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Reflection of X-rays with change of frequency—Part II. The case of diamond

SIR C V RAMAN and DR P NILAKANTAN
Department of Physics, Indian Institute of Science, Bangalore

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1. Introduction

We may now proceed to describe the results obtained by using the Laue method with various crystals which demonstrate the phenomenon of modified X-ray reflection and indicate its origin to be that considered in Part I of this paper. The case of diamond is of exceptional interest for various reasons. Its low atomic weight enables it to be used for such studies with comparatively soft X-rays without sensible loss of intensity by absorption within the crystal. Further, as it is an "ideal" crystal having a rigid lattice and a low specific heat, the effect of thermal agitation and of mosaic structure should be negligible. Diamond is therefore specially suitable for the present investigation. The simplicity of its crystal structure also facilitates the interpretation of the observed results.

Thin plates of diamond with their faces parallel to one of the octahedral cleavages of the crystal are readily obtained. The normal to an octahedral cleavage face is an axis of trigonal symmetry, and is inclined to the normals to the other three pairs of octahedral faces at the tetrahedral angle, namely $109° 28'$. Accordingly, if a pencil of X-rays passes through such a plate normal to its faces, it is incident on the three sets of (111) crystal planes at a glancing angle of $19° 28'$. The reflections from these planes would therefore appear in the Laue pattern as a distinct group of three spots forming an equilateral triangle which are easily recognised and identified (see figures 1 and 2 in plate I). When the crystal setting is not quite normal to the X-ray beam, the triangle appears distorted (see figures 3 and 4 in plate II). These photographs were taken with an X-ray tube having a copper anticathode and run at 41,000 volts. The beam accordingly contains the CuK_α and CuK_β rays in considerable strength, accompanied by white radiations of shorter wavelengths. When figure 1 was photographed the K_β radiations were cut off with a nickel foil, while figures 2, 3 and 4 were obtained, with the unfiltered radiation.

2. Experimental results

The four figures exhibit remarkable differences in the appearances of the (111) reflections (three in each figure) produced by varying the angle of incidence and (in figure 1) also by cutting off the K_β radiation. The differences consist in the shape, size and intensity of the Laue spots, the appearance of fainter companions in their vicinity, and the presence of streamers radiating at an angle from these companions (see figure 3). In order to exhibit clearly how these variations are determined by the glancing angle, eight pictures of the (111) reflections obtained with the unfiltered Cu radiation have been arranged in a vertical row in figure 5, plate III, so that the positions and intensities of the Laue spot and of its companions can be readily compared by inspection.

To appreciate the significance of the experimental results, we may remark that the (111) planes in diamond are those that give the strongest reflections and have therefore a large structure amplitude. Their spacing is 2·055 A.U. while the effective wavelengths of the CuK_α and K_β rays may be taken as 1·537 A.U. and 1·389 A.U. respectively. To obtain a Bragg reflection of the K_α and K_β radiations, therefore, the glancing angles on the (111) planes should be respectively $21° 58'$ and $19° 45'$. For the series of eight pictures shown in figure 5, the actual glancing angle as determined from the position of the Laue spot, and the plate distance alters from $17° 10'$ for figure 5(*a*) to $22° 13'$ for figure 5(*h*), thus covering a range of angles from much below to much above that required for a Bragg reflection of the K_β radiation, while in figure 5(*h*), the glancing angle is nearly that required to give a Bragg reflection for the K_α radiation.

From a study of these photographs, we draw the following conclusions: (1) The companion spots which accompany the Laue reflections appear in the plane of incidence of the X-ray beam on the crystal planes, that is to say, in the same plane as the Laue spots, but unlike the latter, do not satisfy the usual geometrical law of reflection from the crystal planes. (2) The two companion spots are due to the monochromatic CuK_α and K_β radiations respectively. This is shown by the fact that the inner spot vanishes when the K_β radiation is filtered out. (3) The spots are in the nature of well-defined specular reflections being, in fact, nearly as sharply defined as the usual Laue reflections of the white radiation; they tend, however, to be round instead of elliptic in shape. (4) The intensity of the spots increases rapidly as their position approaches that at which they could be identified with a regular geometric reflection from the crystal planes satisfying the usual Bragg formula. The spots continue to be however of perceptible intensity for directions removed by at least 10° on either side of such geometric reflection. (5) When a spot is at or near the position of maximum intensity, it is accompanied by streamers which do not lie in the plane of incidence but which appear to stretch towards or away from the two other (111) Laue spots.

