

THE ANGULAR DIVERGENCE OF THE X-RAY REFLECTIONS BY DIAMOND

BY G. N. RAMACHANDRAN

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

Received September 6, 1944

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

1. Introduction

It is a fairly well-known fact that the geometric character of the X-ray reflections given by diamond varies from crystal to crystal. Mark (1925) found that, with the best specimens, the crystal reflection is so perfect that the $\text{MoK}\alpha_1$ and $\text{K}\alpha_2$ radiations can be photographed beautifully at a distance of 10 metres. On the other hand, certain other specimens were so bad that the X-ray lines were not resolved at all. Ehrenberg, Ewald and Mark (1928) found by means of the double spectrometer that some specimens give extraordinarily precise reflections, while others were far inferior in this respect. However, these workers made no attempt to correlate the X-ray effects with the other properties of diamond. Recently, Lonsdale (1942) found that diamonds of the ultra-violet transparent type give much more intense X-ray reflections than those which are opaque to the ultra-violet, indicating a greater mosaicity in the structure of the former. Krishnan (1944) and Hariharan (1944) have studied this aspect more thoroughly, and have found that, among the opaque diamonds, which fluoresce blue, the intensity of X-ray reflection steadily increases with the intensity of fluorescence, a result which becomes intelligible on the idea (Raman, 1944) that diamonds of the ultra-violet opaque variety consist of the positive and the negative tetrahedral structures interpenetrating each other, and that the intensity of fluorescence is greater the more intimately the two structures are intermixed.

In the present paper, an investigation of the angular divergence of the X-ray reflection given by different diamonds is reported. The method consists in obtaining the reflection of the $\text{MoK}\alpha_1$ and $\text{K}\alpha_2$ radiations from the surface (111) planes of a stationary crystal, using a fine slit, and measuring the widths of the lines registered on a photographic film kept at a large distance from the crystal. Allowing for the lack of monochromatism of the incident X-ray, and the consequent divergence arising from this cause, it is possible to calculate the actual divergence of a monochromatic reflection

given by the crystal. It is clearly found that, in blue-fluorescent diamonds which are fairly free from birefringence, the divergence is greater, the larger is the intensity of fluorescence.

2. *Experimental Arrangement*

The apparatus employed was very simple, being similar to that used by the author (1944) in his investigation of the X-ray topographs of diamond. A fine lead slit, about 0.07 mm. in width and 1 mm. in height, placed in front of the window of a molybdenum target X-ray tube, was the source of X-rays. At a distance of 6.5 cm. from the slit was placed a two-circle goniometer, on which the crystal was to be mounted. The goniometer was so adjusted that its vertical axis was accurately parallel to the height of the slit. The crystal of diamond, in the form of an octahedral cleavage plate, was mounted on the goniometer such that its surface (111) planes were exactly in the vertical plane, and were parallel to the vertical axis of rotation of the goniometer. By trial, the crystal was set so that the characteristic $\text{MoK}\alpha$ line appeared in the distorted 111 X-ray topograph given by the crystal on a film kept normal to the incident beam at a distance of about 3 cm. from the crystal. Then the film was moved away to a distance of 40 cm. from the crystal, and was kept normal to the reflected beam. The $\text{MoK}\alpha_1$ and $\text{K}\alpha_2$ lines were then obtained clearly resolved. A series of pictures were taken with suitable exposures with the film at distances of 20, 40, 60, 80 and 120 cm. from the crystal, for reasons to be explained in a later section. The exposures were adjusted so that the image obtained on the film was just clearly visible, so as to avoid any spreading of the image. No intensifying screen was used, and the development was always carried out in developers made from the same stock solution, and for a standard time of $1\frac{1}{2}$ minutes. In this way, the reflections were recorded with four blue-fluorescent diamonds, exhibiting varying intensities of blue fluorescence, which were carefully chosen from Prof. Sir C. V. Raman's collection.

It may be remarked here that the method employed in the present experiment is similar to that used by Mark (*loc. cit.*), and by Valasek (1930) in his investigation on the fine-structure of X-ray lines. Mark used a pinhole as the source. The advantage of using a fine slit is that the width of the slit can be reduced without appreciable loss in intensity, for the height can be increased. Of course, there is an upper limit to the height on account of the fact that it has a detrimental effect on the sharpness of the line on the film. Under the conditions of the present experiment, however, it can easily be shown that the broadening so produced is negligible, being only of the order of 0.001 mm. at a distance of 50 cm. and less at larger distances.

