

THE DYNAMIC X-RAY REFLECTIONS IN CARBON SILICIDE

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1. INTRODUCTION

THOUGH it has been known for a long time that well-exposed Laue photographs show additional streaks or spots which are not explicable as regular reflections from the crystal planes, the theoretical significance of the phenomenon was first clearly elucidated in the publications of Sir C. V. Raman on the subject in *Current Science* (1940), and *Proceedings of the Indian Academy of Sciences* (1940, 1941). The analysis of the experimental facts observed with diamond (Raman and Nilakantan, 1940-41) revealed three important features of the phenomenon, namely, (1) that it is intimately connected with the dynamics of the crystal, (2) that it is accompanied by a change of frequency, and (3) that it is essentially in the nature of reflections of X-rays by dynamic stratifications in the medium. Further studies of the subject showed that the frequencies of vibration operative in the production of the additional reflections are those of the monochromatic eigenvibrations of the crystal structure excited by the incident X-rays. Besides such reflections, the theoretical treatment also predicts diffuse maxima due to the scattering by the elastic vibrations of the crystal having the largest amplitude. An intensive study of the problem which was stimulated by these publications has led to a clarification of the fundamental ideas regarding the physical nature of these reflections and the vibration spectrum of the crystal lattice.

While it has been conceded by all theorists and experimenters working in the field that the three basic ideas outlined by Raman are essentially valid, there exists some difference of opinion regarding the frequency (or wavelength) region, which is responsible for the observed X-ray effects. According to Born (1941) and his school, the effective wavelengths giving rise to the spot are only the longest in the elastic vibrational spectrum of the crystal. This conclusion is a direct consequence of the hypothesis of Debye, and Born and Karman that the vibrations of a crystal lattice are *non-degenerate* (or single) and distributed over a wide range of frequency. Following Ott

(1935), Born (1942) has also shown that the effect of the type visualised by Raman's theory is theoretically possible, but he *believes* that the intensity of such modified Raman reflections will be extremely small, as the probability of such transitions taking place is not great.

The defect in the argument of Born consists in his assumption that the vibrations in the higher part of the frequency range—the so-called optical series—are non-degenerate in the same manner as the elastic vibrations. By his analysis of the problem which is supported by the experimental spectroscopic facts, Sir C. V. Raman (1943, 1947) has shown that the units of the vibration pattern in crystals are supercells having twice the linear dimensions and therefore eight times the volume of the static units of the crystal structure. The vibrations of the supercell are closely analogous to those of a poly-atomic molecule with the appropriate symmetries, but with this important difference that the atoms in the unit cell are not isolated from the rest of the crystal. There are $(24p-3)$ eigen-vibrations for such a super-cell, where p is the number of atoms in the unit cell. Each of the eigen-vibrations of the super-cell is truly monochromatic and N -fold degenerate, if N is the number of the supercells contained in the crystal. This degeneracy is further increased by virtue of the symmetry of the crystal and is a maximum for cubic crystals. Born's assumption that the lattice vibrations of high frequency are non-degenerate is thus physically untenable, and his objection against the modified X-ray reflections caused by them being sufficiently intense for observation has therefore no theoretical justification. On the other hand, on account of the very high degeneracy of these vibrations one should expect the Raman X-ray reflections caused by them to appear with appreciable intensity. In the above description, a small residue of three degrees of freedom of translation for every supercell appears on ultimate analysis as elastic vibrations having a frequency distribution of the type envisaged by Debye. These elastic waves could be treated as thermal waves which come under the treatment of Faxen (1923) and Waller (1923). The refinement of the latter's theory by Born and Sarginson (1941) leads to a modified expression for the intensity of thermal scattering, and its distribution in terms of the elastic constants of the crystal.

The Raman X-ray reflections are characterised principally by their sharpness and a temperature effect on intensity depending on the eigen-frequency of the lattice vibration but not on the angle of mis-setting of the crystal. The thermal scattering, on the other hand, is characterised by a weak diffuse maximum and a temperature effect whose magnitude depends on the characteristic temperature and on the difference between the glancing angle and the correct Bragg angle of the crystal. In the vast majority of

crystals studied, e.g., rock-salt, sylvine, metals, organic crystals, etc., the modified X-ray reflections due to eigen-vibrations and elastic vibrations are superposed, and it is not easy to differentiate them by their experimentally observed features. In the case of diamond, however, the thermal scattering is so weak and the Raman reflections are so pronounced that a study of this crystal has enabled Raman and Nilakantan (1940) to prove all the characteristics of the phenomenon uniquely. Born (1942) and Lonsdale (1942), however, have attempted to explain the specific results of diamond on the plea that "it is not a normal crystal" or "that a strain which is cubic in symmetry is inherent in the majority of diamonds". In an article in *Nature*, Sir C. V. Raman (1942) has shown that such hypotheses are devoid of justification.

