

A QUANTUM THEORETICAL EXPLANATION OF THE APPEARANCE OF FORBIDDEN X-RAY REFLECTIONS IN DIAMOND

BY P. RAMA PISHAROTY

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

Received September 16, 1941

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

WHEN a narrow pencil of monochromatic X-rays is passed through a thin crystal, dynamic stratifications are excited in the crystal lattice and these give rise to the Raman or quantum X-ray reflections of altered frequency¹ which for the particular setting of the crystal at which they are most intense coincide in direction with the Bragg or classical reflections by the same crystal planes. The present paper deals with the calculation of the structure amplitudes of these dynamic stratifications in the particular case of diamond on the simple assumption that the incident X-rays impart to each degree of freedom corresponding to an infra-red oscillation of the lattice an energy equal to $h\nu^*$, ν^* being the frequency of the oscillation and h the Planck's constant. The simplicity of the structure of diamond and the well-known character of its Raman active, infra-red lattice oscillations, facilitates the calculation. Some of the planes which have zero structure amplitude for the classical Bragg reflections are shown to possess finite dynamic structure amplitudes for the Raman or quantum reflections, thus accounting for the appearance of the so-called "forbidden" reflections in diamond.

2. Oscillations of the Diamond Lattice

As is well known, a crystal of diamond can be pictured as built up either of two interpenetrating face-centred cubic lattices or of two interpenetrating rhombohedrons. On the former view the unit cell consists of eight atoms while on the latter it consists only of two atoms. Adopting the rhombohedral unit cell, Nagendra Nath² as well as Venkatarayudu³ have derived identical expressions for the normal modes of oscillation of the diamond lattice and have shown that there is only one triply degenerate Raman active infra-red oscillation possible for the lattice. In other words, there are three degrees of freedom for the infra-red oscillations and another three for the elastic oscillations, making up the total of six degrees of freedom for the unit

cell of two atoms. We will adopt this point of view and take the Planck oscillator in diamond to consist of two atoms and be of frequency $3 \cdot 996 \times 10^{13}$ sec. $^{-1}$ corresponding to the shift of 1332 cm.^{-1} wavenumbers exhibited by the intense Raman line.

3. The Dynamic Stratifications Associated with the (111) Reflections

The co-ordinates of the lattice points of a unit cell of diamond, referred to rectangular axes, are known to be

$$000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0;$$

and

$$\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}.$$

Here the unit is $3 \cdot 56$ AU as obtained from the X-ray measurements. The structure amplitude F of the $(h k l)$ planes is given by the formula

$$F = \sum_p f_p e^{2\pi i (hx_p + ky_p + lz_p)}, \quad (1)$$

where f_p is the atomic scattering factor of the p th atom whose co-ordinates are x_p, y_p, z_p .

When the atoms are at rest, the value of F for the (111) planes of diamond is given by

$$4f_1(1-i),$$

where we take f_1 , the atomic scattering power of the carbon atom, to be the same for all the atoms of the unit cell.

We will suppose that the incident X-rays excite the infra-red vibrations of the lattice in which one lattice vibrates against the other, the direction of vibration being assumed to be normal to the (111) planes. We are justified in this as we know from the Raman effect data for diamond that its intense infra-red oscillation is triply degenerate and since the oscillations parallel to the planes themselves have no influence on their structure amplitude. We further assume, as a limiting case, that all the unit cells vibrate completely in phase and that each cell is endowed with a quantum of energy $h\nu^*$, where ν^* is equal to $3 \cdot 996 \times 10^{13}$ sec. $^{-1}$, the observed frequency of the lattice oscillations in diamond.

The periodic displacement of the p th atom belonging to one of the lattices is given by

$$\mathbf{D}_p = \mathbf{i} dx_p + \mathbf{j} dy_p + \mathbf{k} dz_p, \quad (2)$$

where

$$dx_p = a_p \sin (2\pi \nu^* t - \zeta) = dy_p = dz_p,$$

since the oscillation is normal to the (111) plane and all the atoms of one

lattice are in phase. The displacements of all the atoms of the other lattice are equal but opposite to those of the first.

