ON THE NEW DIFFRACTION MAXIMA IN LAUE PHOTOGRAPHS.

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It has recently been reported by Sir C. V. Raman and Dr. P. Nilakantan (1940*a*) that a new type of X-ray reflection with change of wave-length has been observed by them in the Laue patterns of diamond obtained with X-rays from a tube with Cu anticathode, the incident beam being nearly parallel to the threefold axis of symmetry of the crystal. In a subsequent paper (Raman and Nilakantan, 1940*b*) the theory of the phenomenon has been given by them and in two other papers (Raman and Nilakantan, 1940*c*) the results obtained by them in the case of diamond and crystals of sodium nitrate have been discussed in detail. The new X-ray reflections observed by them lie very close to the Laue diffraction maxima due to 111 planes, and the intensity of these spots is found to be dependent on the glancing angle made by the X-rays with these planes. The origin of the new X-ray reflections has been interpreted by them to be due to reflections from dynamic stratifications having a spacing identical with that of the 111 planes, but these stratifications are oriented suitably for Bragg reflection by the influence of incident X-rays on the characteristic vibration of the lattice. These authors, however, have overlooked the fact that such new diffraction maxima were observed previously by many workers (Friedrich, 1913 and others). This has been pointed out by Knaggs *et al* (1940). Recently Zachariasen (1940) has put forward a theory of the origin of these new diffraction maxima observed in the vicinity of the Bragg reflection of monochromatic X-rays, and Siegel and Zachariasen (1940) have obtained preliminary experimental results in support of the theory put forward by Zachariasen. The object of the present paper is to point out certain difficulties in the theory put forward by Raman and Nilakantan regarding the origin of these new diffraction maxima, and also to discuss the difference between the fundamentals of this theory and that put forward by Zachariasen.

According to the qualitative theory given by Raman and Nilakantan, the new X-ray diffraction takes place in the following way:—

When a parallel beam of monochromatic X-rays OP, O′P′ (fig. 1) falls on a set of 111 planes the static direction of which is represented by the line AB, if the glancing angle θ_i does not satisfy the Bragg relation, the phases of motion of the different carbon atoms in the characteristic oscillation of the lattice are adjusted by the interaction of the incident X-rays in such a way that momentarily all the members of a 111 family of planes are turned till the glancing angle becomes θ_B which satisfies the Bragg relation; a part of the incident quantum is absorbed in exciting the characteristic vibration of the lattice and the remaining part is reflected. Thus in this reflection of a new type, the wave-length is slightly changed. The change, however, is too small to be observed with X-ray spectrometers. It has also been pointed out that this new theory differs from Brillouin's theory in this respect that according to the latter theory of light scattering by elastic waves due to thermal agitation the waves are actually present in the medium and it is possible to pick up for any direction of incidence a Fourier component of the elastic waves having wave-length satisfying the Bragg relation for the incident radiation, but the characteristic vibration of diamond responsible for the new X-ray diffraction has such a large frequency that such a vibration is not excited by thermal agitation and it is excited only when light waves or X-rays are incident on the crystal.

There are, however, a few fundamental difficulties about such a hypothesis regarding the origin of the observed new reflections. First, when a plane wave is incident on the 111 planes as shown in fig. 1, the disturbance reaches P′ earlier than P, and if it is assumed that the difference of phase at the two points causes a rotation of the planes, the direction of rotation should be such that the 111 plane AB should go to the position AC and the corresponding 111 plane A′B′ of the other interpenetrating lattice should come to the position A′C′ shown in the figure. In such a picture it has been assumed that the vibration of the lattice of frequency 1332 cm.$^{-1}$ which is actually a linear vibration of the two lattices against each other is excited by the incident X-rays earlier at P than at P′. If now θ_i is less than θ^B, the glancing angle for Bragg reflection of CuKα, the orientation AC may give the glancing angle equal to θ_B and so the CuKα may be reflected with the modified frequency. θ_i is actually larger than θ_B for CuKβ and so the orientation A′C′ for the 111 planes of the other lattice may produce the suitable glancing angle for Bragg reflection of CuKβ. If such a picture be assumed to be correct, one has to further assume that the displacement of an atom at P is of the order of at least one-fifteenth of a millimetre, because the new reflection is observed to take place from a surface of the crystal of dimensions more than a millimetre on each side and in a direction which corresponds to a rotation of the 111 planes from the static position by about 4°. It is difficult to believe that such a large displacement of the atom (of the order of ·06 mm.) can actually take place in the oscillation of the lattice mentioned above. In fact, investigations of the intensities of X-ray reflections from atomic planes in crystals show that the displacement of the atoms owing to thermal vibration is of the order of a small fraction of the radius of the atom. So the displacements due to lattice vibrations are expected to be less than 1×10^{-8} cm. But a displacement of the atoms postulated in the theory of the new X-ray diffraction of modified frequency is at least 10^4 times larger than this value.

