Reflexion and scattering of X-rays with change of frequency

II. Experimental

BY SIR C. V. RAMAN, F.R.S.

From the Department of Physics, Indian Institute of Science, Bangalore

It is shown that the quantum theory of X-ray reflexion and scattering in crystals developed in Part I is in full accord with the experimental facts. The theory succeeds in giving a quantitative explanation of the experimental facts concerning these phenomena as observed with diamond, viz. (1) the specular character of the quantum reflexion from the (111) planes, (2) the geometric law of such reflexion and especially the fact that, in general, the reflexion falls outside the plane of incidence, (3) the subsidiary features accompanying the reflexion, viz. faint elliptic spots and elongated streamers noticed in certain special cases, (4) the absolute intensity of the reflexion which is an appreciable fraction of the intensity of the classical reflexion, (5) the failure of the (110) planes to exhibit similar reflexions, (6) the persistence of the reflexions by the (111) planes with undiminished intensity at liquid air temperature and the relatively small increase of intensity at high temperatures, and (7) the appearance of a diffuse scattering having an undiminished intensity at low temperatures. The differences between diamond and other crystals in respect of these X-ray phenomena are explained by taking into consideration the differences in the frequency and character of their lattice vibrations in the infra-red region as revealed by the spectroscope.

1. INTRODUCTION

The two fundamental results emerging from the theory outlined in Part I are, first, that we are here concerned with phenomena of a quantum-mechanical nature, and secondly, that the infra-red or high frequency vibrations of the lattice produce effects radically different in their character from the X-ray scattering by the elastic vibrations, being in fact of an altogether higher order of intensity and in the nature of a geometric reflexion by the lattice planes of the crystal. The latter of these two results escaped recognition in the classical investigations of Debye, Waller and Laue on the temperature problem in X-rays. The reason for this is to be found in their acceptance of Born's postulate that *all the vibrations* of the lattice have wave-lengths forming a three-dimensional harmonic sequence deter-

mined by the dimensions of the crystal; accepting the postulate, it follows at once that the infra-red and the elastic vibrations alike result merely in a diffusion of the X-rays, the effect of the former being even less conspicuous than that of the latter owing to the higher frequency and correspondingly smaller amplitude. The recognition that Born's postulate does not correctly represent the infra-red vibrations of a crystal lattice is thus as important for the present subject as an appreciation of the fact that the classical mechanics does not correctly determine the results of an interaction between the X-rays and the crystal lattice.

Conclusive evidence bearing on these fundamental points of theory was furnished by the experimental work of Dr P. Nilakantan and myself (1940 *a*, *b*). The decisive character of the experimental results set out in those papers was due to the fact that the crystal employed, namely, diamond, shows the effects contemplated in the theory with ideal perfection, and indeed in such manner as totally to exclude all alternative explanations. The experiments disclosed the following features, amongst others of scarcely less interest, namely, the strictly geometric or specular character of the dynamic X-ray reflexions exhibited by the (111) lattice planes of diamond, their great intensity comparable with that of the ordinary Laue spots in specially favourable settings of the crystal, their visibility with undiminished sharpness over a wide range of settings of the crystal though with greatly diminished intensity, and above all, the practically constant intensity of the reflexion over a wide range of temperature. These features, taken together, left no room for doubt that the observed effects were due to the excitation of the characteristic high-frequency vibrations of the lattice by the incidence of the X-rays. Subsequent investigations with this and other crystals have furnished useful information and enabled some details to be more fully elucidated. But the case for the theory as stated in the papers quoted was essentially a complete one.

A good deal of literature has recently appeared on this subject which seeks to show, on the one hand, that the theory of X-ray scattering due to Faxén and Waller explains the facts of the case, and on the other hand seeks to convey the impression that the fundamental observations and conclusions reported by myself and Dr Nilakantan had been anticipated in earlier publications from other laboratories. The first of these claims has already been dealt with in the theoretical part of this paper, and its erroneous character will become even more evident when we proceed to consider the experimental facts. As regards the second claim, while the literature does contain numerous observations on diffuse streaks and spots

in Laue patterns for which very varied explanations had been put forward, *I wish to point out that the existence of a distinct new type of specular X-ray reflexion of a dynamic kind by the lattice planes of a crystal was for the first time recognized and its physical characters elucidated in the publications from this Institute quoted above.*

I shall now set out briefly the relevant experimental evidence under each of the heads mentioned above, commenting at each stage upon its relation to the theoretical aspects dealt with in Part I of the paper.

