THE ABSOLUTE INTENSITY OF THE RAMAN X-RAY REFLECTIONS IN DIAMOND

BY P. RAMA PISHAROTY

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

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1. *Introduction*

IN an earlier paper appearing in this issue of the *Proceedings*, the author has shown how the dynamic structure amplitude of any lattice spacing of diamond may be calculated for the 1332 cm.$^{-1}$ oscillation.† The Planck oscillator of this frequency ν^* is taken to consist of two atoms and the amplitude of the oscillation is calculated by giving an energy $h\nu^*$ to each oscillator. All the oscillators are assumed to be in phase, so that we get the structure amplitude of the Raman or quantum reflection at the correct Bragg setting only. We add the *periodic* displacements of the various atoms of the unit cell to their static co-ordinates and substitute the vectorial sums, for the respective co-ordinates x_p, y_p, z_p, of the pth atom of the unit-cell, in the following expression for the structure amplitude of the reflection from the (hkl) plane:

$$\mathrm{F}_{hkl} = \sum_p f_p \, e^{2\pi i (h x_p + k y_p + l z_p)} \, e^{2\pi i \nu t}.$$

Here f_p is the atomic scattering factor of the pth atom and ν is the frequency of the incident X-radiation. The (hkl) plane would be active for the Raman

TABLE I

Indices of the plane	Spacing in A.U.	Classical or Bragg reflection	Quantum or Raman reflection	Indices of the plane	Spacing in A.U.	Classical or Bragg reflection	Quantum or Raman reflection
111	2·058	A	A	400	0·889	A	F
311	1·073	A	A	420	0·795	F	A
331	0·817	A	A	422	0·726	A	F
333	0·685	A	A	440	0·629	A	F
335	0·542	A	A	620	0·562	A	F
551	0·498	A	A	622	0·537	F	A
..	..	..	..	660	0·419	A	F
200	1·778	F	A	662	0·409	F	A
220	1·258	A	F	844	0·363	A	F
222	1·029	F	A				

A—Allowed. F—Forbidden.

† Recently Nayar has found that there are discrete lattice frequencies for diamond as low as 127 cm.$^{-1}$ They are not discussed here since their modes of oscillation are not as yet known. It is possible that some of them may be active where the quantum reflections for the 1332 oscillation is forbidden. These quantum reflections, if any, would be then more temperature-sensitive.

reflection whenever there is a term with frequency $(\nu \pm \nu^*)$ in the reflected radiation. The above table gives the active planes for the quantum reflection produced by the lattice oscillation of 1332 cm.$^{-1}$ The first series of planes have all their indices *odd* and every one of them is allowed for the Raman reflections. When all the indices are *even*, the Raman reflections are 'forbidden' if $h+k+l=4n$, and are 'allowed' if $h+k+l=4n+2$, the Bragg reflection being 'forbidden' for the latter case. A face-centred cubic lattice has planes in common with the diamond lattice which are 'forbidden' for the classical reflections. All of them are 'forbidden' for the quantum reflections as well.

The author has calculated in his previous paper already mentioned, that the intensity of the Raman reflection for the (111) planes of diamond in the correct Bragg setting would be about 7% of the total reflected intensity. The experiments of Raman and Nilakantan[1] showed that the intensity of the quantum reflection is fairly large when close to the Bragg setting, and that it falls off rapidly as the setting is continuously altered. But they have given no quantitative data and have not approached very close to the Bragg setting. The present paper gives an account of an experimental determination of the absolute intensity of the quantum reflections from the (111) planes, in terms of the intensity of the direct monochromatic beam.

2. *Experiments and Results*

Copper X-radiations generated in a Siefert tube of the demountable type, worked at 56 k.v. peak and 22 ma., was passed through a lead slit 0·2 mm. wide, 4 mm. high, and 130 mm. deep. The emergent narrow pencil was monochromatised by reflection at the octahedral cleavage face of a thin plate of diamond ($10 \times 6 \times 0{\cdot}8$ mm.^{3}) set at the Bragg angle of the K_α radiation. The reflected beam was easily visible on a fluorescent screen, held beyond a second slit 0·2 mm. wide and 2 mm. high, cut in a sheet of lead, and placed at a distance of 2 cm. from the crystal.

The monochromatic beam, coming through the second slit, passed through a second crystal of diamond (0·8 mm. thick), set with its octahedral cleavage face nearly normal to the incident beam. A rod of 10 cm. length attached to the goniometer of this crystal enabled it to be turned through small angles. A plane mirror attached to the goniometer was used together with a scale and telescope to measure small angular displacements of the crystal. A millimetre shift on the scale corresponded to a shift of the crystal through 1·3 minutes of arc.

After a series of trials, the second crystal was set to give Bragg reflection from the interior (111) planes, as registered on a photographic film kept normal to the direct beam and at a distance of 4·5 cm. from the crystal. The crystal was rotated through known angles from this position, and the corresponding quantum reflections were recorded. In each case the direct beam was allowed to be incident on the film all the time, but with its intensity reduced to a known fraction by the interposition of a definite number of thin standard nickel foils supplied by the firm of Adam Hilger. Each foil was 0·033 mm. thick. The number of foils were adjusted so that the direct spot and the quantum reflection recorded on the same film were of comparable intensities. Up to five foils were used in the experiments.

A density-log. intensity curve, for the Kodak "Duplitized" X-ray films used, was drawn employing the step-wedge method of Baltzer and Nafe[2], with the incident X-rays nearly monochromatised by a nickel filter 0·066 mm. thick. All the films were developed with the same stock of developer under the same conditions of time and temperature. A Moll microphotometer supplied by Kipp and Zonen was employed for the photographic density determinations.