If A be the amplitude of the oscillator taken along the [111] direction, we have

$$a = \frac{A}{\sqrt{3}}.$$

It is well known that the diamond lattice has three degrees of freedom corresponding to the elastic and another three corresponding to its infra-red, lattice oscillations. Hence each Planck oscillator composed of two atoms—one from each lattice—has an energy $h\nu^*$ associated with it. Therefore, if A be the amplitude of oscillation of one carbon atom and m its mass, we have

$$h\nu^* = \frac{1}{2} \sum m v^2 = 2 \times \frac{1}{2} m (2\pi A \nu^*)^2$$

$$\text{i.e.,} \quad A^2 = \frac{h}{4\pi^2 m \nu^*}$$

$$\text{and} \quad a^2 = \frac{h}{12\pi^2 m \nu^*}.$$

Substituting the values for h , m and ν^* we obtain,

$$a = 0.0268 \times 10^{-8} \text{ cm.} \quad (3)$$

We will calculate the structure amplitude of the dynamic (111) planes on the assumption that the atoms do not move appreciably in a time interval equal to the period of the X-ray vibration.

The co-ordinates of the vibrating atoms in a unit cell are

$$\begin{aligned}
 & \frac{dx}{u}, \frac{dy}{u}, \frac{dz}{u}; \quad 0 + \frac{dx}{u}, \frac{1}{2} + \frac{dy}{u}, \frac{1}{2} + \frac{dz}{u}; \\
 & \frac{1}{2} + \frac{dx}{u}, 0 + \frac{dy}{u}, \frac{1}{2} + \frac{dz}{u}; \quad \frac{1}{2} + \frac{dx}{u}, \frac{1}{2} + \frac{dy}{u}, 0 + \frac{dz}{u}; \\
 & \text{and} \quad \frac{1}{4} - \frac{dx}{u}, \frac{1}{4} - \frac{dy}{u}, \frac{1}{4} - \frac{dz}{u}; \quad \frac{1}{4} - \frac{dx}{u}, \frac{3}{4} - \frac{dy}{u}, \frac{3}{4} - \frac{dz}{u}; \\
 & \quad \frac{3}{4} - \frac{dx}{u}, \frac{1}{4} - \frac{dy}{u}, \frac{3}{4} - \frac{dz}{u}; \quad \frac{3}{4} - \frac{dx}{u}, \frac{3}{4} - \frac{dy}{u}, \frac{1}{4} - \frac{dz}{u}.
 \end{aligned} \quad (4)$$

Here $u = 3.56 \text{ AU}$ —the side of a unit cell. Substituting these values in equation (1) and putting $h = k = l = 1$, we obtain

$$F_{111} = 4 f_1 \left\{ e^{\frac{6\pi a}{u} i \sin(2\pi\nu^* t - \xi)} - i e^{-\frac{6\pi a}{u} i \sin(2\pi\nu^* t - \xi)} \right\}$$

We have the well-known relation

$$\begin{aligned} e^{i\alpha \sin \beta} = & J_0(\alpha) + 2i J_1(\alpha) \sin \beta + 2 J_2(\alpha) \cos 2\beta \\ & + 2i J_3(\alpha) \sin 3\beta + 2 J_4(\alpha) \cos 4\beta \\ & + \dots \end{aligned}$$

where $J_n(\alpha)$ represents the n th order Bessel function of α .

Let us put

$$\frac{6\pi\alpha}{u} = \alpha$$

and $(2\pi\nu^*t - \xi) = \beta$.

Then we obtain that

$$\begin{aligned} F_{111} = & 4f_1(1-i)[J_0(\alpha) - 2 J_1(\alpha) \sin \beta + 2 J_2(\alpha) \cos 2\beta \\ & - 2 J_3(\alpha) \sin 3\beta + 2 J_4(\alpha) \cos 4\beta \\ & - \dots] \end{aligned}$$

The reflected radiation at a great distance ρ from the unit cell is given by

$$F e^{2\pi i(\nu t - \rho/\lambda)}$$

where ν is the frequency of the X-ray beam and λ its wave-length. Remembering that

$$\sin \beta = \frac{e^{i\beta} - e^{-i\beta}}{2i}, \text{ and } \cos \beta = \frac{e^{i\beta} + e^{-i\beta}}{2}$$

the expression for the secondary radiation becomes

$$\begin{aligned} & 4f_1(1-i) J_0(\alpha) e^{2\pi i(\nu t - \rho/\lambda)} \\ & \pm 4f_1(1+i) J_1(\alpha) e^{2\pi i\{(\nu \pm \nu^*)t - \xi_1\}} \\ & \pm 4f_1(1-i) J_2(\alpha) e^{2\pi i\{(\nu \pm 2\nu^*)t - \xi_2\}} \\ & \pm \dots \end{aligned} \tag{5}$$