The following table shows the measured distances of the Laue spots and of its two companions in the series of pictures figures 5(*a*) to (*h*) measured from the centre of the Laue diagram, the plate distance being 3·98 cms.

Table 1. Distances of spots from centre

Figure 5	Laue spot (cm)	Inner companion (K_β) (cm)	Outer companion (K_α) (cm)
(*a*)	2·72	3·13	3·55
(*b*)	2·85	3·20	3·60
(*c*)	3·04	3·22	3·65
(*d*)	3·31	Not separated	3·72
(*e*)	3·38	Not separated	3·74
(*f*)	3·50	3·30	3·76
(*g*)	3·54	3·34	3·78
(*h*)	3·60	3·36	3·81

The distances of a spot from the centre of the pattern for Bragg reflections of the CuK_α and CuK_β radiations respectively from the (111) spacings would be respectively 3·83 cms and 3·28 cms. It will be noticed that these distances coincide with the observed position of the spots when they are near the position of maximum intensity, but tend to deviate systematically from it in one direction or the other when they move away from this position.

3. Interpretation of the results

The general nature of the results described above leaves little doubt that we are here dealing with modified X-ray reflections of the kind discussed in Part I of the paper. We may however go a little more deeply into the matter in the light of the known crystal structure and properties of diamond.

The (111) planes have the largest spacings and give the strongest reflections amongst the crystal planes in diamond. It is therefore not surprising that they should give the modified X-ray reflections with notable intensity. The reason for this becomes clearer when we examine the nature of these spacings. As is well known, diamond consists of *two* interpenetrating face-centred cubic lattices of carbon atoms which we may refer to as the A and B lattices. The (111) spacings consist of planes of atoms belonging to lattice A interleaved by planes of atoms belonging to lattice B, the distance between the nearest layers of A and B atoms being one-fourth of the distance between the successive planes of A or of B atoms. It is this arrangement that makes the reflection from the (222) planes weak or evanescent, and makes the structure-amplitude of the (111) spacings correspondingly strong. If, now, we imagine the A and B lattices to oscillate as rigid wholes relatively to one another, the structure-amplitude of the (111) spacings should exhibit a strongly marked variation. For, the electron density between the most nearly adjacent A and B planes of atoms would increase when these planes approach each other and *per contra*, diminish when they recede. At the same time, the electron density between the less nearly adjacent A and B planes would behave in the opposite way, that is, would diminish in one case and increase in the other. The oscillation of the two elementary lattices with respect to one another in a direction normal to an octahedral cleavage face should therefore produce a stratification of the electron density which is periodic in time and has the same spacing as the (111) planes. These planes should thus be in a position to give a modified reflection of the incident X-rays.

When a crystal of diamond is illuminated with monochromatic light, the spectrum of the scattered light exhibits a single sharp line of great intensity with a spectral shift of 1332 wave-numbers. It is a well-established result that this frequency-shift is due to the same oscillation which we have considered here, namely, a linear vibration of the two interpenetrating lattices A and B with reference to one another. The oscillation is triply degenerate, in other words, may take place in any arbitrary direction or simultaneously in different directions with arbitrary phases, the frequency being the same in every case. It is evident that the structure-amplitude of a particular (111) spacing would be influenced only if the movement of the lattices has a component normal to that spacing and would be unaffected if the movement is parallel to it. So long, however, as the two interpenetrating lattices move as rigid units and the phase of the motion is identical in all the individual cells, the periodic stratifications of electron density produced by such motion remain everywhere parallel to the respective crystal planes and have identically the same spacing as these planes. On these assumptions, therefore, the modified reflection of the X-rays by any set of crystal planes would appear only in the same direction as the ordinary Laue reflections.

Actually, as we have seen, the modified X-ray reflections associated with a particular set of the (111) planes in diamond continue to appear with practically undiminished sharpness, though with rapidly diminishing intensity, as we move away from the correct Bragg orientation for the particular X-ray wavelength. Further, as shown by the figures in table 1, if the modified reflection is regarded as a Bragg reflection from a periodic stratification of electron density inclined to the crystal spacing, not only does the effective 'structure-amplitude' of such stratifications diminish rapidly as they are tilted away from the crystal planes, but the effective spacing of such tilted wave-fronts progressively deviates from the actual crystal spacing. A glance at the figures in table 1 shows that this apparent change of spacing occurs in such a direction that the modified reflection is nearer to the direction of the Laue reflection than would otherwise be the case. These results become intelligible when we recognize that the circumstances most favourable for the modified reflection to make its appearance are precisely those in which the unmodified reflection is also obtained. In any other case, a modified reflection is only separable from the unmodified reflection if the oscillation of the structure-amplitude departs from the ideal condition of having the same phase everywhere. A diminution of the intensity of the resulting reflection is only to be expected in such circumstances.

