays, on the other hand, enable us directly to ascertain the geometrical characters of the vibration and only indirectly to infer the frequency changes involved.

The clear-cut enunciation of the new facts and ideas put forward in April 1940 was made possible largely by the deliberate choice of diamond as the crystal round which the investigations have principally centred. The known perfection of this crystal, the simplicity of its structure, the possibility of using relatively soft X-rays in working with it, and above all, the geometric precision with which it exhibits the new phenomena have enabled the latter to be understood much more clearly than would have been otherwise possible. For this reason, the present article will be devoted wholly to the results of the experimental studies made with diamond. It will be shown, on the one hand, how the experimental facts totally exclude any explanation of the type based on the original theories of Debye, Waller and Faxén, with or without such further modifications as have been recently suggested. It will, on the other hand, be shown how completely the experimental facts fit into the scheme of new ideas expounded and developed quantitatively in the two preceding papers. It must not be imagined however that the case for the new theory rests exclusively on the facts observed with diamond. So far from this being the case, it may be said that a careful and unprejudiced examination of the facts with any crystal is sufficient to show that the efforts recently made by several workers, notably Zachariasen, Max Born and the group at the Royal Institution to base an explanation of the new X-ray facts observed at this Institute on the basis of the existing theories or modifications thereof are not on the right lines. In the earlier paper on basic ideas, the effects indicated by the theories of the Debye type are set out and contrasted with those indicated by the quantum theory of X-ray reflection, and a series of experimental

criteria are put forward enabling a discrimination between the two. In the papers which follow in these *Proceedings*, these criteria have been applied in several cases, and in every case the verdict of the facts has been in favour of the new ideas. Equally striking has been the success of the new ideas in dealing with problems of the solid state which have hitherto proved baffling, *e.g.*, the large deviations of the observed specific heats of elementary solids, such as metals, from those indicated by the Debye specific heat formula. Far from such a failure of the Debye theory being surprising, it is a necessary consequence of the idea that the lattice spectrum of every crystal includes Einstein or monochromatic frequencies of vibration. Mr. Bisheswar Dayal has shown in a series of papers which will appear in the next issue of these *Proceedings* that the specific heat curves for metals and other elementary solids find a very simple and complete examination on the basis of these new concepts in crystal dynamics.

2. *Structure and Lattice Spectrum of Diamond*

The specific heat of diamond has been accurately measured by Pitzer (1938) over the range of temperature from 70° T. to 288° T. His data do not fit into the Debye formula, showing deviations as large as fifteen per cent. within this range, if the limiting frequency in the formula is chosen to fit the data at the lower limit of temperature. The cause of this failure becomes apparent when we consider the real nature of the lattice spectrum. The Debye theory of specific heats rests on the belief that the infra-red vibrations of the lattice are physically of the same nature as the vibrations of the acoustic type and form a continuous spectrum of frequencies. That the same idea forms the basis of the crystal dynamics of Max Born and his school is evident from the postulate of the " cyclic lattice " on which the work of that school rests and which has been discussed earlier in these *Proceedings* and shown to be untenable. The Born postulate places the elastic and infra-red vibrations mathematically on the same footing. Its implications become clear when we examine the results of the calculations worked out on its basis by Blackmann, Kellerman and others of that school. The calculations lead to representations of the vibration spectrum which while differing in detail from that assumed in the Debye theory, have nevertheless the same fundamental feature, namely that the vibrations of the extended solid forms a continuous spectrum of frequencies. The lattice spectra of actual crystals as revealed to us by spectroscopic investigations, especially those made at low temperatures, present us with a totally different picture. Indeed, it may be said that the assumptions made in the Debye theory and in the Born crystal dynamics bear no resemblance whatever to the actual facts at such temperatures.

veral different lines of investigation agree in showing that, except y in the region of the lowest frequencies where the experimental [ues have not at present been good enough to give a definite answer, .tice spectrum of diamond consists of sharply defined or mono-
ιtic frequencies. Bhagavantam (1930) investigated the scattering of . diamond and found numerous sharp lines in the spectrum giving the ng frequency shifts in wave numbers per centimetre: 1585, 1480, .382, **1332**, 1288 and **1158**. Amongst these, the 1332 line is at least [red times more intense than the next most intense line 1158, while ers were just detectable in the spectrum of a large clear white diamond. 32 line, besides being intense, is also extraordinarily sharp, in fact as sharp as the exciting radiations. It remains sharp (though with [ly diminishing frequency shift) over the whole range of temperature ·3° T. to 1130° T. Further evidence on the lattice spectrum of .d has been furnished by the recent investigations of Nayar at this e on its luminescence and ultra-violet absorption spectra at low atures. As was first noticed by Ramaswamy, diamond exhibits эscent band at 4157 A.U., the same band also appearing in absorp-On cooling down the crystal to liquid-air temperatures, this band ɔ 4152 A.U., at the same time becoming much sharper. Subsidiary ιre also noticed at lower frequencies in fluorescence and at higher cies in absorption, the frequency differences between these and the and being the same but of opposite sign in fluorescence and in ion. These frequency differences therefore represent the lattice n of diamond. The band at 4152 A.U. is not as sharp at liquid-perature as could be desired, and it is greatly to be hoped that this ·ill be repeated at liquid hydrogen temperatures in some cryogenic ɔry. Nevertheless even at liquid-air temperatures and using the igh dispersion provided by an E_1 Hilger spectrograph, Nayar has hat the fluorescence and absorption bands appear resolved into us *discrete frequencies*. These are (within about ten wave numbers) ι52, 1148, 1090, 1010, 960, 784, 681 and 532. There are indications эr frequency shifts in the same region as those observed by ιntam, as also of several discrete frequency shifts smaller than 532 ιg very feebly in the spectra. Plate XVI, Figs. 4 (*a*), (*b*) and (*c*) ce the lattice spectrum of diamond as observed respectively in light-ιg, in fluorescence and in absorption, and exhibit these frequency