In the present investigation the author has studied the dynamic X-ray reflections by carbon silicide (carborundum) which has a structure similar to that of diamond and the results are discussed in relation to the current theories of the phenomenon.

2. CRYSTAL STRUCTURE AND LATTICE SPECTRUM OF CARBORUNDUM

The crystal structure of carborundum has been extensively studied by Ott (1925, 1926). He has discovered four different types, three of which are hexagonal and one is cubic. Sommerfeld (1928) has given a fifth one which is also hexagonal. In the present investigation the author has made use of a thin plate of a natural crystal which is bluish-green in transmitted light. The Laue pattern taken with X-rays normal to the plate shows that it belongs to type II, hexagonal (Fig. 1 *a*). The Bravais elementary cell of this type contains six molecules of SiC. Atoms of one kind are bound to those of the other tetrahedrally. The smallest Si-C distance is 1.9 A.U. and those of the other tetrahedrally. The smallest Si-C distance is 1.9 A.U. and the binding between the atoms is non-polar. The axial lengths of the unit cell are $a = 3.095$, $b = 5.38$ and $c = 15.17$ A.U., where c -axis is perpendicular to the cleavage plane. The structure thus bears a close resemblance to the diamond lattice. According to Schaefer and Thomas (1923) this type of carborundum shows only one strong sharp infra-red-reflection at 12μ (830 cm.^{-1}). This obviously corresponds to an oscillation of silicon against carbon atoms.

3. SPECULAR CHARACTER OF THE DYNAMIC REFLECTIONS

The X-ray generator used in the present investigation was a demountable Coolidge tube with a Mo-anticathode and operated at 45 kilo-volts and a fairly steady milliampereage of 20 m.A. The crystal was mounted with its

(0001) plane vertical. A narrow beam of X-rays limited by a system of lead slits is let fall on the crystal normally to this plane. The film was placed at a distance of 43.5 mm. from the crystal. Figs. 1 *a* and *b* in the accompanying plate illustrate the Laue pattern obtained after an exposure of one hour; Fig. 1 *a* was taken with a wide circular beam and Fig. 1 *b* with a fine slit. It will be seen that all the six spots arising by reflection from $\overline{(2021)}$ planes are accompanied by sharp circular modified spots. The extreme sharpness of the latter may be seen from Fig. 1 *b*. As the white radiation in the source was pronounced, the radial streaks are fairly prominent. Much more satisfactory photographs are obtained using a narrow linear slit. Figs. 2 *a-g* are taken with a linear slit for various settings of the crystal.

The outstanding feature in all these photographs is that the dynamic reflection is as sharp as the Laue reflection itself for a range of 4° on either side of the Bragg setting. The intensity of the spot falls off rapidly as the crystal is turned away and almost completely disappears for an angle of 2½° from the latter position. Unlike diamond, however, the modified spot remains more or less in a stationary position for the whole range. Table I gives the measurements of the angular distances of the Laue (θ_i) and the Raman reflections (θ_m) and the lattice spacing *d* of $\overline{(2021)}$ planes calculated according to Raman-Nath (1940) formula both for k_α and k_β radiations of the source. It will be seen that the spacing has nearly a constant value for both the rays and agrees well with the theoretical data.

TABLE I
Carborundum

$\overline{2021}$ reflections $d = 2.68 \text{ \AA}$
 $M_0 k_\alpha = 0.708 \text{ \AA}; k_\beta = 0.620 \text{ \AA}$

$2\theta_i$	$2\theta_m$		<i>d</i> in Å	
	k_α	k_β	k_α	k_β
19° 33'	15° 10'	13° 7'	2.68	2.72
17° 38'	15° 25'	13° 24'	2.64	2.66
16° 24'	15° 10'	13° 7'	2.68	2.72
15° 10'	15° 10'	13° 7'	2.68	2.72
11° 36'	15° 25'	13° 24'	2.64	2.66
8° 30'	15° 10'	13° 7'	2.68	2.72
7°	15° 10'	13° 7'	2.68	2.72
				Mean <i>d</i> = 2.69 Å

Another interesting feature of the circular spots (Fig. 1 *a*) which is worth mentioning is the fact that the intensity distribution is *annular with a minimum at its centre*. In order to see whether this is the result of each of the spots being a composite of six others situated hexagonally, the experiment was repeated with a fine aperture lead slit (Fig. 1 *b*); but it was not possible to resolve them any further. In the case of linear slits, however, it was observed that each modified line is accompanied on either side by faint close companions (see Fig. 2). It is possible that each of the spots has a fine structure due to the co-existence of six 'phase waves' similar to three waves in diamond (Pisharoti, 1941).