Empirically, it is found that the formula

$$\lambda^* \sin(\theta + \phi) = \lambda \cos \phi, \tag{1}$$

nearly fits the results for diamond shown in table 1. Here θ, ϕ are the glancing angles of incidence and reflection with respect to the crystal planes, λ^* is the spacing of the latter, and λ the X-ray wavelength. It will be noticed that the formula is unsymmetrical in θ and ϕ, in other words, they are not interchangeable. On the other hand, a formula of the symmetrical type

$$2\lambda^* \sin \tfrac{1}{2}(\theta + \phi^*) = \lambda \tag{2}$$

for the modified reflection would make it completely analogous to the Bragg formula and give an angular separation $(\theta + \phi^*)$ of the incident X-ray beam and of the modified reflection which is the same for all orientations of the crystal and therefore identical with that for the unmodified reflection. Comparing (1) and (2), it is easily seen that

$$\begin{aligned} &\text{If } \phi > \theta, \quad \text{then } \phi < \phi^* \\ &\text{If } \phi < \theta, \quad \text{then } \phi > \phi^*. \end{aligned}$$

This is what the figures given in table 1 indicate. Both the formulae (1) and (2) reduce to the Bragg formula when $\theta = \phi$ or ϕ^*.

We may now remark on the explanation of the oblique streamers [seen in figure 3 and figure 5(h)] which as already mentioned, accompany the modified X-ray reflection in diamond when it is of sufficient intensity. It will be noticed that they radiate towards or away from the two other Laue spots due to the (111) spacings, instead of towards the centre of the pattern. Their explanation is to be found in the fact already remarked that the lattice oscillation in diamond is triply degenerate, and may therefore co-exist in different directions and in different phases. In general, therefore, variations of the structure factor of each of the three sets of (111) planes would occur simultaneously. An X-ray beam incident on any one set of these planes and reflected by it would also be influenced by the stratifications having the same spacing and frequency parallel to the two other sets of these planes. The streamers accompanying the modified reflection are evidently secondary effects due to the superposition of the three sets of stratifications. This is clearly shown by the directions which they assume.

The radial streamers which stretch from the Laue reflection towards the centre of the pattern have a different origin. They are best seen with diamond when the modified reflections due to the K_α and K_β rays both lie outside the Laue spot, and may therefore be identified with the modified reflection of the *white* radiations of shorter wavelengths present in the incident X-ray beam.

4. Significance of the diffuse halo

Referring again to figures 1, 2, 3 and 4 in the plates, a very striking feature of these Laue patterns is the strong though diffuse halo which appears surrounding the primary X-ray beam. Its outer limit is ill-defined, and indeed towards its periphery the halo mingles insensibly with the diffuse scattering by the crystal which overlays the entire Laue pattern. It is, however, evident that the intensity of the halo is relatively great over a limited area which lies well within the triangle formed by the (111) Laue spots. That the phenomenon is really due to the diamond has been fully established by blank exposures without the crystal which give a clear film except over a narrow ring due to the primary beam surrounding the blocked-out circle at the centre. Allowing for this narrow ring, it appears that the maximum intensity of the halo is not at the centre of the pattern, but very definitely further out, in fact about half-way between the centre and the (111) Laue spots. In well-exposed pictures, the falling off in the intensity of the halo towards its centre is clearly seen. In considering the origin of the halo, we must, of course, take into account the composition of the incident X-radiations, which includes besides the CuK_α and K_β rays, also a considerable intensity of while radiation of shorter wavelengths. The elimination of the latter, if it had been possible, would undoubtedly have accentuated the falling off in intensity of the halo towards the centre of the pattern and made the existence of a well-defined maximum at a distance from the centre more strikingly evident. There can be little doubt, however, that the most intense region of the halo owes its origin to the monochromatic K_α and K_β radiations of the copper anticathode.