2. THE SPECULAR CHARACTER OF QUANTUM REFLEXION

In the earliest published photographs, the dynamic reflexions by the (111) planes of diamond appear as round spots whose diameter in strongly exposed pictures is about the same as or a little less than the major axis of the elliptic Laue spots, thereby indicating that their size is determined by the thickness of the crystal and the divergence of the incident X-ray beam and *not* by any inherent diffuseness of the reflexion. This inference has since been thoroughly tested by using thin plates of diamond with a fine slit as the source of X-rays and giving long exposures to bring out the reflexions with full intensity. Two such pictures are shown as figure 1 *a* and *b* in plate 32 for two different settings of the diamond. The quantum reflexions (indicated by arrows) appear in the record as fine lines, their measured widths being exactly that resulting from the finite thickness of the plate and the width of the slit used. Further, it is most significant that there is no change in the width of the reflexion as between the two settings. The experimental situation indicated in figure 1 *b* in plate 32 may be compared directly with the curve for the same glancing angle, namely 25° 58′, drawn in figure 2 of Part I. The 'diffuse maximum' of scattering in the latter curve extends over fully 12° of arc, while the reflexion appearing in figure 1 *b* as stated above has no measurable width. *The observed facts thus completely discredit the idea that the scattering of X-rays by elastic waves is in any way responsible for the phenomenon with which we are now concerned.* They also show that the term 'diffuse reflexion' is inappropriate as a description of it, since such diffuseness is clearly not an essential feature of the phenomenon. The observed sharpness of the quantum reflexions in diamond is equally decisive against the postulate of Born as applied to the infra-red vibrations of the lattice. For it demonstrates that the orientation and azimuth of the phase-waves are uniquely defined and independent of their wave-length, instead of having an infinite number of possible values as assumed in Born's postulate.

The sharpness of the quantum reflexion is closely related to the geometric law of such reflexion, being in fact a measure of the precision with which such law can be stated. It is evident that the reflexion can be perfectly specular only when the crystal is *dynamically homogeneous*, which would be the case if the lattice vibrations are represented by sharp lines in the spectrum of the light scattered by the crystal, as is actually found with diamond. Any cause, e.g. thermal agitation, which disturbs the dynamic homogeneity and results in increasing the width of these spectral lines must therefore also impair the specular character of the quantum reflexions. The lattice vibrations appear in the spectra of the great majority of crystals as rather diffuse lines which, however, become sharper at low temperatures. Accordingly, it is not surprising that the phenomenon of quantum reflexion is not shown with the same perfection as in diamond by other crystals. Nevertheless, in many cases, e.g. calcite or rock-salt, the quantum reflexions appear fairly sharp, their angular spread being only a small fraction of the angular separation between the Laue and the quantum reflexions. Indeed, the experimental facts as observed with the majority of crystals bear no resemblance to the situation represented in the series of curves in figure 2 of Part I. It is thus patent that the Faxén-Waller theory of X-ray scattering is completely irrelevant to the phenomenon now under consideration.

The manner in which a dynamic inhomogeneity of the lattice would influence the quantum reflexions may be readily appreciated by reference to the three-dimensional representation of the lattice vibrations against the reciprocal wave-length $\overrightarrow{1/\lambda}$. As already remarked in §4 of Part I, the N representative points lie densely clustered at the origin, the stragglers being distributed along a specific line (or lines) defining the permitted orientation and azimuth of the phase waves. The intersection of this line (or lines) with the sphere of reflexion determines the direction in which the reflexion is observed. A dynamic inhomogeneity of the lattice would result in this line, instead of being rigid and fixed in direction, becoming ill-defined. Since, however, the origin from which the line is drawn is firmly fixed, *it follows that the resulting spread of the quantum reflexion would be negligible when it lies very near the Laue reflexion and would progressively increase as its angular separation from the latter increases.* This is exactly what was observed and pointed out in the case of sodium nitrate and rock-salt (Raman & Nilakantan 1940 b, c) and is indeed a general feature. As the lattice lines in the spectra of most crystals sharpen at low temperatures, a corresponding sharpening of the quantum reflexions may be expected in the same circumstances.