: dynamical theory of the diamond lattice has not at present been out with sufficient thoroughness to enable us to explain all these

experimental results. It is noticed, however, that the most intense fluorescence and absorption frequencies fall roughly into two groups. The head of one of these groups is close to the 1332 frequency which appears as an extremely intense and sharp line in light scattering. The nature of the 1332 vibration has been very fully discussed by Nagendra Nath (1934) and was indicated by him as an oscillation relative to each other of the two Bravais lattices of carbon atoms which constitute diamond. Since each carbon atom belonging to one lattice is bound by valence bonds to four carbon atoms in the other lattice, and *vice versa*, such an oscillation would necessarily have a high frequency. Indeed, a calculation based on the known force constants gives a frequency in fair agreement with the observed 1332. The symmetry characters of such an oscillation (Venkatarayudu, 1938) also indicate that it should be active in light-scattering. The identification of the 1332 frequency as that of an oscillation of the two interpenetrating lattices of carbon atoms relative to each other is thus firmly established. The second group of frequencies of which the head is at 784 is completely inactive in light scattering. It is therefore very probable that the oscillations of this group involve movements of the atoms in each Bravais lattice against themselves, alterations of the tetrahedral valence angles rather than the extensions or compressions of the valence bonds determining the observed frequencies.

Examining the structure of diamond, we find that the carbon atoms belonging to the two Bravais lattices appear in the planes parallel to the octahedral faces in separate layers which are alternately at *unequal distances*. It follows from this fact and the considerations set out in the preceding paper that the (111) planes would have their structure amplitudes strongly varied by the 1332 oscillation. A similar situation would also arise in respect of any oscillation in which the movements of some of the atoms in one Bravais lattice are balanced by opposite movements of an equal number of atoms in the other lattice. If, on the other hand, we consider a type of vibration in which the movements of the atoms in one lattice are balanced by opposite movements of the remainder of the atoms in the same lattice, it is easily seen that the structure amplitudes of the octahedral planes would remain unaffected. It is thus evident that only the **1332** vibrations or other vibrations of similar character would influence the structure amplitudes of these planes. A simple calculation on the basis of the theory set out in the preceding paper shows that in spite of the high frequency involved in such oscillations, dynamic reflections of notable intensity should be given by the (111) planes. On account of the high frequency of the associated vibrations of the lattice, such reflections should be practically insensitive to variations of temperature.

The crystal spacings in diamond giving the classical X-ray reflections are of two kinds. In one set which includes the spacings parallel to the octahedral faces, the alternate layers of carbon atoms appear unequally spaced in the ratio of 1:3. In the second set, which includes the planes parallel to the forms of the cube and the dodecahedron, the planes appear equally spaced. In the planes parallel to the dodecahedral faces, the carbon atoms belonging to the two Bravais lattices appear interspersed with each other in equal numbers. It follows that these planes are incapable of giving a dynamic reflection as a result of the relative oscillation of these two lattices. This conclusion, however, only refers to this particular mode of vibration having the high frequency of 1332 wave-members. There are numerous other modes of vibration of the lattice with discrete frequencies, some of which are as low as 127, 178, 303 and 421 wave-numbers (Nayar, 1941). In such vibrations, there can be no doubt that the atoms in each Bravais lattice oscillate against each other, that is, some of the atoms move one way and the others move the opposite way to balance the oscillation. The extreme feebleness with which the frequencies lower than 532 appear in fluorescence and absorption probably indicates that such vibrations have a relatively small *a priori* probability. Nevertheless, a low frequency involves a correspondingly larger amplitude of vibration. Hence, the planes in the crystal which cannot give a dynamic reflection associated with the 1332 vibration may nevertheless give observable reflections associated with some of the vibrations of the lattice with lower frequencies. Such reflections would be indicated by their intensity being more temperature-sensitive than the reflections associated with the high-frequency vibrations.

3. Specular Character of Quantum Reflections

Amongst the many items of supporting experimental evidence set out in the publications by the present writers (1940) announcing the discovery of quantum or modified reflection, one of the most cogent which was duly emphasized was the truly geometric or specular character of the reflections associated with the (111) planes of diamond. This feature by itself and apart from all other evidence was sufficient proof that the phenomena described in those papers lay entirely outside the scope of X-ray optics as it existed before the announcement of the discovery. In view of the importance of this feature and especially of the fact that it is absolutely fatal to the attempts made by Max Born and others to interpret the phenomena on the basis of the Debye-Born crystal dynamics, we shall here consider it in some detail.

Even in the photographs published with our earliest communications (*Current Science*, April 1940 and *Nature*, 27th April 1940), it was evident

that the quantum or dynamic reflections given by the (111) planes of diamond were just as sharp as the ordinary Laue reflections by the same planes. While the Laue reflections appeared as elliptic spots, the quantum reflections were round in shape and had about the same diameter as the major axis of the Laue spots. These features are readily understood when the angular divergence of the incident beam is considered and it is borne in mind that a quantum reflection can occur at any incidence of the X-rays on the crystal planes. A detailed discussion of the geometric aspects of the quantum X-ray reflections in diamond by Mr. P. R. Pisharoty has already appeared in a recent issue of these *Proceedings* (1941). Mr. Pisharoty has proved that the appearance of the quantum reflections as observed in the photographs for all possible settings of the crystal is just what we should expect if they were perfectly geometric.

In actual experimental work with X-rays, the radiation from the source is necessarily divergent. The extent and manner in which such divergence may be advantageously limited depends both on the aim of the investigation as well as upon the material under study, *viz.*, upon the thickness or area of the crystal. In investigating phenomena of low intensity, an undue restriction of the divergence of the beam would merely increase the difficulties of the investigation without advancing its purposes in any way. Thus, for instance, in the present problem, when we wish to decide whether we are dealing with a sharp reflection or a diffuse scattering, instead of reducing the aperture excessively, it is preferable to retain it at a reasonable value and prolong the photographic exposures as much as possible. In such circumstances, a geometric reflection would not enlarge in area, while a diffuse scattering would progressively widen out. Using the technique here indicated, it is easy to decide the question whether the quantum reflections in diamond enlarge their angular extension when the crystal is moved away from the setting at which the quantum and classical reflections coincide. By not reducing the width of the X-ray beam unduly, it is possible to record the spots with fair intensity even when the crystal setting is altered by as much as 6° in either direction. It will be seen from the photographs reproduced in Plate XVII, Figs. 5 (*a*) to (*k*) that the extension of the quantum reflections remains constant over this whole range of settings, while if it were due to a scattering of the X-rays associated with the reflections of the usual kind, it should enlarge rapidly in area. One has only to glance at the photographs in Fig. 5 and then turn to the set of curves reproduced in Fig. 3 of the preceding paper showing how the distribution of intensity of scattering of X-rays varies with the setting of the crystal to realise the futility of any attempt to explain the actual phenomena in terms of the scattering theory.