It will be remembered that in Part I of the paper, we have referred to Brillouin's theory of the reflection of monochromatic X-rays by sound-waves of thermal origin. This theory indicates the appearance of a continuous diffusion halo in the X-ray pattern extending from the centre outwards and falling off in intensity to zero at an angle corresponding to the short wavelength limit of the acoustic spectrum. Brillouin's expression for the intensity of the halo includes a Planck factor which is equal to unity for the lowest frequencies and tends to zero for acoustic frequencies for which $h\nu \gg KT$. Accordingly, for the case of diamond, the intensity of the Brillouin halo should be vanishingly small except very near its centre. Actually, as is evident from the photographs, the halo is a conspicuous phenomenon and exhibits a maximum at an angular radius from the centre of about 20°. It is therefore clear that though the halo is evidently due to the reflection of the X-rays by acoustic waves as postulated by Brillouin, its intensity is much larger than that indicated by his theory. The basic idea of his theory, namely, that the sound-waves responsible for the scattering of X-rays are of thermal origin, cannot therefore be accepted. If, however, we consider the acoustic waves to be actually excited by the X-ray quanta, the difficulty would disappear, as the intensity of the scattering would then be vastly greater and in better accord with the observed facts. The distinct concentration of the scattering in a ring-shaped halo suggests that the acoustic spectrum has a marked intensity maximum at a wavelength roughly about double the shortest permissible.

We must not, of course, omit to mention the Compton scattering. Theory indicates that this is of zero intensity for the forward scattering and increases to its full value at large angles. In the case of diamond, the Compton scattering is probably responsible for most of the radiation diffused by the crystal through large angles. Nearer the centre of the pattern, however where the intense diffuse halo is observed, the Compton scattering is less important, and the observed effect is mostly due, as we have seen, to the acoustic waves excited by the incidence of the X-radiation.

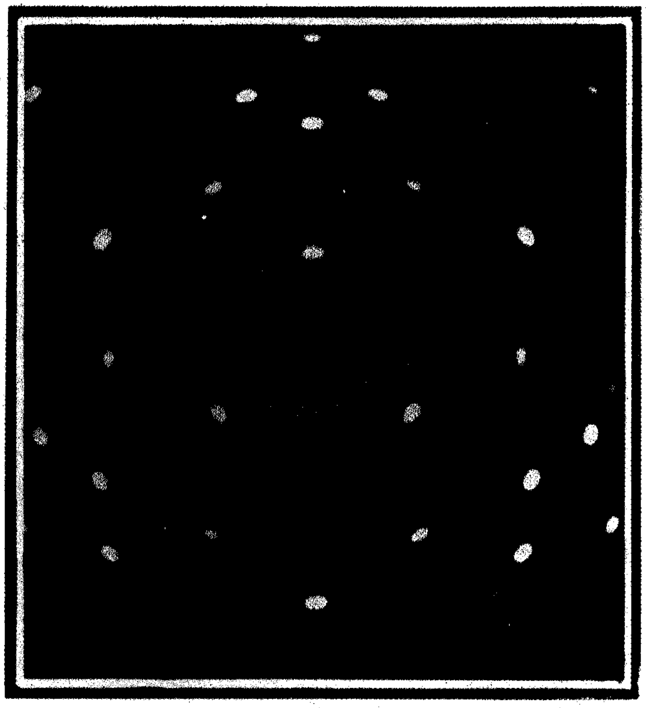
5. Influence of temperature

As explained earlier in the paper, the choice fell on diamond as the crystal for these experiments, mainly because phenomena of purely thermal origin would, prima facie, be negligible in dealing with it. This is evident when we consider the magnitude of the Planck factor $1/(\exp(h\nu/KT-1))$ which indicates the extent of thermal excitation of any oscillation of frequency ν. At room temperature ($\tau = 300°$), $h\nu = KT$ for a frequency $\approx 6 \times 10^{12}$, whereas the characteristic frequency of diamond corresponding to $1332\,\mathrm{cm}^{-1}$ is 40×10^{12}. The magnitude of the Planck factor for this frequency is entirely negligible, while it is small even for a frequency which is only half of it. The appearance of a modified X-ray reflection due to the lattice oscillation in diamond and indeed also of the scattering by the acoustic waves for lower frequency must therefore be regarded as quantum effects. A very convincing demonstration that this is the case would be to cool down the diamond to liquid air temperatures and to observe whether the effects under consideration persist undiminished, as is to be expected. Experiments of this kind are in progress and will be reported as soon as they are completed. As corresponding experiments with light show that modified scattering persists with undiminished intensity at the lowest temperatures, we may confidently anticipate an analogous result also with modified X-ray reflection at angles close to the usual Laue reflections. The falling off in the intensity of the modified reflection when the crystal is tilted away from the correct position for a Bragg reflection may however conceivably show a more marked temperature dependence. This is a matter for further investigation.