3. Geometric law of quantum reflexion

The earliest measurements with diamond showed that the dynamic spacing d^* of the (111) planes altered continuously with the setting of the crystal, coinciding with the static spacing d only when the classical and quantum reflexions appeared superposed. This made it evident that the phase waves were not transverse to the crystal spacing in diamond, though in other cases, e.g. sodium nitrate, rock-salt and calcite, the measurements appeared to support the assumption of transversality. The explanation of
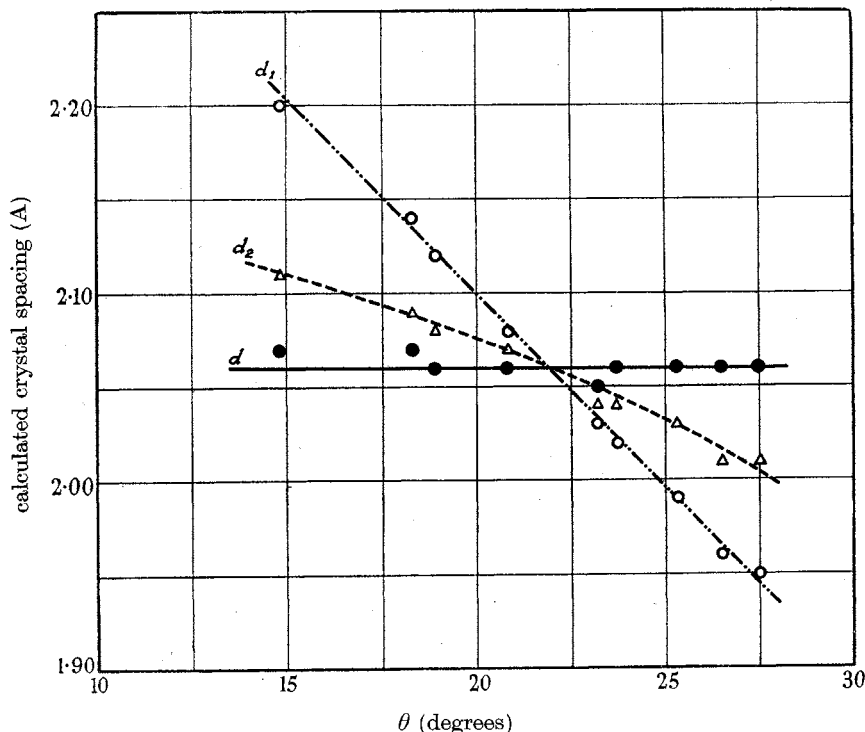

FIGURE 2. Showing the failure of the Faxén formula.

these and other facts was furnished by the general theory of quantum reflexion (Raman & Nagendra Nath 1940) which yielded the formula

$$2d \sin \psi \sin (\vartheta + \epsilon) = n\lambda \sin \vartheta, \qquad (1)$$

ϑ and ϵ having the significance already indicated in Part I. *Since the plane of the reflexion is that of incidence of the X-rays on the dynamic stratifications, it will not in general coincide with the plane of incidence on the static crystal*

planes. In the particular case, however, when $\epsilon = 0$ and the classical and quantum reflexions therefore coincide, and also generally when the plane of the phase waves is transverse to the plane of incidence on the static spacings, the reflexion indicated by (1) would appear in the same plane. We may then write (1) in the form

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

θ and ϕ being respectively the glancing angles of incidence and quantum reflexion measured with reference to the crystal planes. The earliest measurements as well as more elaborate ones made a few months later over a wider
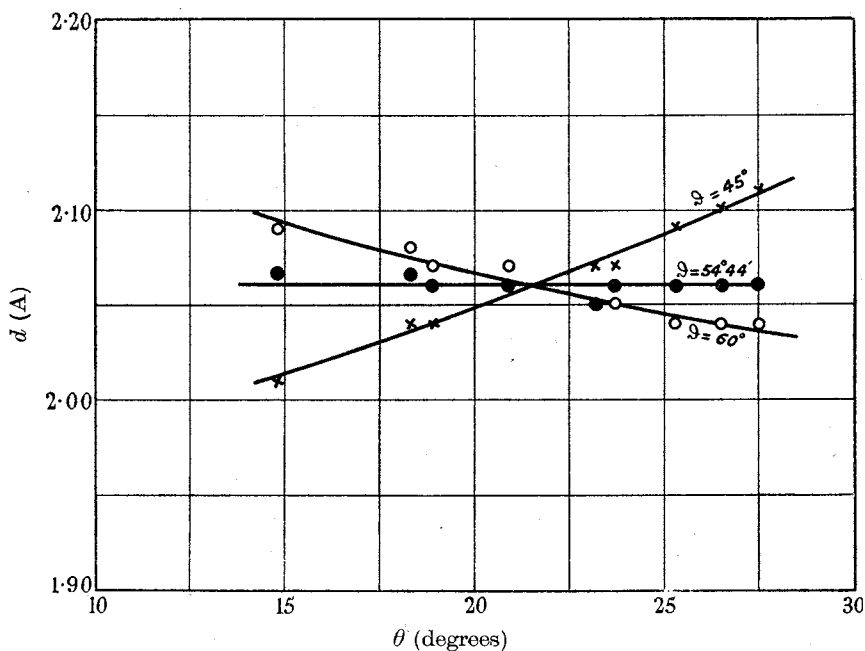

FIGURE 3. Fixing the orientation of the phase waves in diamond.

range of settings for the quantum reflexions by the (111) planes of diamond fitted the formula (1) rigorously, ϑ coming out as $54°\,44'$, that is half the tetrahedral valence angle. The measurements made for the particular case in which the plane of incidence is transverse to the (100) planes are shown graphically in figure 2.