The classical and quantum reflections have a different origin and obey different geometric laws. Nevertheless, they are both geometric reflections, and optical principles indicate various simple criteria which can be employed to test their nature as such and which would reveal the correct position immediately if the quantum reflection were not an independent phenomenon. Various factors in the experimental technique are capable of variation, *e.g.*, the area and angular divergence of the incident X-ray beam, as well as the area and the thickness of the crystal irradiated by it. These variations would influence the intensity and the angular spread of the two effects in a very different manner if they were not essentially similar phenomena. Actually, we observe a complete parallelism in the behaviour of the classical and quantum reflections when the experimental factors are varied separately or together. It is well known, for instance, that the spots in a Laue pattern diminish in extension when the X-ray beam is made narrower, and that such diminution in size cannot be prevented from occurring by merely prolonging the photographic exposures. Precisely the same effect is observed with the quantum reflections by the (111) planes in diamond. These are reduced in extension by limiting the area of the X-ray pencil in much the same way and in the same proportion as the ordinary Laue reflections, longer exposures not altering the situation. It is also noticed that the relative intensity of the Laue and quantum reflections remains unaltered by such procedure, thus proving that we are dealing with true geometric reflections in both cases and not a reflection in one case and a scattering in the other.

The classical X-ray reflections by the lattice planes of crystals appear in directions which are geometrically definable with a degree of precision depending on the perfection of the crystal. Diamond, for instance, may be so perfect that the setting at which it reflects monochromatic rays with the maximum intensity is probably definable with as great an accuracy as the wave-length can itself be specified. In the case of the quantum reflection, we are concerned not only with the geometric perfection of the crystal but also with its *spectroscopic* perfection, that is to say, with the monochromatism of the infra-red vibrations of its lattice. As will be seen from Fig. 4 (*a*) in Plate XVI, the monochromatism of the 1332 vibration of the diamond lattice, even at ordinary temperature, is of the most remarkable kind. Accordingly, we should expect that the quantum reflections by the (111) planes which owe their origin to it should have a precisely definable geometric character and should be unaffected in their sharpness by the setting of the crystal. A rigorous test of this question is not so easy as in the case of the classical reflections, for the quantum reflections can occur independently of the angle of incidence of the X-rays on the crystal.

Hence, an angular divergence of the incident beam and therefore also of the reflections can easily be mistaken as indicating a lack of geometric perfection of the latter. The severity of the test which can be made depends on the possibility of obtaining an X-ray beam with small lateral extension and angular divergence but of sufficient intensity to record the quantum reflections in a reasonable time. As the intensity of the reflections falls off with extreme rapidity when the crystal setting is turned away so as to separate the classical and quantum reflections, it is evidently not easy to push the question to the final limit. It may be stated, however, that, *the quantum reflections by the* (111) *planes of diamond are geometrically as perfect as can be experimentally ascertained at the present time.* .This is shown by the photographs reproduced by Figs. 6 (*a*) and (*b*) in Plate XVIII. In these photographs, the quantum reflections by the (111) planes have been recorded using a fine rectangular slit 100 millimetres deep and 0·15 millimetre wide, and a cleavage plate of diamond 0·76 millimetre thick. The width of the reflections as measured on the plates is no greater than that to be expected from the finite lateral extension of the beam, its angular divergence and the thickness of the plate used. It is specially noteworthy that the reflection as recorded on the plates shows no detectable widening when the crystal setting is altered so as to make the quantum reflection move away from the Laue reflection in one direction or the other by several degrees.

These facts show that there is no ground for the belief entertained by some X-ray workers in the Debye-Waller-Faxén theory of X-ray scattering as a possible explanation for the phenomena discovered with diamond at this Institute. So striking are the facts that even the advocates of the scattering theory have been compelled to take the illogical step of referring to the phenomena as a " diffuse reflection " instead of as a " diffuse scattering " which would be the correct nomenclature for them to adopt on the basis of that theory. Indeed, the designation of " diffuse reflection " as applied to the case of the (111) quantum reflection of diamond is quite misleading. Actually, these reflections are probably as sharp or sharper than the classical reflections of X-rays by the lattice planes of many crystals of the ordinary or imperfect type.

4. Geometric Law of Quantum Reflection

Any discussion regarding the geometric law of the quantum reflection presupposes its specular character. Indeed, unless we are dealing with a phenomenon which is recognizable as a reflection over a wide range of settings of the crystal and whose position can be observed and stated with some precision, there can be no point in discussing the validity of any geometric formula

descriptive of it. No useful purpose would be served, for instance, in seeking to find empirically the point of maximum intensity in a field of diffuse scattering such as those represented theoretically in the curves of Fig. 3 of the preceding paper. The precision with which the positions of the X-ray reflections can actually be located and measured is an indication that the experimental situation in this respect is very different indeed from that arising in the case of X-ray scattering.