In the case of the modified scattering of light, the intensities of the Stokes and anti-Stokes components are respectively proportional to $1/(1-\exp(-h\nu/KT))$ and $1/(\exp(h\nu/KT-1))$. The first of these quantities is approximately independent of temperature so long as $h\nu \gg KT$. For a characteristic frequency 40×10^{12}, the temperature dependence of the intensity of the Stokes component should only become sensible when $T > 1000°$. Investigations on light scattering in diamond made recently at Bangalore show that when the crystal is heated, it exhibits an appreciable alteration of the characteristic frequency, and it is probable also that at higher temperatures the frequency broadens out into a band. Accordingly, we should not be surprised to find in the X-ray phenomena temperature effects more pronounced than those indicated by the formula quoted.

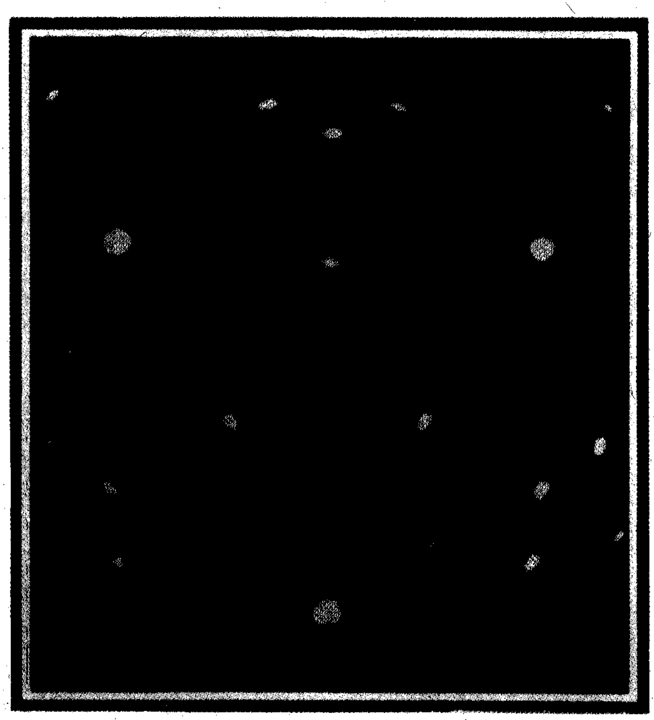
Photographs of the Laue pattern of diamond at 25° C and at 500° C show at the higher temperature a slight enfeeblement of the ordinary Laue reflections, and a detectable but not very striking enhancement of the intensity of the modified reflections, as also of the diffuse halo appearing in the pattern. The thermal expansion of the crystal with consequent shifting of the relative positions of the Laue and modified reflections however complicates the issue, as the intensity of the modified reflections depends greatly on their relative position. A more detailed study is therefore necessary before any definite conclusions can be drawn. Nevertheless, the observations so far as they go indicate pretty clearly that the modified reflection of X-rays and the diffuse halo are not *primarily* thermal phenomena. This statement, it will be noticed, does not exclude observable thermal influences on the phenomena, such as sharpening of the reflections at low temperatures, or their brightening up and becoming more diffuse at high temperatures.

(1)



Filtered, CuK_α radiation only

(2)