In figure 2 the line marked d represents the crystal spacing calculated from the experimental data and equation (2), while the lines d_1 and d_2 were respectively drawn assuming the formulae

$$2d_1 \sin \tfrac{1}{2}(\theta + \phi) = \lambda, \tag{3}$$

$$d_2 \sin (\theta + \phi) = \lambda \cos \phi. \tag{4}$$

In figure 3 the same data are plotted from the formula (2) assuming different values of ϑ to illustrate the accuracy with which this angle can be evaluated and also the agreement between the evaluated and the known crystal spacing (2·055 A). Formula (4) was derived by Faxén to give the position of the diffuse maximum in the intensity of scattered X-radiations. *The total lack of agreement between the calculated and known crystal spacings, and the curvature of the line indicate that the considerations on which the Faxén formula is based are altogether irrelevant to our present subject.*

The experimental result stated above (Raman & Nilakantan 1941) is of extraordinary interest, for it indicates that the *phase waves of the infra-red vibration which give the* (111) *reflexions have a completely fixed orientation parallel to the* (100) *planes of the crystal.* Its significance from the point of view of crystal dynamics becomes clear when it is remarked that the (111) planes are normal to the valence bonds between the carbon atoms, while the (100) planes bisect the angles between them, and that the atomic layers in both these planes belong alternately to the two interpenetrating lattices of carbon atoms of which the oscillation as rigid wholes relative to each other gives the characteristic infra-red frequency (1332 cm.$^{-1}$) of diamond.

As remarked above, the reflexion given by the formula (1) ceases to appear in the plane of incidence (except in the special case where $\epsilon = 0$) if the phase waves are not transverse to that plane. *If, therefore, the diamond is so set that the* (100) *planes are inclined to the plane of incidence, the Laue and quantum reflexions by the* (111) *spacings should appear in different planes.* This remarkable result indicated by the theory was verified experimentally by Dr P. Nilakantan and myself and is illustrated in figure 4 in plate 32; the observed and calculated inclinations between the plane of incidence and the plane in which the quantum reflexion appears are found to be in full agreement.

Other remarkable results also follow from the theory. From considerations of symmetry, it is evident that if there is a set of phase waves parallel to the (100) planes, there must also be two other sets parallel respectively to the (010) and (001) planes. *Diamond must therefore show three quantum reflexions from the* (111) *planes and not one*, their relative positions being determined

by the angle of incidence of the X-rays and the azimuth in which the crystal is set, while their relative intensities would depend on the numerical values of the three reciprocal phase vectors $\overrightarrow{1/\varDelta_1}$, $\overrightarrow{1/\varDelta_2}$ and $\overrightarrow{1/\varDelta_3}$. These conclusions, extraordinary as they may seem, have been completely confirmed by the experimental investigations made at this Institute. Mr P. R. Pisharoty has worked out the geometrical implications of the theory in a most detailed manner and shown that in spite of the perfectly specular character of the quantum reflexion, by taking into account the angular divergence of the incident X-ray beam, all the observed phenomena, including especially the oblique streamers diverging from the Laue spots in some settings and the elongated elliptic spots on the opposite side in other settings are quantitatively explained (see figures $5a, b, c, d$ in plate 32). The oblique streamers are, in fact, the result of two of the phase vectors being nearly tangential to the sphere of reflexion instead of meeting it sharply. The intensity and extension of the streamers are determined by precisely the same considerations as the brightness and positions of the discrete spots. *Thus, the theory of phase waves put forward in April* 1940 *has found a most detailed and satisfactory experimental confirmation in the case of diamond.*

Formula (3) follows from the general formula (1) as an approximation if ϑ is assumed equal to $\frac{1}{2}\pi$, and ϵ is small. It suffices roughly to describe the observed geometric behaviour of the quantum reflexion in many cases. An appropriate choice of the angle ϑ in the general formula should lead to better concord with observation in all cases.