The earliest measurements made with diamond (Raman and Nilakantan, May 1940) showed that the spacing d^* of the dynamic stratifications altered rapidly with the setting of the crystal, being identical with the static spacing d of the (111) planes only at the particular setting when the two types of reflections appear superposed. It was found later that even these early measurements fitted perfectly into the general geometric law of quantum reflection

$$2\, d \sin \psi \sin (\vartheta \pm \epsilon) = \lambda \sin \vartheta, \tag{1}$$

the angle ϑ coming out the same within a degree or two as the value of $54°\,44'$ established by the measurements over a wider range of settings of the crystal made in July and August 1940. The angle $54°\,44'$ is half the tetrahedral angle between the valence bonds joining the carbon atoms in diamond. It is also the angle between the faces of the cube and the octahedron in the regular crystal system. In other words, *the phase-waves for the quantum reflection of X-rays by the octahedral planes of diamond are parallel to the cube faces of the crystal.* This remarkable result which was discovered experimentally in September 1940 forms a striking confirmation of the basic ideas underlying the quantum theory of X-ray reflection. It emerged from the extended studies made in the preceding months as mentioned above. The photographs from which the measurements were made are reproduced in Plate XVII, Figs. 5 (*a*) to (*k*). A brief reference to this result was made in a footnote to the paper by Raman and Nath (November 1940) in which the theoretical formula (1) was first announced. The result itself was communicated in a letter to *Nature* dated the 11th November 1940 and published in its issue of the 25th January 1941. In view of the great significance and importance of the result, it appears worth while to give a detailed account of the experimental work which led to its recognition.

These early experiments were carried out with a ' Spektro Analyt ' Rontgen apparatus manufactured by Siefert & Co., Hamburg. The X-ray tube was of the sealed hot-cathode type with a copper target, the X-rays emerging through four windows of Lindemann glass. The tubes worked at 41,000 k.v., with a tube current of 12 ma. A flat film type of camera was employed for taking the photographs. The X-ray beam was restricted by a

circular hole bored through cylindrical lead blocks of effective depth 93 mm., the diameter of the hole being 1·6 mm.

Diamond has a perfect cleavage parallel to an octahedral face of the cubic crystal. Plates evidently obtained by cleavage in this manner and subsequently polished can be readily obtained from jewellers in India. The plate actually used was about half a square centimetre in area with a thickness of 0·76 millimetre. The crystal was mounted on the goniometer with its faces nearly vertical and nearly normal to the X-ray beam. The crystal was set by trial so that the (111) planes within the crystal from which the reflections were to be studied were vertical, as also the adjoining lattice spacings parallel to the form of the cube. Thus, when the crystal was rotated about the vertical axis of the goniometer, the plane of incidence of the X-rays on the (111) spacings remained horizontal throughout, coinciding with a plane of symmetry of the crystal parallel to the form of the dodecahedron. Particular care was taken in mounting the crystal to ensure that the goniometer axis passed through the portion of the crystal irradiated by the X-ray beam. Small rotations of the crystal introduced no sensible change in the distance from the crystal to the photographic film. This however, was checked up at every setting of the crystal. The actual distance from the diamond to the film was 3·99 centimetres for Figs. 5 (a) to (g) and 3·95 cm. for Figs. 5 (h) to (k) in Plate XVII. With the aperture used, the X-ray beam traversing the diamond had an appreciable angular divergence. The round shape and sharpness of the spot as recorded on the film, however, enabled the position of its centre to be located with such accuracy that the use of a finer X-ray pencil would merely have prolonged the exposures necessary and thereby increased the difficulties of the investigation without any material gain in precision.

Since, in these experiments, the reflections occur in a plane of symmetry of the crystal, it follows that we may write the geometric law (1) in the form

$$2\,d\sin\tfrac{1}{2}\,(\theta+\phi)\sin\left(\vartheta\pm\frac{\theta-\phi}{2}\right)=\lambda\sin\vartheta \qquad (2)$$

θ and ϕ being the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Since the actual value of the crystal spacing is known, viz., 2·056 A.U., the most convenient representation of the data is to regard the spacing as an unknown function of θ to be determined from the observed values of θ and ϕ and the formulæ used. The angle ϑ disappears from equation (2) when $\theta=\phi$. Thus, whatever be the chosen value of ϑ, the graphs representing the calculated values of the spacing as a function of θ calculated with different assumed values of ϑ all necessarily cross at the same point. This should agree with the known spacing of the crystal

within the limits of experimental error. When however, $\theta \neq \phi$, the spacing calculated would diverge progressively from the actual value unless the correct value of ϑ has been chosen. The appearance of the graph as a horizontal line in a position agreeing with the known crystal spacing thus furnishes an exact test of the formula employed.

Fig. 1 shows three graphs in which the experimental observations have been set out in the manner indicated. The graphs marked d_1 represents the
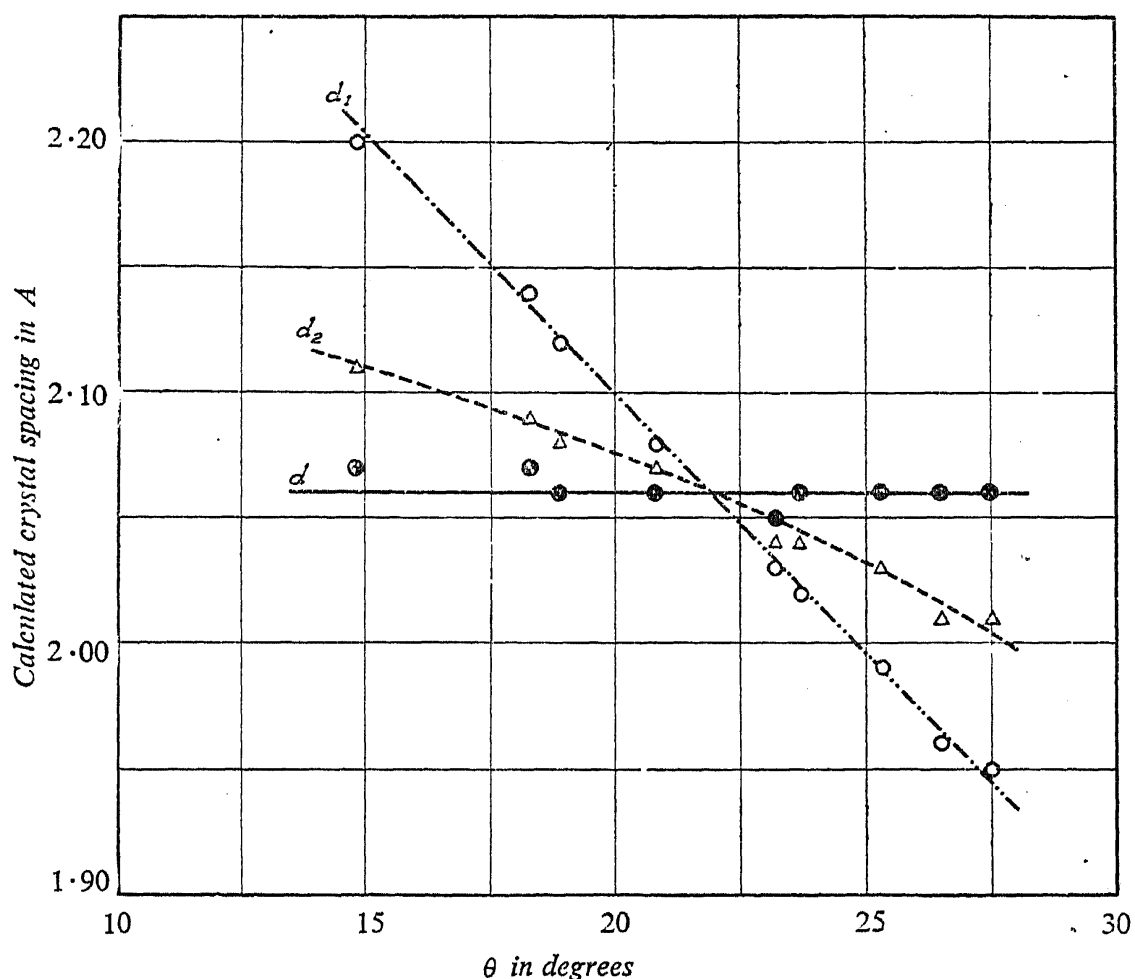