This means that the secondary radiation in the direction of the classical reflection consist partly of altered frequencies. Since α is small, terms containing $J_2(\alpha)$ and higher orders may be omitted. On quantum mechanical principles the intensity of the antistokes ($\nu + \nu^*$) will be much smaller than that of the stokes ($\nu - \nu^*$), so that the modified radiation consists practically only of ($\nu - \nu^*$). The ratio of the structure amplitude of this stokes' to that of the unmodified reflection is

$$\frac{J_1(\alpha)}{J_0(\alpha)} = 0.071$$

Thus in the correct Bragg setting of the crystal, these dynamic stratifications also are capable of giving a total reflection of the X-rays with modified frequency. But due to the phenomenon of 'extinction' for the primary beam in the correct setting of the crystal, the actual percentage of the modified reflection can never exceed about 7% of the total reflected intensity. Of course this can happen only when all the Planck oscillators are in phase—a limiting case.

4. The Dynamic Stratifications Associated with the (222) Reflections

Employing the values for the co-ordinates of the atoms given by the expression (4) and substituting $h = k = l = 2$, we obtain

$$F_{222} = 4f' \left\{ e^{i \frac{12\pi a}{u} \sin(\nu^* t - \xi)} - e^{-i \frac{12\pi a}{u} \sin(\nu^* t - \xi)} \right\},$$

where f' is the atomic scattering factor in the required direction.

Let us put,

$$\frac{12\pi a}{u} = a' = 2a$$

and $(2\pi\nu^* t - \xi) = \beta$

so that

$$F_{222} = 8f' i [2J_1(a') \sin \beta + 2J_3(a') \sin 3\beta + \dots]$$

Hence the expression for the secondary radiation is

$$\begin{aligned} & \pm 8f' J_1(a') e^{2\pi i \{(\nu \pm \nu^*) t - \xi_1\}} \\ & \pm 8f' J_3(a') e^{2\pi i \{(\nu \pm 3\nu^*) t - \xi_3\}} \\ & \pm \dots \dots \end{aligned} \quad (6)$$

We find that there can be secondary radiations of only modified frequency. In other words, if the atoms are at rest there can be no Bragg reflection at all. a' being small, Bessel functions of higher orders than the first can be omitted. The intensity of the antistokes ($\nu + \nu^*$) being negligible in comparison with ($\nu - \nu^*$), the (222) reflection will practically consist of X-rays of frequency ($\nu - \nu^*$) and the structure amplitude of the spacings will be

$$8f' J_1(a').$$

Its ratio to the structure amplitude of the static (111) spacings is

$$\frac{2f' J_1(a')}{(1-i)f_1}$$

Taking the Hartee interpolation values for f' and f_1 , the above ratio works out to be nearly 0.14.

It is well known that the (222) reflection in diamond is observed^{4,5} in contradiction with the ordinary theory. It has been suggested⁴ that this may be due to the two neighbouring carbon atoms of diamond being non-centro-symmetric regarding their scattering power. This hypothesis is supported neither by the calculations of L. Pauling⁶ for the charge distribution in the carbon atom nor by the calculations of Hartee⁷ for the scattering power of the atom. The above hypothesis is further contradicted by the non-appearance of the (200) reflection.

For a specimen of diamond behaving as an ideal crystal Ehrenberg, Ewald and Mark⁵ estimate the intensity of the (222) Mo K_α reflection from a rotation picture about the (110) axis to be about a third of the (400) Mo K_β reflection. According to Hull the intensity ratio K_α : K_β for Mo is nearly 2.4. The above authors have found that the (400) reflection is about half as intense as the (111) reflection. Thus in their estimate the (222) reflection is about 0.07 times the (111) reflection.

For a perfect crystal the 'integrated reflection' is proportional to

$$\frac{F(1 + |\cos 2\theta|)}{\sin 2\theta} = F \cot \theta, \quad (\theta < 45^\circ).$$

Hence the ratio of the (222) modified reflection to the (111) unmodified reflection would be

$$0.14 \times \frac{\cot 20^\circ}{\cot 10^\circ} = 0.068$$

for the Mo K_α radiation employed by those authors. This value is in excellent agreement with their observation. We may therefore reasonably infer that the (222) reflection actually observed is entirely a quantum or Raman reflection.