4. INFLUENCE OF HIGH AND LOW TEMPERATURES

While the geometric character of the modified spot and the rapid fall of intensity with the rotation of the crystal indicate that we are dealing with a modified reflection, investigations of the relative intensities of these reflections at temperatures varying from -180°C . to 600°C . have yielded decisive results in favour of the Raman's theory. For low temperature work, the technique of high vacuum low-temperature X-ray spectroscopy described in a previous paper (Venkateswaran, 1941) was employed. A linear slit was made use of, instead of a circular one and the relative intensities were determined by varying the time of exposure at the room temperature till its intensity is equal to that at the low or high temperature as judged visually. For high temperatures, the crystal was mounted in a copper block which is heated by a heating coil. The temperature of the crystal was determined by means of a calibrated thermocouple. The crystal was set at different angles and the intensities at various temperatures compared for each setting with that at the room temperature. The results of measurements are given in Tables II and III. Typical photographs taken at 600°C ., 300°C ., room temperature 30°C . and the liquid-air temperature -180°C . for the same time of exposure are given in Figs. 3 and 4 (Plate).

TABLE II

Low Temperatures

$2\theta_i$	$2\theta_m$	2ϵ	λ in A.U.	$I_{30^{\circ}}/I_{-180^{\circ}}$
$11^{\circ} 15'$	$15^{\circ} 10'$	$3^{\circ} 55'$	89	1
$11^{\circ} 54'$	"	$3^{\circ} 16'$	94	1
$15^{\circ} 48'$	"	$0^{\circ} 38'$	512	1.1
$16^{\circ} 29'$	"	$1^{\circ} 19'$	307	1.05
$16^{\circ} 48'$	"	$1^{\circ} 38'$	192	1.05
$17^{\circ} 48'$	"	$2^{\circ} 38'$	118	1
$19^{\circ} 5'$	"	$3^{\circ} 55'$	89	1

TABLE III
High Temperatures

$2\theta_i$	$2\theta_m$	2ϵ	λ in A.U.	$\frac{I_{20}}{I_{100}}$	$\frac{I_{30}}{I_{600}}$
17° 18'	15° 20'	1° 58'	154	1	1.1
17° 46'	15° 10'	2° 36'	118	1.2	1.2
20° 19'	15° 25'	4° 54'	63	1.2	1.4

According to Raman's formula, the intensity of dynamic reflection is proportional to $\frac{e^{h\nu^*/k\nu T} + 1}{e^{h\nu^*/kT} - 1}$, where ν^* is the frequency of the lattice vibration and T is the absolute temperature. If we assume that $\nu^* = 830 \text{ cm.}^{-1}$ given by the infra-red absorption for carborundum (*loc. cit.*), there should not be any pronounced variation of the intensity of the spot for the range of temperature used. The relative intensity between the different temperatures should also be independent of the angular distance ϵ between the Laue spot and the appropriate Bragg position θ_m . These predictions of the theory are fully supported by the experimental facts. It should, however, be mentioned that due to the diminution of the lattice spacing at low temperatures there is a slight increase in the intensity of the spot compared with that at the room temperature. A similar error prevents an accurate estimate of the intensities at the higher temperatures as well.

If on the other hand, we treat the spot as a diffuse scattering of X-rays by the solid elastic waves, according to Born (1942) the maximum intensity at the Bragg position is proportional to $T e^{-T/T_0}$, where

$$T_0 = \frac{mk\theta^2}{3h^2} \cdot \frac{a^2}{h_1^2 + h_2^2 + h_3^2}$$

(T, absolute temperature, m , atomic mass in grams, a , lattice constant in cm., θ , Debye temperature, k , and h , Boltzman and Planck constants, h_1 , h_2 and h_3 are the Miller indices of the nearest Bragg reflection.) The characteristic temperature θ for SiC is estimated roughly from the specific heat data and is about 1750. This gives for the (20 $\bar{2}$ 1) plane a value for $T_0 \approx 10^5$. Hence for the temperatures used, the intensity of the diffuse scattering at the Bragg position is nearly proportional to the absolute temperature T. The wavelength λ of the elastic wave effective at each setting of the crystal is calculated according to the approximate relation $\lambda = \frac{d}{\sin \epsilon}$ and given in column 4 of Tables II and III. The thermal theory of diffuse

scattering thus leads us to expect that the intensity at the liquid-air temperature should be one-third and those at 300° C. and 600° C. to be respectively twice and thrice at the room temperature. These relative intensities should also show a dependence on the wavelength of the wave corresponding to the angle of setting of the crystal. Both these conclusions drawn from Born's theory are not supported by the results of the present investigation.