Fig. 1. Geometric Law of Quantum Reflection

crystal spacings calculated from the approximate formula

$$2 d \sin \tfrac{1}{2} (\theta + \phi) = \lambda. \qquad (3)$$

The graph marked d_2 represents the crystal spacings calculated from the formula

$$d (\sin \theta + \cos \theta \tan \phi) = \lambda. \qquad (4)$$

This formula which is of the same form as that derived originally by Faxén on the basis of the scattering theory, would also represent the geometric formula of quantum reflection if the phase-waves of the infra-red lattice vibration had an arbitrary orientation within the crystal, and the actual

geometric position of the reflection were determinable from a consideration of the minimum phase wave-length. The graph marked d in the figure was calculated from the formula (2) above, assuming ϑ to be 54° 44′. It will be seen that it is a horizontal straight line with a spacing very closely agreeing with the known value. On the other hand, the graphs d_1 and d_2 diverge rapidly from the known spacing at except the point where all the three graphs intersect.

To indicate the degree of accuracy with which the angle ϑ is determinable from the observations, the graphs drawn for three different values of the angle are shown in Fig. 2. It will be seen that the angle lies certainly within one degree of half the tetrahedral valence angle.
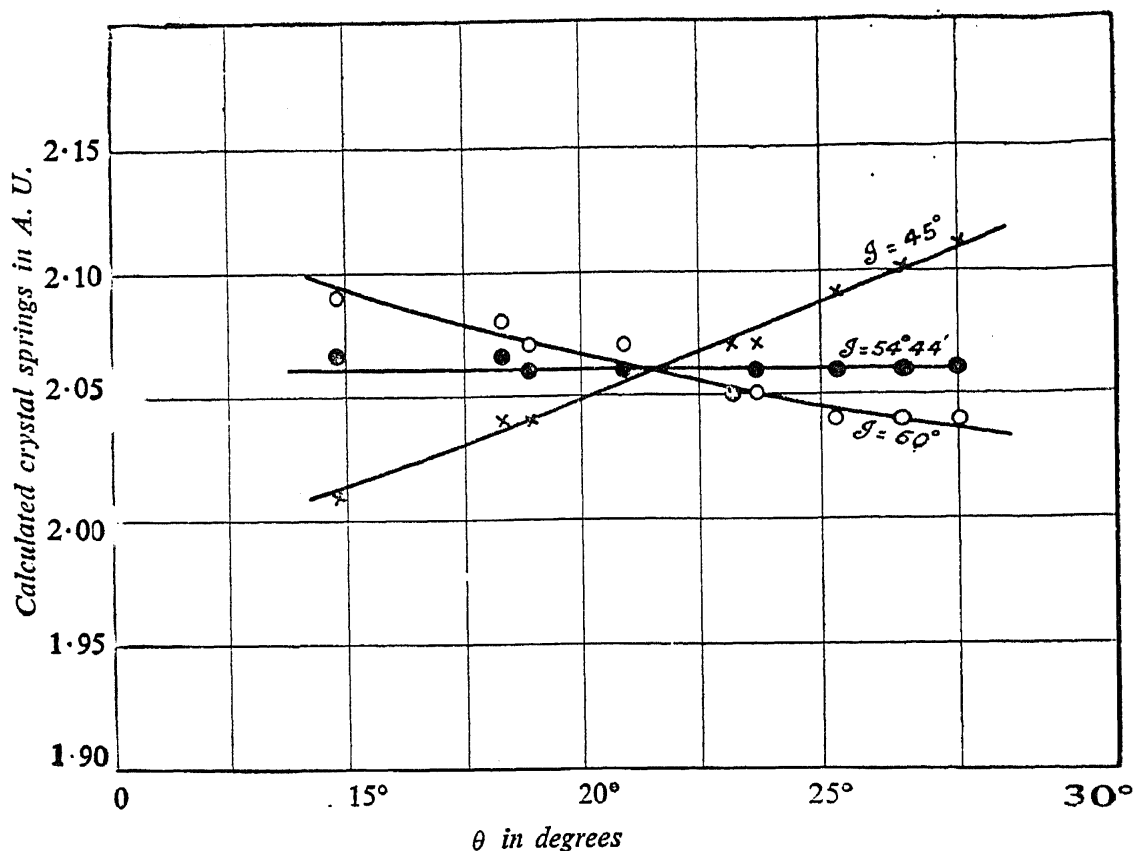