5. The Dynamic Stratifications Associated with the (220) Reflections

If we substitute $h = k = 2$, and $l = 0$ in equation (1) and use the co-ordinates of the atoms of the unit cell as given by the expression (4) we obtain for the structure amplitude of the dynamic (220) planes, the following expression:

$$\begin{aligned} F_{220} &= 8f_2 \cos \left\{ \frac{8\pi a}{u} \sin (2\pi v^* t - \xi) \right\} \\ &= 8f_2 \{ J_0(a_1) + 2J_2(a_1) \cos 2\beta + 2J_4(a_1) \cos 4\beta + \dots \}. \end{aligned}$$

Here

$$a_1 = \frac{8\pi a}{u}$$

$$\beta = (2\pi v^* t - \xi)$$

and f_2 is the corresponding atomic structure factor.

Hence the expression for the secondary radiation is

$$\begin{aligned}
 & 8 f_2 J_0(a_1) e^{2\pi i(\nu t - \rho/\lambda)} \\
 & + 8 f_2 J_2(a_1) e^{2\pi i\{(\nu + 2\nu^*)t - \xi_2\}} \\
 & + 8 f_2 J_4(a_1) e^{2\pi i\{(\nu + 4\nu^*)t - \xi_4\}} \\
 & + \dots \dots \dots \quad (7)
 \end{aligned}$$

As before if we neglect the second and higher order Bessel functions of the small quantity a_1 , we find that the (220) planes cannot give rise to any modified reflection of appreciable intensity. The failure of Dr. Nilakantan to record the (220) modified reflection in spite of a large number of trials is thus explicable.

6. The Dynamic Stratifications Associated with the (200) Reflections

According to the classical theory, the (200) reflection is another of the forbidden reflections in diamond. But the assumption of Planck oscillators excited by the incident X-ray quanta gives the following expression for the reflected radiation from these planes:

$$\begin{aligned}
 & + 8 f_3 J_1(a_2) e^{2\pi i\{(\nu + \nu^*)t - \xi_1\}} \\
 & + 8 f_3 J_3(a_2) e^{2\pi i\{(\nu + 3\nu^*)t - \xi_3\}} \\
 & + \dots \dots \dots \quad (8)
 \end{aligned}$$

Here $a_2 = \frac{4\pi a}{u}$ and f_3 is the atomic scattering factor of the appropriate direction. This indicates a Raman reflection unaccompanied by any Bragg reflection. But the intensity of this modified reflection of frequency $(\nu - \nu^*)$, the others being negligible, can only be a third of the (222) reflection. In a rotation photograph about the (110) axis the number of the co-operating planes for the (200) reflection is only two while for the (222) it is four. Ehrenberg, Ewald and Mark⁵ remark that in a rotation picture about the (110) axis the (222) reflection was just recorded while there was no indication of any (200) reflection. Their observation finds a ready explanation on this idea of lattice oscillations according to which the (200) spot has to be six times weaker than the weak (222) spot.

7. The Dynamic Stratifications Associated with the (662) Reflections

Since $h + k + l \equiv (4n + 2)$ for this case, the (662) reflection is also 'forbidden' by the classical theory. Substituting these values of h , k and l

in (1) and using the co-ordinates given by expression (4), we obtain for the reflected radiation from the (622) planes the expression:

$$\begin{aligned} & \pm 8 f_4 J_1(a_3) e^{2\pi i \{(v \pm v^*) t - \xi\}} \\ & \pm 8 f_4 J_3(a_3) e^{2\pi i \{(v \pm 3v^*) t - \xi_3\}} \\ & \pm \dots \dots \end{aligned} \quad (9)$$

Here

$$a_3 = \frac{28\pi a}{u}$$

and f_4 is the atomic scattering factor in the direction of this reflection.