5. CONCLUSION

The main results of the present investigation of the non-Laue spots in the diffraction of X-rays by carborundum may be stated as follows:

1. The modified spots show a hexagonal pattern similar to the Laue spots and are closely related to the internal structure of the crystal.
2. They are sharp for an angular range of nearly 4° on either side of the correct Bragg setting.
3. They are fairly intense near the Bragg position; but the intensity falls off rapidly as the crystal is rotated away from this position.
4. The spots obtained with a circular beam of X-rays have an annular distribution of intensity.
5. The intensity of the modified spot is nearly independent of temperature for all orientations of the crystal.

These results for carborundum are exact parallels to those for diamond. As has been remarked by Sir C. V. Raman (1948) in a recent note in *Nature*, the very fact that the modified spots have a regular geometric pattern bearing an observable relationship to the structure of the crystal is itself a sufficient indication of the connection between them and the eigen-vibrations of the super-cell. The characteristics of the spots enumerated above follow as a necessary consequence of such an origin for these spots.

The above experimental work was carried out in the Physics Laboratory of the Indian Institute of Science, Bangalore, and I desire to place on record my heartfelt gratitude to Sir C. V. Raman for his kind suggestions and inspiring interest in the work.

SUMMARY

Raman's theory of dynamical X-ray reflections and the thermal theory of diffuse X-ray scattering are critically reviewed. An investigation of the extra-spots in X-ray diffraction by the {2021} planes of a hexagonal type of carborundum crystal shows that the spots are sharp and their intensity is nearly independent of temperature for a wide range from - 180° C. to 600° C. and for different orientations of the crystal. It has been shown that they