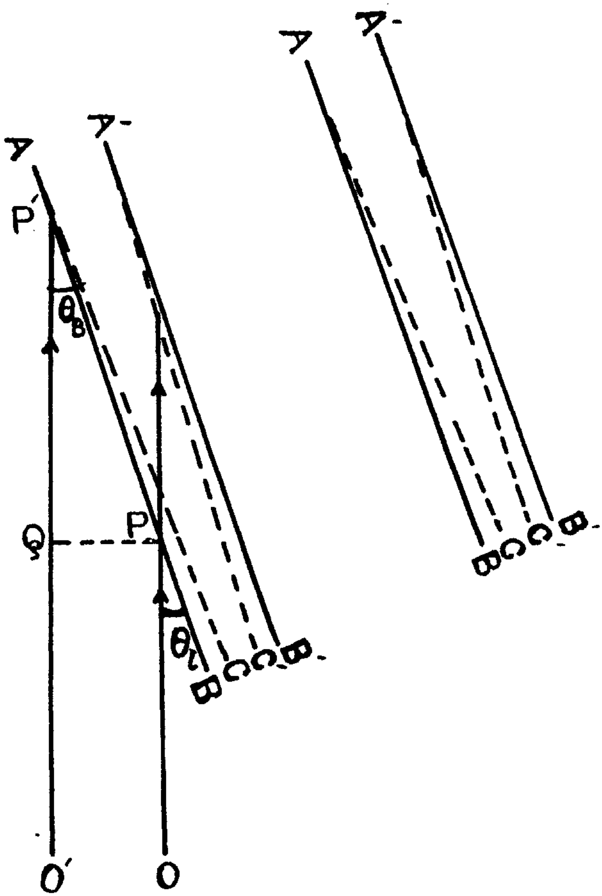

FIG. 1.

We can also calculate the ratio of the mean velocity u of the atom to that of the X-rays from the picture of the new type of X-ray reflection given above. The maximum displacement of the atom at P takes place in the time in which X-rays travel from Q to P′. If the length PA be taken to be equal to a millimetre and the displacement of the atom at P perpendicular to the plane be assumed to be about ·05 mm. the ratio of the velocity $u/c = \cdot 05$. Such a high velocity of the atoms in the crystal seems to be highly improbable.

The above arguments hold good even if we assume that only a small volume of the lattice oscillates at a time and the observed reflection is a statistical effect of reflections from different portions of the lattice at different times. For any appreciable intensity of the sharp Bragg reflection, the smallest dimensions of the volume contributing to the reflection should be of the order of at least about 25 A.U. (i.e., about 10 grating spaces) on each side and in that case the displacement of the atom corresponding to a rotation of

$4°$ is about 1·7 A.U., which again is too large to actually take place in the crystal.

Secondly, if the angular displacement of the 111 planes would take place as postulated by Raman and Nilakantan owing to the interaction of the incident X-rays, the amplitude of displacement would have a certain definite value, and the intensity of reflection by these oscillatory planes would not depend on the magnitude of the variation of the glancing angle from the Bragg angle for the reflection of the monochromatic radiation. But actually, the intensity of the new spots is found to diminish rapidly with increase in the variation mentioned above.

Thirdly, if the new spots are due to Bragg reflection from the dynamic stratifications as suggested by Raman and Nilakantan, it is difficult to understand why the Bragg relation does not hold accurately when the spacings of the 111 planes are taken for calculation. In fact, assuming that the Bragg relation holds good for the mean position of the planes corresponding to the initial glancing angle and the angle of scattering, the spacings have been calculated for different values of glancing angles and different values of the spacings have been obtained. The reason for this discrepancy is not explained in the theory put forward by Raman and Nilakantan.

It has already been mentioned, however, that the appearance of the new maxima in the X-ray diffraction pattern has been observed by various workers, and Zachariasen has recently put forward a theory to explain the phenomenon. He has shown that the expression for the intensity of radiation scattered by a simple lattice containing one kind of atoms as modified by thermal vibrations of the crystal contains two terms, the first one giving the Laue diffraction maxima, and the second one the diffuse scattering as given below:—

$$J = J_1 + J_2,$$

where $J_1 = J_0 \,.\, e^{-2M}$ as given by Debye; but J_2 differs from the second term in Debye's expression, and has a maximum in a particular direction.