The expression shows that there is no unmodified or Bragg reflection. Neglecting the 'antistokes' and the second and higher order Bessel functions the ratio of the dynamic structure amplitude of this reflection to that of the (222) reflection is

$$\frac{f_4 J_1(a_3)}{f' J_1(a')}$$

The values of f_4 and f' of the carbon atom for the respective glancing angles of 60° and 10° , when Mo $K\alpha$ radiation is employed, are found from the interpolation values obtained by the Hartee method and given in the "International Tabellen Zur Bestimmung Von Kristalstrukturen". They are 0.8 and 1.8 respectively. Substituting these values and the values of a' and a_3 , the above ratio works out to be nearly 0.9.

Since in a rotation picture the intensities of the spots on the equatorial line are proportional to

$$\frac{1 + |\cos 2\theta|}{\sin 2\theta} = \begin{cases} \cot \theta & \text{when } \theta < 45^\circ \\ \tan \theta & \text{when } \theta > 45^\circ \end{cases}$$

the ratio of the intensity of the (662) to the (222) quantum reflection will be nearly

$$0.9 \frac{\tan 60^\circ}{\cot 20^\circ} = 0.57.$$

Ehrenberg, Ewald and Mark⁵ remark that this 'forbidden' (662) reflection does appear in a rotation photograph and that it is weaker than the 'forbidden' (222) reflection; but they suggest a ratio 0.3. The discrepancy is not large when one remembers that these reflections are extremely weak and that the experimental value of the ratio of their intensities is only an estimate.

8. Other Lattice Oscillations

As mentioned in the Introduction we have here considered the rhombohedral unit cell having only one lattice oscillation which was identified as

that giving the Raman frequency of 1332 cm.⁻¹. The recent work of Nayar^{8,9} on the luminescence and ultra-violet absorption spectra of diamond at low temperatures has revealed that the lattice spectrum of diamond contains a whole series of discrete frequencies ranging down to about 127 cm.⁻¹. Amongst these, 1332 and 780 appear most prominently and are the principal members of the two important groups of frequencies. Until these modes of vibration with lower frequencies are fully investigated and can be dynamically specified, it is not possible to discuss their influence on the dynamic structure amplitudes of the various crystal planes. It may be anticipated, however, that such influence should be relatively unimportant in respect of the lattice planes for which the 1332 oscillation is active. On the other hand, it is quite possible that for those planes for which the 1332 vibration is inactive, e.g., the (220) planes, the lower frequencies may influence the structure amplitudes appreciably and give rise to dynamic reflections. If this were the case, such reflections would necessarily exhibit a more marked temperature dependence of intensity than the planes which are chiefly excited by the 1332 oscillation.

I am very much indebted to Sir C. V. Raman, F.R.S., for his kind and helpful guidance in the course of this work.

9. Summary

On the Raman idea of quantum exchanges of energy and momentum between a crystal lattice and an X-ray photon traversing it, the dynamic structure amplitudes of the various crystal planes of diamond are worked out assuming that each Planck oscillator takes up one quantum of infra-red vibrational energy from the incident X-rays. It is shown that such an interaction gives rise to X-ray reflections of altered frequency in most cases. The structure amplitude of the (111) planes for this modified or Raman reflection is found to be about 7% of that of the same planes for the Bragg reflection. The (222) planes, the (200) planes, and the (662) planes, the Bragg reflections from which are 'forbidden' according to the classical theory, are found to possess finite structure amplitudes for the quantum reflections. The values of these structure amplitudes are shown to quantitatively account for the intensities of the reflections appearing from these planes as recorded by Ehrenberg, Ewald and Mark. It is therefore suggested that the so-called 'forbidden' reflections which appear in diamond are pure Raman or quantum reflections of modified frequency.

REFERENCES

1. C. V. Raman and P. Nilakantan *Proc. Ind. Acad. Sci.*, 1940, **11**, 379.
2. Nagendra Nath, N. S. .. Ph.D. Thesis, Cambridge University (unpublished).
3. Venkatarayudu, T. .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 349.
4. Bragg, W. H. .. *Proc. Phys. Soc. Lond.*, 1921, **33**, 304.
5. Ehrenberg, Ewald and Mark *Zeit. Fur. krist.*, 1928, **66**, 582.
6. Pauling, L. .. *Proc. Roy. Soc. Lond.*, (A), 1927, **114**, 181.
7. Hartee, E. R. .. *Phil. Mag.*, 1923, **46**, 1091; 1925, **50**, 289.
8. Nayar, P. G. N. .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 483.
9. _____ .. In the course of publication.