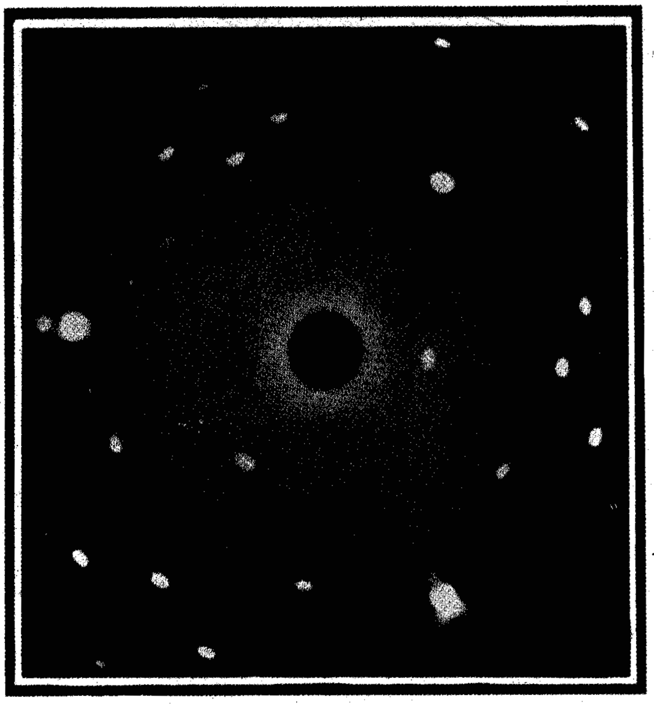


Unfiltered. CuK_α and CuK_β radiation

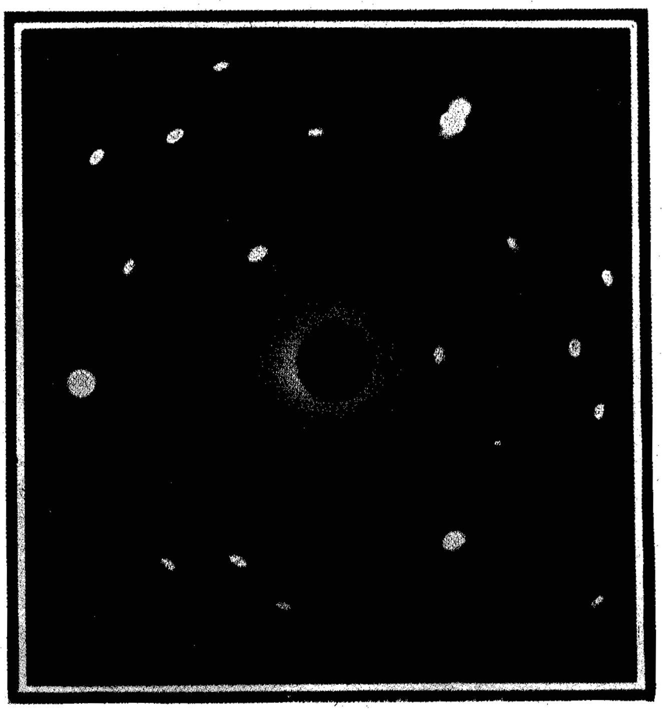
Figures 1 and 2. Symmetrical Laue pattern of diamond (normal to cleavage plane).

Plate I

(3)



(4)



Figures 3 and 4. Asymmetrical Laue pattern of diamond (approximately normal to cleavage plane).

Plate II

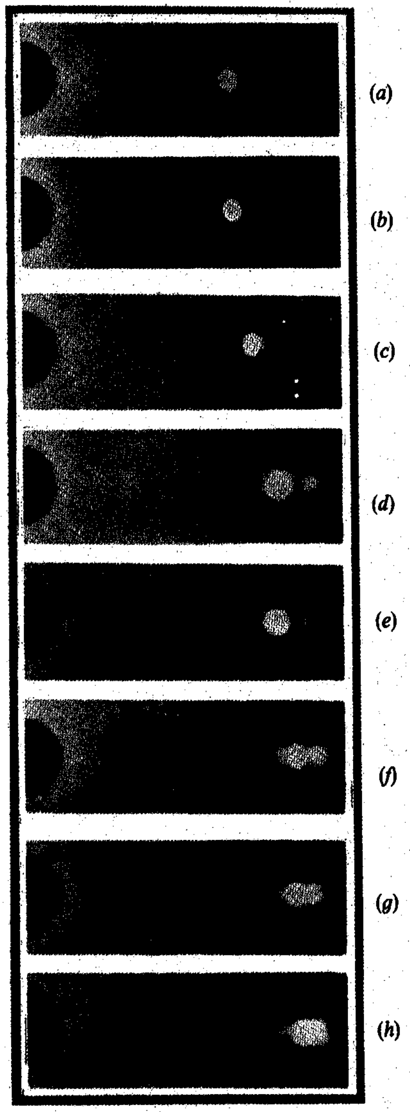


Figure 5. Showing Laue spot due to reflection from [111] planes of diamond and modified reflections due to K_α and K_β radiations.

Plate III