$$J_2 = I_0 \left(\frac{e^2}{mc^2 R}\right)^2 \frac{1+\cos^2 2\theta}{2} f^2 e^{-2M} N \frac{4 \sin^2 \theta}{\lambda^2 m_a v^2} \times \frac{2\pi (NV)^{\frac{2}{3}} Q(\tau_0)}{1+2\pi (NV)^{\frac{2}{3}} \tau_0{}^2}, \quad \ldots (1)$$

where v is the mean velocity of propagation of the elastic waves, θ is the glancing angle of scattering, V is the volume of the unit cell,

$$Q_j = \frac{h\nu_j}{e^{h\nu_j/kT} - 1} + \tfrac{1}{2} h\nu_j,$$

and $\nu_j = \tau v_j$; $\therefore \tau_j = \nu_j / v_j$;

τ_0 is the propagation vector given by the relation

$$\vec{K} - \vec{K_0} + \vec{\tau_0} = H_1 \vec{b_1} + H_2 \vec{b_2} + H_3 \vec{b_3},$$

where $\vec{K_0}$ and $\vec{K}$ are vectors in the directions of the incident and diffracted rays respectively such that $K_0 = K = \frac{1}{\lambda}$; $\vec{b_1}, \vec{b_2}, \vec{b_3}$ are vectors representing the inverses of the edges of the cell, and H_1, H_2, H_3 are integers. J_2 changes rapidly with the scattering angle and has maximum value when τ_0 assumes minimum values. The direction of maximum intensity lies in the plane of incidence but the glancing angle of scattering is in general not equal to the glancing angle of incidence. When $\theta_i - \theta_B = \Delta$, where θ_i is the actual glancing angle and θ_B is that for Bragg reflection, θ_m corresponding to the maximum in diffuse scattering is given by

$$2\theta_m \doteqdot 2\theta_B + 2\Delta \sin^2 \theta_B \qquad \ldots \quad \ldots \quad \ldots \quad (2)$$

This expression shows that θ_m is larger than θ_B if Δ is positive and *vice versa.* This has been verified by Siegel and Zachariasen in the case of scattering of CuKα radiation by rock salt, and there is quantitative agreement between the observed values of θ_m and that calculated according to (2). The values of θ_m observed in the case of diamond by Raman and Nilakantan as shown in Table I, reproduced from their paper, agree almost quantitatively

TABLE I.

Maxima in diffuse scattering of Cu radiation from 111 *planes of diamond.*

Glancing angle.		$2\theta_B$	$\theta_i - \theta_B = \Delta$	$2\theta_m$	$2\theta_B + 2\Delta \sin^2 \theta_B$
Incidence θ_i	Reflection ϕ				
17° 11′	24° 33′ (Kα)	43° 56′	−(4° 47′)	41° 44′	42° 36′
18° 41′	23° 50′ ,,	,,	−(3° 17′)	42° 31′	43° 1′
20° 49′	22° 43′ ,,	,,	−(1° 9′)	43° 32′	43° 37′
21° 4′	19° 6′ (Kβ)	39° 30′	+(1° 19′)	40° 10′	40° 58′

with those calculated according to (2); also there is qualitative agreement in this respect that $\theta_m > \theta_B$ when Δ is positive and *vice versa.* Again, according to Zachariasen's theory the intensity of the maxima in diffuse scattering diminishes rapidly with increase in the value of Δ and increases with the increase in the temperature of the crystal. These effects have actually been observed in the case of diamond by Raman and Nilakantan.

Thus it is evident that the theory given by Zachariasen can explain the nature of the new diffraction maxima more satisfactorily than that put forward by Raman and Nilakantan. The fundamental difference between the two theories is that the diffuse scattering is due to Debye heat waves which are present in the crystal owing to thermal agitation, while according to the latter theory the lattice vibration responsible for the new reflection is excited by the X-rays, and does not exist at ordinary temperatures. The increase in the intensity of the new diffraction maxima with increase of temperature of diamond observed by the said authors probably supports Zachariasen's theory and contradicts the theory put forward by them.

As regards the explanation of the oblique streamers which, as mentioned by Raman and Nilakantan, radiate towards or away from the two Laue spots due to 111 spacings, those authors assume that the streamers arise from the interaction of the vibration of the other two sets of 111 planes on that of one set of these planes, and that they are originated by the modified monochromatic radiation. The present authors obtained some Laue photographs of diamond, two of which are reproduced in figs. 2 and 3. X-rays were nearly normal to the cleavage plane, i.e. almost parallel to the threefold axis of symmetry. The photograph shown in fig. 2 was obtained with X-rays