FIG. 2. The Inclination of the Phase Waves

The experimental facts emerging from Figs. 6 (a) and (b) in Plate XVIII, and from Figs. 1 and 2 above in the text are thus of a completely decisive character. The Debye-Faxén-Waller theory of X-ray scattering demands a distribution of the intensity of the scattered X-rays over an area whose angular extension is expressed in as many degrees of arc as the setting of the crystal is moved away from the position required for the classical X-ray reflection. It also demands that the position of maximum intensity in such scattering, though not capable of being measured with any particular precision, should follow the course of the curve marked d_2 in Fig. 1. On the other hand,

the actual spread of the quantum reflection is not experimentally detectable and if it is finite, is measureable in minutes of arc rather than in degrees, as indicated by Figs. 6 (*a*) and (*b*). The geometric direction of the reflection is capable of being determined with precision and follows a wholly different law, namely that defined by equation (2) above. The facts thus definitely negative any possibility of explaining the phenomena in terms of the Debye-Faxén-Waller theory. *The observed specificity of the value of ϑ also forms a direct experimental contradiction of the Born postulate of the cyclic lattice,* since the latter assumes the phase-waves of the vibration of the crystal lattice to have all possible orientations instead of a definitely restricted orientation as shown by the X-ray results. We have thus no choice left except that of assuming the infra-red or high-frequency vibrations of the lattice to be the factor responsible for the observed X-ray reflections.

We may now consider the question why the phase-waves of the 1332 vibration which are evidently responsible for the (111) reflections are parallel to the form of the cube. The answer to this is evidently that the nature of this vibration is determined by the geometry of the crystal structure. Each carbon atom in one Bravais lattice is joined by four valence bonds in a symmetrical fashion to four other carbon atoms belonging to the other Bravais lattice. The individual valence bonds are normal to the octahedral planes in diamond, while the planes parallel to the cube faces bisect the angles between the valence bonds taken in pairs. The vibration responsible for giving the reflection by a particular set of octahedral planes is normal to them and therefore parallel to one of the valence bonds. Since the three other bonds are also possible directions for such a vibration, it is to be expected that the plane of the phase-waves would take an intermediate direction, which by symmetry should bisect the angle between them. On the basis of this argument, it is evident that there should be three sets of possible phase-waves which are respectively parallel to the three pairs of faces parallel to the forms of the cube. This result demanded by considerations of symmetry is found as we shall see presently, to be fully supported by the experimental facts.

5. The Azimuth Effect

A further remarkable confirmation is forthcoming for the result that the phase-waves associated with the 1332 vibration are restricted to a specific crystallographic orientation. This is the so-called azimuth effect, which was foreseen theoretically before it was sought for and confirmed experimentally by the authors. Since the phase-waves for a (111) reflection are parallel to the adjoining cube face, it follows that if the crystal plate be rotated in its own plane so as to make the plane of incidence no longer a plane of symmetry of

the crystal, the quantum reflection should move out of such plane of incidence. Why this effect occurs becomes evident when we recall that the plane in which the quantum reflection should appear is the plane of incidence of the X-rays on the dynamic stratifications; in the circumstances considered, these are no longer perpendicular to the plane of incidence of the X-rays on the static crystal planes. This situation is readily appreciated with the aid of a vector diagram in which the reciprocals of the crystal spacing and of the phase-wave normal are geometrically represented. The point at which the phase-wave normal intersects the sphere of reflection necessarily moves out of the plane of incidence when the crystal is rotated in its own plane, the angle of incidence being retained constant. It is evident that such displacement would be zero if the reciprocal phase wave-length is zero; it changes sign when the direction of the wave-normal is reversed either by a change of the crystal setting or by a change of the X-ray wave-length. In other words, the displacement of the quantum reflection out of the plane of incidence would be zero when it coincides with the Laue reflection, and would be of opposite signs when it lies respectively on the two sides of it. It should also increase progressively as the quantum reflection moves away from the Laue spot in either direction. The theory of the effect has been very fully discussed and illustrated by appropriate diagrams in the paper by Pisharoty already cited. We need not therefore enter into the matter here in further detail. The necessary mathematical formulæ will be found in Pisharoty's paper. The effect is illustrated in Figs. 10 (a) and (b) in Plate XIX. The angular displacements of the reflections out of the plane of incidence as measured from the photographs are in quantitative agreement with those deduced from the formulæ.

6. *Explanation of Multiple Spots and Streamers*

Another striking confirmation of the theory of phase-waves is afforded by the phenomena arising from the fact that there are three sets of phase-waves and therefore three quantum reflections corresponding to the points where the phase-wave normals meet the sphere of reflection. As these normals are at right angles to each other, it is not to be expected that all the three reflections would be observable in every case. The setting of the crystal would obviously determine the effects actually recorded. It is evident that if the phase-wave vector nearly grazes the sphere of reflection, the finite divergence of the incident X-ray beam would result in the reflection appearing as an oblique streak or an elongated elliptic spot, instead of as a round circular spot; the latter would be the observed result only when the vector cuts the sphere of reflection normally. The intensity of the streamers or elliptic spots would vary with the reciprocal phase wave-length at each point,

being greatest when this is a minimum and tending to zero when it is large. Hence, these streamers and subsidiary spots would be most prominent when the setting of the crystal is such that the Laue and quantum reflections nearly coincide. On the other hand, when the quantum reflection is far removed from the Laue reflections, all trace of them should disappear. These effects are well illustrated as the series of photographs reproduced in Figs. 5 (*a*) to (*k*). A detailed discussion of them and of various other cases is given in the paper by Mr. Pisharoty already cited to which the reader may be referred for further particulars. Remarkable changes in the appearances of the streamers and subsidiary spots occur when the azimuth of the setting of the crystal is altered. Some of these features are illustrated in Figs. 10 (*a*) and (*b*) and 11 (*a*) and (*b*) in Plate XIX, and are in full accord with the indications of the theory.