4. INTENSITY OF QUANTUM REFLEXIONS

Optical theory indicates that when the secondary radiations from N dipoles are of identical frequency and in coherent phase relationship, their resultant appears as a directed geometric pencil of intensity proportional to N^2, while if there is no such identity of frequency, the resultant is a diffuse radiation of which the intensity is proportional to N. The translatory movements of the lattice units in a crystal due to its elastic vibrations have a continuous spectrum of frequencies, and the case therefore comes under the second category. On the other hand, the characteristic infra-red vibrations are shown by the spectroscope to have precisely definable frequencies and their effect therefore comes naturally under the first category. The geometric character of the quantum reflexions, their physical origin and observed intensity are thus seen to be related to each other in a very intimate fashion, while the diffuse character of the quantum scattering, its physical origin and its intensity are similarly connected.

The intensities of the quantum reflexions like those of the classical ones are thus necessarily proportional to the square of the volume of the irradiated crystal (if this be not too large), while that of the scattering is proportional to the volume. This situation may be readily verified experimentally by reducing the effective volume to the minimum possible, e.g. by using the thinnest possible crystal and the finest possible X-ray beams. The classical and quantum reflexions are then seen physically to stand in the same category, continuing to be visible in the photographic record, while the diffuse or background scattering becomes too feeble to produce any sensible effect.

As explained in Part I, the intensity of the quantum reflexion may be evaluated theoretically by setting the energy of the individual oscillators equal to $h\nu^*$ and assuming them to be in an identical phase of vibration. This procedure yields the limiting intensity at the lowest temperatures and for the most favourable setting of the crystal, and comes out as a small but easily observable fraction of the intensity of the classical reflexion, of the order of about 1/100 to 1/1000, depending on the particular circumstances. *Though no precise experimental determinations are available, this indication of theory is at least of the right order of magnitude.* In making an exact test of the theory, it would be preferable not to rely on comparisons between the classical and quantum reflexions, but to make a calculation of the absolute intensity as well as a direct experimental determination of the same. Investigations of this kind have been undertaken at this Institute by Mr Pisharoty and are now in progress.

As already mentioned in Part I, theory indicates that the intensity of the quantum reflexions by different lattice planes in a crystal need not necessarily stand in the same ratio as the intensities of the classical reflexions by the same planes. We may, as an example, consider the case of diamond. The atoms belonging to the two interpenetrating lattices in the crystal appear interleaved in the (111) and the (100) planes, dividing these spacings in the ratios 1:2 and 1:1 respectively. On the other hand, they appear interspersed in equal numbers in the (110) planes. From these facts and formula (9) of Part I, it follows that neither the (110) nor the (100) planes can give any modified reflexion as the result of an oscillation of the inter-penetrating lattices, though the (111) planes can. Though the classical reflexions by the (110) planes have an intensity one-third of that of the (111) planes, *prolonged exposures fail to yield any modified reflexions by the* (110) *planes, in agreement with the indications of the theory.*

5. QUANTUM REFLEXION AT LOW TEMPERATURES

In the scattering of light with altered frequency by crystals, the quantum mechanical nature of the effect is strikingly revealed in the spectroscope by the enormous disparity in intensity of the radiations with frequencies $(\nu - \nu^*)$ and $(\nu + \nu^*)$ respectively, the disparity increasing rapidly with the magnitude of ν^*. In the X-ray problem, the components $(\nu \pm \nu^*)$ overlap, but this does not obscure the situation altogether, since the sum of their intensities continues to behave quite differently in the classical and quantum theories. As illustrated in figure 3 of Part I, the course of the intensity curve depends on ν^*. The greater its value, the more nearly horizontal is the curve at ordinary temperatures and the greater the deviation from the simple proportionality to the absolute temperature indicated by the classical mechanics. Per contra, the smaller the value of ν^*, the lower the temperature we must reach before the curve flattens out and becomes horizontal. Hence, the quantitative study of the intensity at low temperatures is of decisive importance for the subject. Not only does it furnish a test of the quantum mechanical nature of the phenomenon, but the course of the curve also enables us to measure the frequency of the lattice vibrations responsible for the reflexion and thus to establish the physical reality of the frequency shift. It also enables us to demonstrate the error of seeking an explanation of modified X-ray reflexion in the Faxén-Waller theory of X-ray scattering. For, in the latter theory, the elastic-solid waves giving the 'diffuse maxima' of the scattered radiation are those of which the frequency is the lowest possible, diminishing without limit as the position of the 'maximum' approaches the Laue spot. Hence, the intensity of the 'maximum' should diminish proportionally with temperature down to the absolute zero and indeed for all crystals, including even diamond.