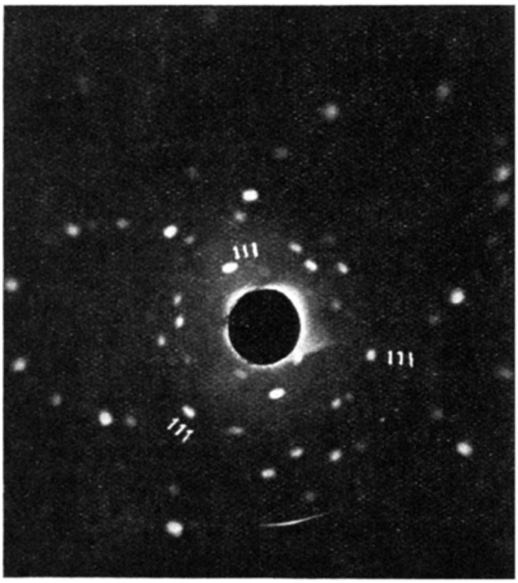

FIG. 2.

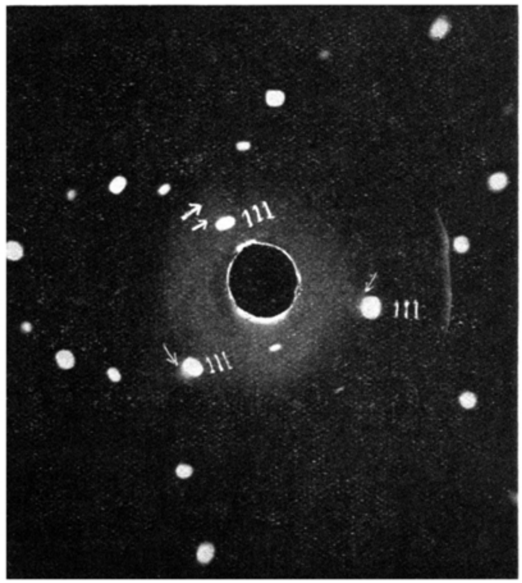

FIG. 3.

Laue photographs of diamond.

Fig. 2, due to white radiation from W target.
Fig. 3, ,, ,, radiation from Cu ,,
The spots marked with arrows in fig. 3 are due to new diffraction maxima.

from a Coolidge tube having tungsten anticathode and operated at 40 K.V. The other photograph was obtained for exactly the same orientation of the crystal but with radiation from a copper anticathode of a Hadding tube operated at about 30 K.V. The new diffraction maxima due to CuKβ lie close to the Laue spots due to 111 planes produced by the white radiation and are quite intense but those due to CuKα are the weaker, the further away they are from the Laue spots. These photographs show the reflections from the planes of the three zones $1kl$, hll, and hkl, the three 111 reflections being situated at the intersections of the three loops representing the three zones mentioned above. It will be seen by comparing these photographs with those reproduced by Raman and Nilakantan that the directions of the streamers are along the loops starting from the Laue spots due to 111 planes. It is, therefore, evident that the planes of reflections producing these streamers are also the planes of incidences on some planes of the crystal which might be imagined to belong to these zones but whose indices are very complicated. For a simple lattice the presence of such planes could not be imagined but as diamond consists of two interpenetrating lattices and the 111 planes of the two lattices are very close to each other, being separated from each other by one-fourth the spacing of these planes, some planes slightly inclined to the 111 planes may have some appreciable reflecting power. If suitable wave-lengths are used to get the new diffraction maxima from 100 planes, these streamers are expected to disappear.

Also the streamers extend up to such large angles from the directions of the static positions of the 111 planes that it is highly improbable that the influence of angular oscillations will extend up to such a large angle.

The arguments set forth above show that the new X-ray diffraction maxima observed in the case of diamond cannot be explained satisfactorily by the theory put forward by Raman and Nilakantan and on the other hand some of the observed facts definitely contradict the hypothesis put forward by them. The results obtained by them in the case of diamond seem to support the theory of diffuse scattering due to thermal vibration put forward by Zachariasen. The crystals of sodium nitrate contain a large number of interpenetrating lattices and so the interpretation of the results is difficult and is not attempted here.

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Summary.

The qualitative theory put forward by Raman and Nilakantan regarding the new diffraction maxima observed in the Laue photographs of diamond has been examined and it has been shown that there are some difficulties in the assumptions made by the said authors. It has been pointed out that the observed facts contradict the theory put forward by them while the theory of diffuse scattering due to thermal vibrations of the lattices put forward previously by Zachariasen can explain satisfactorily all the facts observed by Raman and Nilakantan in the case of diamond. The angles made by the directions of maxima in the diffuse scattering with the 111 planes for different angles of incidence agree closely with those calculated from Zachariasen's theory. The streamers radiating from the positions of the Laue spots due to 111 planes of diamond observed by Raman and Nilakantan are shown to be

due to reflections in the planes of incidence of certain complicated planes in the zones $1kl$, $h1l$ and $hk1$.

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