7. *Intensity of Quantum Reflection*

Extremely rapid changes occur in the intensity of the quantum reflection as it approaches from the Laue spot with an alteration of the setting of the crystal. This effect is seen in the series of pictures reproduced in Figs. 5 (*a*) to (*k*) and is even more pronounced than would appear from the photographs since the exposures were considerably prolonged for the first few and the last few pictures of the series. A better idea of the situation is obtained from Fig. 7 which is reproduced from the article in *Current Science* for April 1940. It will be noticed that both the K_α and K_β reflections fall beyond the spot marked A and are so feeble as only just to be visible in the reproduction. The quantum reflection of K_α is beyond the spot marked C, while the K_β reflection actually coincides with the latter and therefore also with the classical monochromatic reflection. The spot marked C therefore appears very intense. The K_α and K_β quantum reflections appear respectively on the two sides of the spot marked B, the former being of great intensity. The illustration shows clearly that as the quantum reflection approaches the Laue spot, its intensity rapidly increases and ultimately becomes quite large.

It is evident from the pair of pictures appearing in Fig. 8 (*a*) and (*b*) that the intensity of the quantum reflection of the monochromatic X-rays may actually exceed the intensity of the Laue reflection by the same spacings of the white radiations accompanying the characteristic X-rays of copper. That the classical and quantum reflections of the same wave-length are of comparable intensity when they are superposed is indicated by the photographs reproduced as Figs. 11 (*a*) and (*b*) in Plate XIX. It will be noticed when the crystal is set so that the classical and quantum reflections coincide, the streamers emerging from the reflections on both sides are easily visible. Since these streamers are necessarily much weaker than the principal

quantum reflection, it follows that the latter should be comparable in its intensity with the classical reflection of the same wave-length which appears superposed on it. The experimental facts are thus in general accord with the conclusions arrived at from the quantum theoretical calculations set out in the preceding paper.

Experiments have also been made varying the thickness of the plate of diamond as also the width of the beam of X-rays used. These factors are found within wide limits to be without influence on the relative intensities of the classical and quantum reflections under otherwise similar conditions, thus supporting the indications of theory. On the other hand, the diffuse continuous background of scattered radiation appearing in the Laue patterns of diamond [e.g., in Figs. 5 (a) to (k) and in Fig. 7] is practically suppressed by using thin plates or fine X-ray beams.

8. Influence of High and Low Temperatures

The spectroscope enables us directly to observe the changes of frequency in the scattered radiations which arise when energy and momentum are exchanged between a beam of light and the crystal which it traverses. The quantum-mechanical character of such scattering is indicated by the difference of the intensities of the radiations of increased and diminished frequencies respectively. The theoretical ratio of these intensities is simply the Boltzmann factor $e^{-h\nu^*/kT}$, actual measurements giving values closely agreeing with it. In the parallel X-ray problem, neither the spectroscopic observation of the change of frequency nor the comparison of the intensities of the two components $(\nu \pm \nu^*)$ is at present possible. What we observe is the superposed effect of both components of frequency which, as shown in the preceding paper, is proportional to

$$\frac{e^{-h\nu^*/kT} + 1}{e^{-h\nu^*/kT} - 1}. \tag{5}$$

Measurements of the variation of intensity with temperature within the range for which the formula (5) may be expected to be valid should therefore enable us to demonstrate the quantum-mechanical character of the effects and to evaluate the frequency ν^* of the vibrations responsible for them in any particular case.

As shown earlier in this paper, the 1332 vibration is the only one which can be expected to give an appreciable variation of the structure amplitude of the (111) planes in diamond. It follows from this fact and from formula (5) that the intensity of the quantum reflection by the (111) planes should be sensibly independent of temperature. This result was indicated as a consequence of theory in the Current Science article of April 1940. In the more

detailed paper of May 1940, experiments were described in which the diamond was heated up to 500° C. without any notable enhancement of the intensity of the reflection resulting therefrom. Experiments at low temperatues were also indicated as a further test of the theory. A suitable high vacuum low-temperature X-ray camera suitable for quantitative work was then developed, and the tests made with it with the crystal cooled down to liquid-air temperature showed that the reflections continued to be visible at such temperatures. This was reported in a letter to *Nature*, dated the 20th September 1940 published in its issue of the 23rd November 1940. Further comparisons showed that the intensity of the reflections by the (111) planes at room and at liquid-air temperatures were practically identical. This result was communicated in a letter to *Nature* dated the 23rd November 1940 and published in its issue of the 25th January 1941.
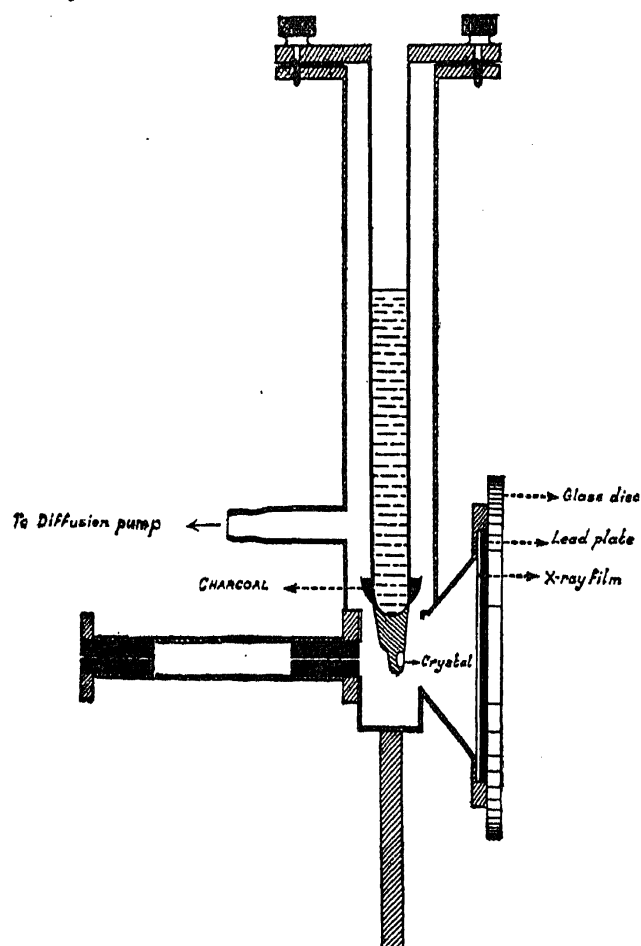