Measurements were taken only up to thirty minutes of arc from the Bragg setting by this method. The time of exposure for this setting was ten hours. For wider settings of the crystal monochromatisation was dispensed with, as very long exposures were required. A narrower slit was employed and the beam directly passed through the second crystal. Raman reflections for half-a-degree and one degree off the Bragg setting were recorded on the same film, one below the other, and with suitable exposures to make both of them nearly of the same photographic density. Similarly, the quantum reflection when $(\theta_B - \theta) = 2°$ was compared with the one for which $(\theta_B - \theta) = 1°$. The actual intensities were compared by assuming the value of the exponential of time, in the expression for the photographic density poduced by X-rays, to be one.

The following table gives the intensities of the quantum reflections, for various settings of the crystal, as fractions of the intensity of the direct beam.

TABLE II

$2(\theta_B - \theta)$	$\frac{\text{Intensity of the Raman reflection}}{\text{Intensity of the direct beam}}$
5′·2	0·010
10′·4	0·0029
18′	0·00085
20′	0·00028
1° 2′	0·0000020
2° 0′	0·0000004
4° 0′	0·00000008

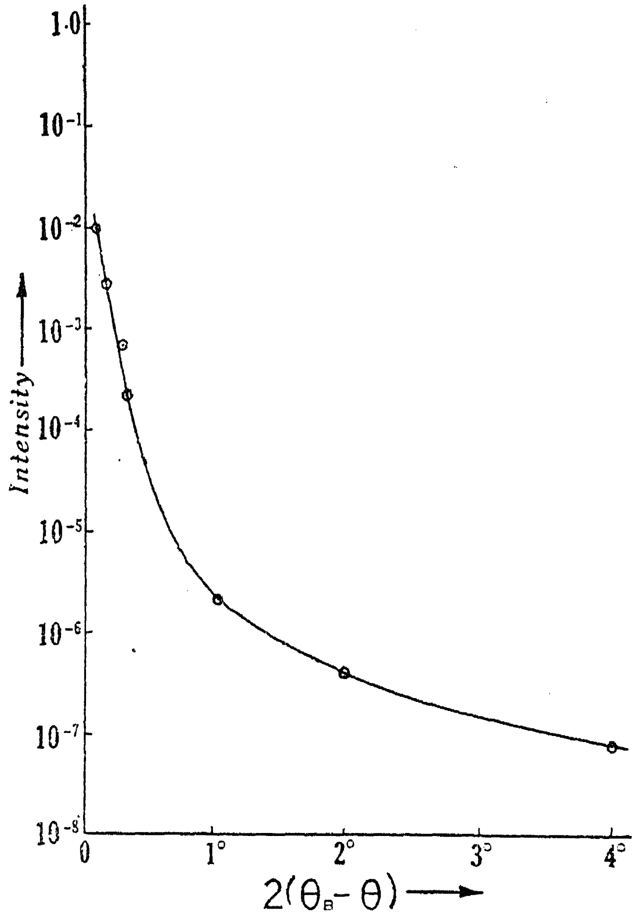

FIG. 1

Graph of Intensity against Crystal Setting

The results are plotted in Fig. 1, the ordinates being the intensities and the abscissæ being twice the difference between the Bragg angle θ_B and the glancing angle θ. It can be shown from the Raman and Nath formula[3] that,

$$2\,(\theta_B - \theta) \simeq 2\,\frac{d}{\Delta}\,\frac{\cos\,(\theta_B + \vartheta)}{\cos\,\theta_B}$$

where d is the crystal spacing, Δ is the phase-wave-length of the lattice oscillations, and ϑ is the inclination of the phase-waves to the lattice spacings. Hence, the curve represents the variation of the intensity of the quantum reflections with the reciprocal of the phase-wave-length of the lattice oscillations involved.

The natural divergence of the beam is determined by the width of the second slit and the far end of the first slit. This works out in the present experiment to be about four minutes of arc on either side of the central beam. To this is to be added the divergence of the Bragg reflection. But this is of the order of a few seconds of arc, for a perfect crystal of diamond, and hence negligible. Therefore there can only be some doubt about the accuracy of the first value in the above table.

3. *Discussion*

It is found that the intensity of the Raman reflection does approach a few hundredths of that of the incident beam and therefore, of the Bragg reflection itself. This is in general agreement with the theory, which indicates an intensity of about 7% of the Bragg reflection in the most favourable setting. The intensity of the quantum reflection falls with extreme rapidity at first and then more slowly with increase of the value of $(\theta_B \sim \theta)$, or from another point of view, with decrease of the operative phase-wave-length of the lattice oscillations. The facts thus suggest that, in diamond, the lattice oscillations with long phase-wave-lengths are far more probable than those with smaller phase-wave-lengths.

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4. *Summary*

The lattice planes of diamond which are 'allowed' and 'forbidden' for the Raman reflections produced by the lattice oscillation of 1332 wave-numbers are tabulated. The intensity of the quantum reflections from the (111) planes are directly compared with the incident monochromatised X-rays, at settings ranging from a few minutes of arc to two degrees away from the Bragg setting. The results show that the intensity of the Raman reflection at the closest setting is a few hundredths of the intensities of the incident beam, in general agreement with the theoretically estimated value of 7% at the exact Bragg setting. The intensity falls off rapidly at first and then more slowly as the crystal setting is continuously altered. When the angle of incidence differs by two degrees from the Bragg value, the intensity is roughly a ten-millionth part of the incident beam.

REFERENCES

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2. Baltzer and Nafe .. *Phys. Rev.*, 1940, **57**, 1048.
3. Raman and Nath .. *Proc. Ind. Acad. Sci.*, 1940, **12**, 427.