The theoretical relation between the intensity of quantum reflexion and temperature was clearly set out (Raman & Nilakantan 1940a, b) dealing with the case of diamond, and observations at high temperatures were also described which supported its indications. It was confidently predicted that the intensity of the quantum reflexion by diamond should remain undiminished at liquid air temperature. When the necessary experimental technique had been developed, this prediction was found to be in complete accord with the facts (Raman & Nilakantan 1940d).

A proper experimental procedure is obviously imperative for all quantitative investigations of intensity. The simple method of dipping the crystal into liquid air which has been adopted in this connexion by the workers at the Davy-Faraday Laboratory (Preston 1941) is obviously

incapable of giving trustworthy results, as the absorption and diffusion of X-rays by the liquid air would mask the effects due to the crystal. *The conclusions which have been drawn from photographs in which the halo due to the liquid air appears superposed on the crystal pattern are*
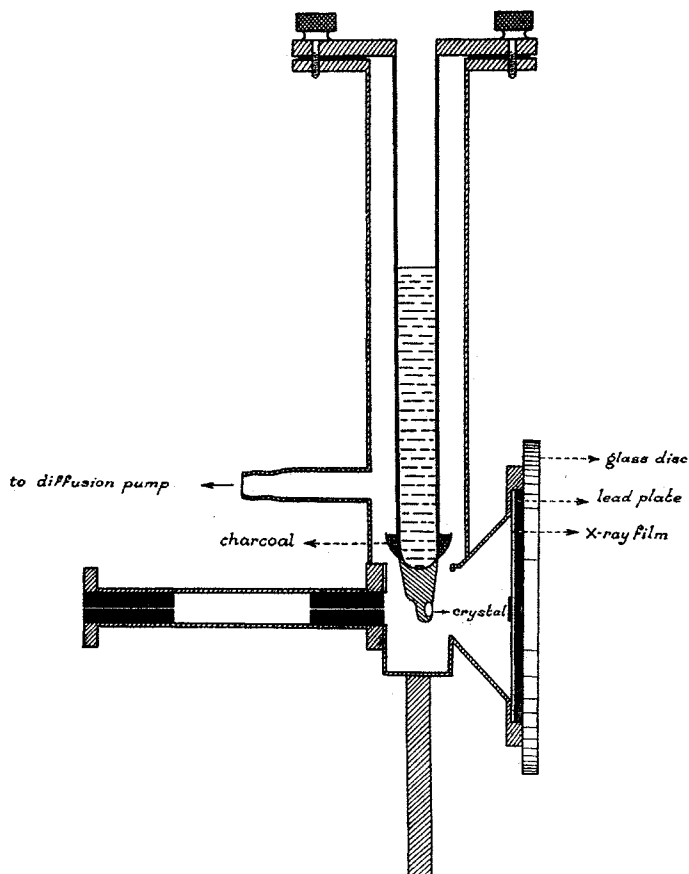

FIGURE 6. Design of low-temperature high-vacuum X-ray camera.

therefore quite illusory. To obtain results having a real significance, a high-vacuum low-temperature X-ray camera was constructed and employed by Dr P. Nilakantan at this Institute with very satisfactory results for the investigations with diamond. The design of the apparatus is illustrated in figure 6. Both the crystal and the photographic film are placed inside a high vacuum, the crystal being held firmly in contact with a metal block attached to the vessel containing liquid air or other refrigerant. It should be remarked also that for such quantitative work, *intensifying screens should*
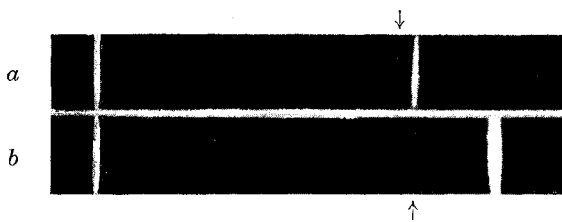
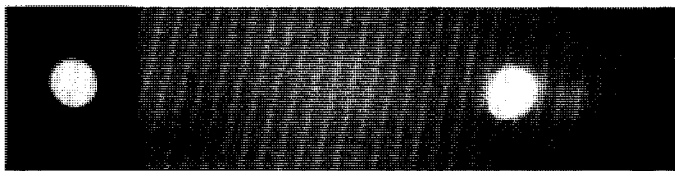FIGURE 1. Showing sharpness of quantum reflexions in diamond.