FIG. 3. High-Vacuum Low-Temperature X-Ray Camera

The special X-ray camera designed and constructed for the experimental study of quantum X-ray reflections at liquid-air temperatures is illustrated in Fig. 3 above. The diamond is imbedded in a copper block which forms the lowest end of the receptacle for holding the liquid air. A hole bored through the block allows passage for the X-ray beam. Both the crystal and the photographic film recording the X-ray pattern are held inside a high

A4

vacuum, the latter being produced by an oil diffusion pump. No intensif
screen was used in these experiments. A small lead disc attached to the
served to cut off the central beam of X-rays. Photographs were taken un
identical conditions with and without cooling the crystal by liquid
Figs. 12 (a) and (b) in Plate XX, reproduce two typical photographs obtai
in this way, the former at liquid air and the latter at room temperat
No sensible difference is noticeable in these photographs between the in
sities of the quantum reflections appearing in the vicinity of the three L
spots. Figs. 13 (a), (b) and (c) in Plate XX present a similar compariso
the intensities for the quantum reflections photographed under similar co
tions at 25° and at 400° Centigrade. Here again, no difference in intensi
perceptible. The experimental results thus completely establish that the (
reflections arise from a quantum-mechanical excitation of the infra-red vi
tions of high frequency. It is important to notice that the reflections see
Fig. 12 (a) are situated in the near vicinity of the Laue reflections. Acc
ingly, if the effects had arisen from elastic vibrations of the lattice, t
would have been of very low frequency and would therefore have been to
suppressed by the cooling of the crystal to liquid air temperature.

9. Quantum Scattering

The diffuse halo surrounding the primary beam is a very striking fea
of the Laue pattern reproduced in Fig. 7, the radiations here used being t
of a copper target. Fig. 14 in Plate XXI reproduces a similar picture taken
the X-rays from a molybdenum target and shows a noticeable contractio
the halo, but not so great as should have resulted if the halo had been
entirely to the monochromatic X-radiations present. That the halo is
due solely or even principally to the scattering of the X-rays by elastic vi
tions of *thermal origin* is shown by the fact that it persists at liquid air temp
tures as seen in Fig. 12 (a) in Plate XX. Since the halo is recorded witl
diamond inside a high-vacuum camera, it is evident that the effect cannc
due to the diffusion of the X-rays by the air. This is also otherwise (
from the fact, already mentioned, that the use of thin plates of diamond t
to supress the intensity of the halo in comparison with those of the reg
reflections. We are thus obliged to conclude that the halo is a quar
mechanical effect, the X-rays exciting the vibrations of diamond lattice ha
much lower frequencies than 1332 and somewhat similar characters to
vibrations of an elastic solid. The extent to which the intensity of ;
scattering would be diminished by lowering the temperature would be gre;
for the vibrations of the lowest frequency and least for those of the hig
frequency. The intensity of the halo should therefore fall off in the c

vicinity of the direct beam, and remain sensibly unaffected in directions far removed from it. The distinct sharpening of the halo at low temperatures noticed on a comparison of Figs. 12 (*a*) and (*b*) is probably to be explained in this way. The outermost parts of the halo may reasonably be attributed to a diffuse scattering of the X-rays by the lattice planes of the crystal in combination with the elastic vibrations of the structure.

10. Summary

The paper presents the experimental evidence furnished by the X-ray studies with diamond which confirms the theoretical ideas and mathematical formulation contained in the two preceding papers. The nature of the vibrations of the crystal lattice of diamond is first discussed with special reference to the mode having a frequency of 1332 wave-numbers. This vibration gives a large variation of the structure amplitude of the (111) crystal planes, while other vibrations of a different character leave it unaffected. Various experimental tests show that the X-ray reflections of the second kind given by these planes are truly specular or geometric in character. Measurements of the geometric positions of the reflections over a wide range of crystal settings show a complete agreement with the theoretical formula, the phase-waves of the vibrations appearing parallel to the (100) planes of the crystal. Symmetry demands that there should be three such sets of phase-waves, and this is fully substantiated by the experimental facts. The quantum reflection moves out of the plane of incidence when the crystal plate is rotated in azimuth. The appearance of multiple spots and streamers is also explained by the theory. The intensity of the reflections is of the order of magnitude indicated by the theory and is sensibly independent of the temperature in agreement with it. The phenomenon of quantum scattering is also briefly described and discussed.

REFERENCES

QUANTUM REFLECTION OF X-RAYS

Raman and Nilakantan	*Curr. Sci.*, 1940, **9**, 165.
	Proc. Ind. Acad. Sci. 1940, **11**, 179.
	Ibid., 1940, **11**, 189.
	Ibid., 1940, **11**, 398.
	Nature, 1940, **5**, 667.
	Ibid., 1940, **145**, 860.
	Ibid., 1940, **146**, 523.
Raman and Nath	*Proc. Ind. Acad. Sci.*, 1940, **12**, 83.
———— and Nilakantan	*Ibid.*, 1940, **12**, 141.
———— and Nath	*Ibid.*, 1940, **12**, 427.

Raman and Nilakantan	..	*Nature*, 1940, **146**, 686.
————————	..	*Ibid.*, 1941, **147**, 118.
————————	..	*Ibid.*, 1941, **147**, 118.
Raman	..	*Proc. Ind. Acad. Sci.*, 1941, **13**, 1.
——— and Nilakantan	..	*Curr. Sci.*, 1941, **10**, 241.
Pisharoty	..	*Proc. Ind. Acad. Sci.*, 1941. **14**, 56.
Raman, Nilakantan and Pisharoty		*Nature*, 1941, **147**, 805.
——— and Nilakantan	..	*Phys. Rev.*, 1941, **60**, 63.

DYNAMICS OF DIAMOND LATTICE

Bhagavantam	..	*Ind. Jour. Physics*, 1940, **5**. 169 and 573.
Nagendra Nath	..	*Proc. Ind. Acad. Sci.*, A, 1934, **1**, 333.
Venkatarayudu	..	*Ibid.*, 1938, **8**, 349.
Pitzer	..	*Jour. Chem. Physics*, 1938, **6**, 68.
Nayar, P. G. N.	..	*Proc. Ind. Acad. Sci.*, A, 1941, **13**, 483 and 534; **14**, 1.