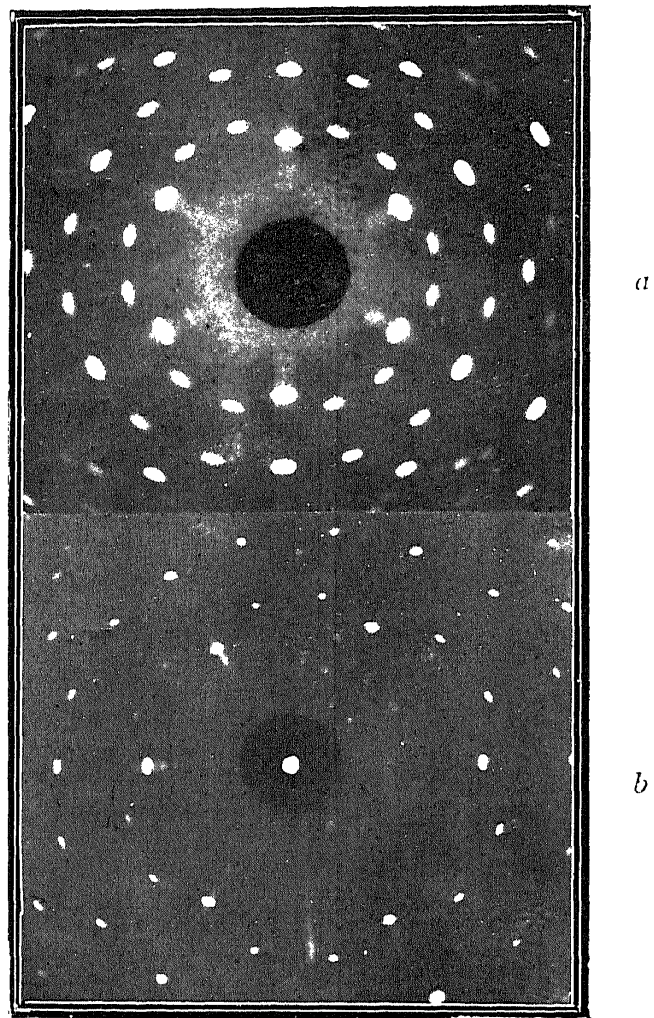


FIG. 1. Carborundum—Laue Photographs
(a) Broad Slit. (b) Fine Slit

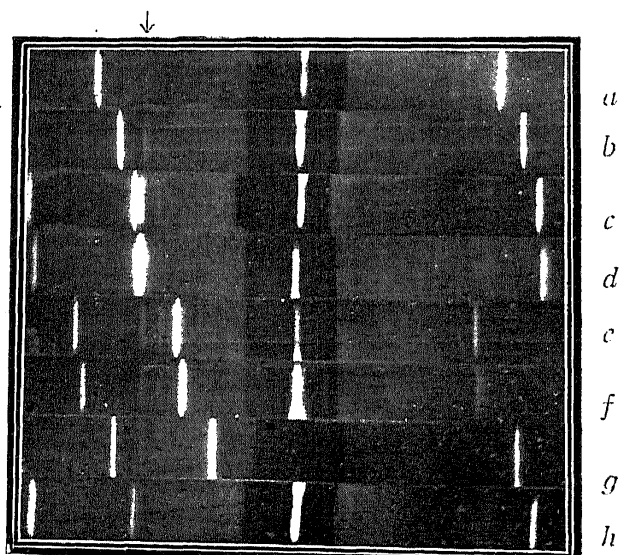


FIG. 2. Carborundum—Orientation Studies

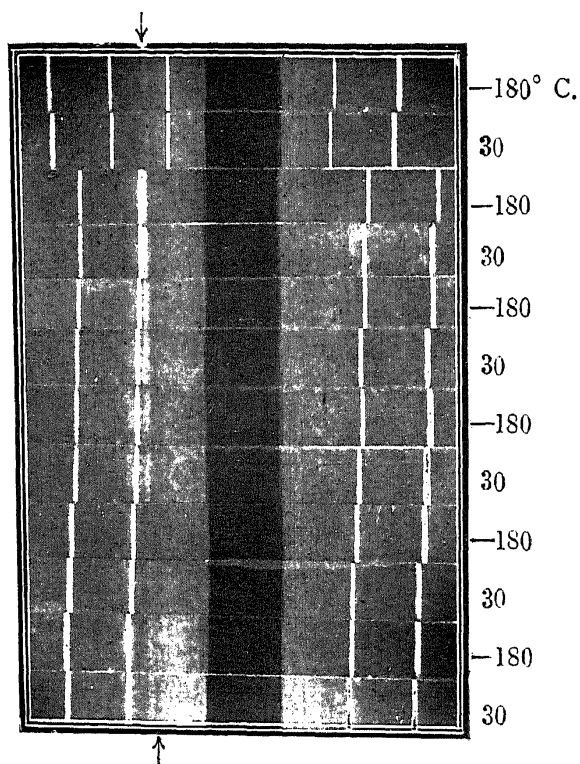


FIG. 3. Carborundum. Low Temperature Studies

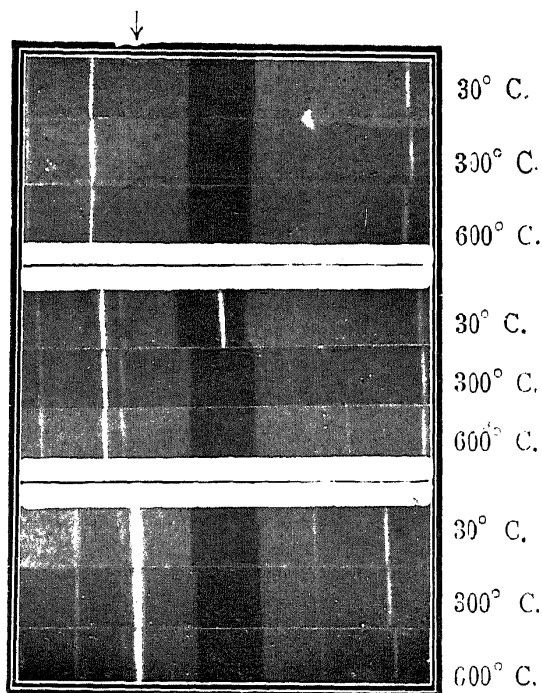


FIG. 4. Carborundum. High Temperature Studies

can be explained as due to the coherent modified reflections of X-rays by the eigen-vibrations of the crystal lattice having a frequency of 830 cm.^{-1} which is observed in the infra-red absorption as well and that the diffuse thermal scattering due to the long elastic waves is not responsible for their appearance.

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