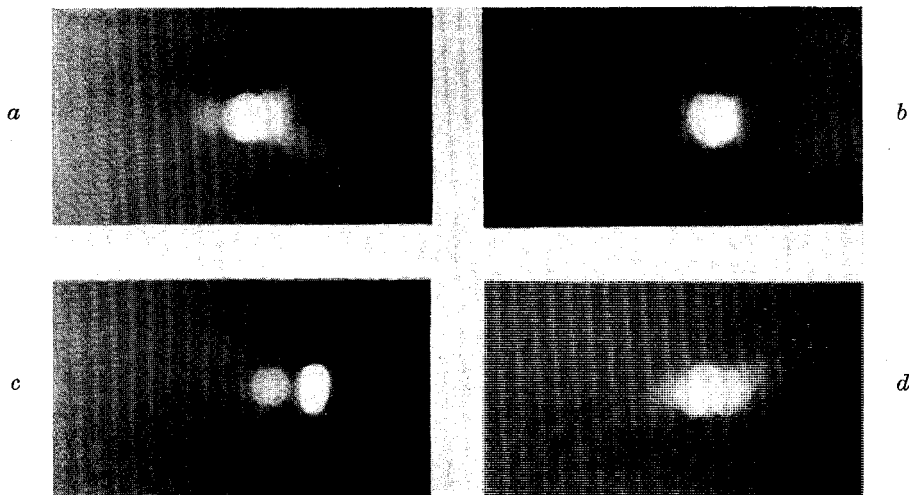FIGURE 4. Showing reflexions from diamond not in
the plane of incidence.

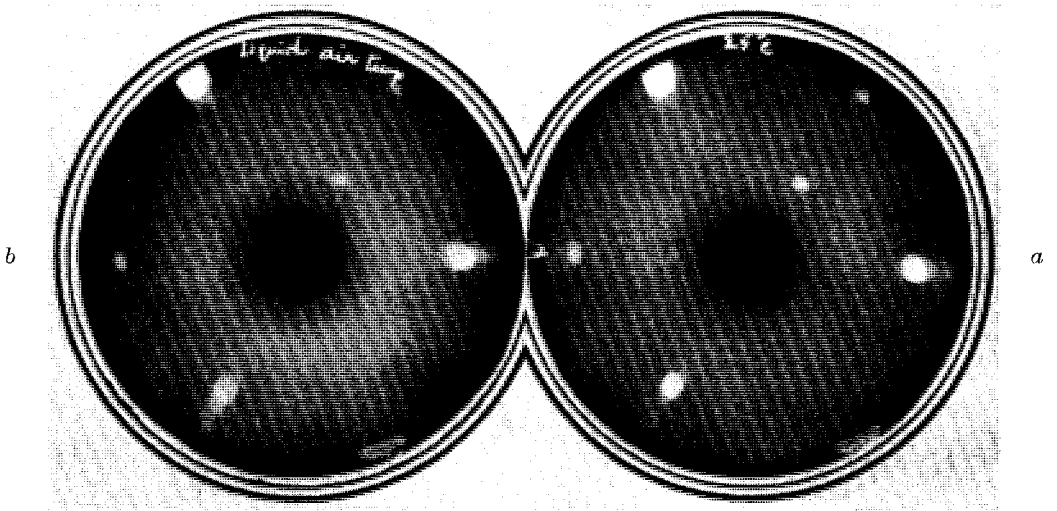FIGURE 5. Showing streamers and other subsidiary phenomena.

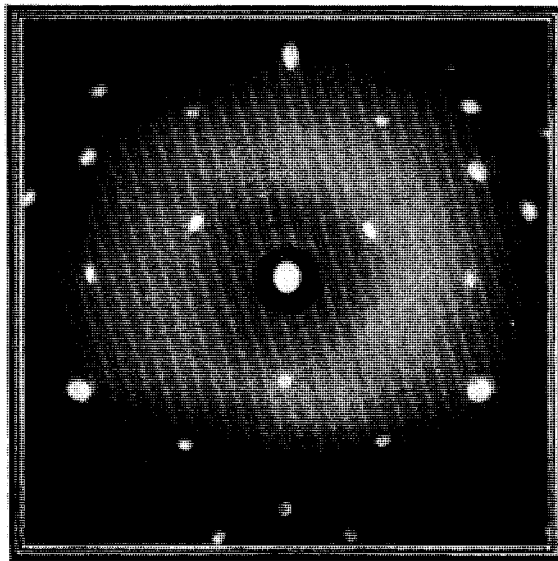FIGURE 7. Comparison of intensities at room and
liquid air temperatures.

FIGURE 8. Quantum scattering in diamond.

not be used, as they cannot be relied upon to maintain a constant behaviour. Two photographs for diamond taken with this camera at room and liquid air temperatures respectively are shown in figure 7 *a* and *b* in plate 33. A camera of improved design which enables rectangular X-ray films of larger size to be used has more recently been constructed and employed by Dr C. S. Venkateswaran in highly successful investigations with crystals of carborundum, rock-salt and pentaerythritol. These crystals were chosen as having high, medium, and low frequencies respectively in the infra-red spectrum. The results obtained with them at various temperatures completely confirm the theoretical conclusions already set out in the foregoing pages.

6. QUANTUM REFLEXION AT HIGH TEMPERATURES

The majority of crystals have numerous characteristic infra-red frequencies. The different modes of vibration are, however, far from being of equal importance in relation to our present subject. At the lowest temperatures, the intensity of the quantum reflexions is proportional to $h/4\pi^2\mu\nu^*$, while at sufficiently high temperatures it becomes proportional to $kT/2\pi^2\mu\nu^{*2}$. Thus in nearly all cases and particularly at high temperatures, the infra-red modes which have the lowest frequencies would make the largest contribution to the observed intensities of the modified reflexions. It may also be remarked, as shown by the formula (11) and (12) of Part I, that the static and dynamic structure amplitudes of the different lattice planes would be influenced even by the same mode of vibration to different extents. Hence by a comparative study of the modified reflexions from several lattice planes at various temperatures, it should be possible to correlate the X-ray facts with the known spectroscopic behaviour of the crystal, particularly in regard to the infra-red vibrations of the lowest frequencies.

The intimate relationship between modified X-ray reflexion and the infra-red spectrum is strikingly illustrated by the behaviour of the (210) planes of sodium nitrate investigated by Dr Nilakantan and the present writer. It is found that pari passu with the rapid decrease in the intensity of the classical reflexions by these planes which occurs in the temperature range from 180 to 275° C, there is an enormous increase in the intensity of the modified reflexions by the same planes. *This behaviour is not shared by other planes in the crystal*, the intensity of reflexion by which is altered by rise of temperature to a relatively small extent; it is thus evident that *we are concerned with a particular mode of vibration of the sodium nitrate lattice which is strongly excited in this temperature range*, and not with the general increase

of the thermal agitation. The same inference is indicated also by the specific heat data, and by spectroscopic observations on the light scattered in sodium nitrate crystals.

7. Quantum scattering of X-rays

Since the scattering of X-rays by the elastic vibrations of the crystal lattice involves a change of frequency, it is a quantum effect which should persist at the lowest temperatures. The observed intensity would, however, be then sensible only if $h\nu^* > kT$, in other words when the scattering is due to elastic waves of high frequency for which this condition is satisfied. Such an effect is actually exhibited by diamond, the scattering appearing as a diffuse halo at a considerable angular distance from the primary beam (figure 8 in plate 33). The dark ring at the centre of the halo and the distinct maximum of intensity towards its outer margin are noteworthy features of the phenomenon. It will be seen on a comparison of figure 7 a and b in plate 33 that the halo does not disappear at liquid air temperature, but that, on the other hand, it is actually more conspicuous and better defined. The effect presumably arises from the scattering of X-rays by longitudinal elastic waves of high frequency. The peculiar distribution of intensity in the halo is probably due to the increasing value of $h\nu^*$ to which the intensity is proportional for larger angles of scattering. The variation in the number of elastic modes of vibration with the reciprocal wave-length $\overrightarrow{1/\lambda}$ will, of course, also have to be taken into consideration.

8. Concluding remarks

Though the present report is written by me, it is largely based on the work of past and present members of the department, including especially Dr P. Nilakantan with whom these investigations were first undertaken, Dr N. S. Nagendra Nath, Dr C. S. Venkateswaran and Mr P. R. Pisharoty, all of whom have contributed notably to the development of the subject. I desire to place on record my warmest appreciation of their collaboration.

References

Preston, G. D. 1941 *Nature, Lond.,* **147,** 467.
Raman, C. V. & Nagendra Nath, N. S. 1940 *Proc. Indian Acad. Sci.* A, **12,** 427.
Raman, C. V. & Nilakantan, P. 1940*a Curr. Sci.* **9,** 165.
Raman, C. V. & Nilakantan, P. 1940*b Proc. Indian Acad. Sci.* A, **11,** 379, 389, 398.
Raman, C. V. & Nilakantan, P. 1940*c Proc. Indian Acad. Sci.* A. **12,** 141.
Raman, C. V. & Nilakantan, P. 1941 *Nature, Lond.,* **147,** 118.