3. Theory of the Experiment

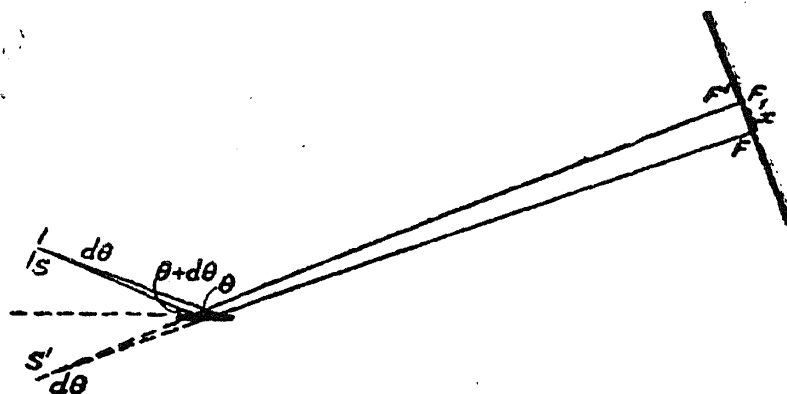


FIG. 1. X-Ray Reflection from a Stationary Crystal

Fig. 1 represents a horizontal cross-section of the experimental arrangement. S is the slit, which is the source of X-rays, and FF' is the photographic film, placed normal to the reflected beam at a large distance from the crystal. Suppose that the crystal were such that it gives a reflection only at the precise Bragg angle (θ say), and further assume that the X-rays are strictly monochromatic. It is then obvious from Fig. 1 that, if the crystal were oriented properly, then the width of the reflected line obtained on the film at F would be equal to the width of the slit, and would be independent of the distance of the film from the crystal.

Actually, neither of the above two conditions is satisfied. The Bragg reflection for a monochromatic beam takes place over a finite range of angles, and besides, the X-ray line (the $MoK\alpha_1$ or $K\alpha_2$ say) covers a small range of wave-lengths. The effect of both of these is to produce a divergence of the reflected beam, and as will be obvious from Fig. 1, if $d\theta$ is the range of angles over which the reflection occurs, the reflected beam would have a divergence equal to this, and would appear to diverge from a point S' , which is the image of S in the plane of the crystal. The width of the line obtained on the film would, therefore, be greater than the width of the slit, and it would increase with increasing distance of the film from the crystal.

The above is the case with a perfect crystal. Now, suppose that the crystal possesses a certain amount of mosaic structure, *i.e.*, it consists of a large number of blocks which are slightly disoriented with respect to one another. It is then obvious that the Bragg reflection can occur over a wider range of angles than with a perfect crystal, and that the reflected beam would consequently be more divergent. It may also be remarked in this connection that a variation of the lattice spacing of the crystal would also produce precisely the same effect. In fact, such a variation of lattice spacing cannot be distinguished from the presence of mosaic structure by

the present experimental technique. What one can determine is only the magnitude of the resulting divergence, which may be due to either cause, or both. Consequently, we shall denote by the term '*divergence* of the crystal reflection,' the total angular divergence arising from the finite width of the Bragg reflection which occurs even in a perfect crystal, as well as from the presence of mosaicity or a variation in the lattice spacing as the case may be.

We shall now consider what the half-width of the line would be at a distance R from the source. Since the reflected beam appears to diverge from the image S' of the source, R is the sum of the distance of the film from the crystal, and that of the crystal from the slit. The intensity distribution in the line has a shape similar to that of a Gaussian error curve, as will be seen below. The term "half-width" consequently stands for the half-width at half-maximum.

Ever since the classical work of Ehrenberg, Ewald and Mark (1928) on the width of X-ray reflection, it is customary to represent the reflection curve for a perfect crystal in the form

$$I_{\phi} = \exp [- (\phi^2/c^2) \log 2] \quad (1)$$

where ϕ is the angular departure from the Bragg angle corrected for refractive index, and c is the half-width at half maximum. In the same way, for an imperfect crystal, we shall represent the variation of the intensity of the reflected beam with angle in the form

$$I_{\phi} = \exp [- \phi^2 (\log 2)/w^2] \quad (2)$$

where ϕ is the angle measured from that for which I is a maximum, and w is the half-width of the "divergence." We shall not consider in this section the relation between w and the half-width of a perfect crystal reflection c .

Now, the X-ray line also has a distribution of intensity of the form

$$I_{\lambda} = \exp [- (\lambda - \lambda_0)^2 (\log 2)/w_{\lambda}^2] \quad (3)$$

where λ_0 is the wavelength of maximum intensity, and w_{λ} is the half-width at half-maximum. If D is the dispersion ($d\phi/d\lambda$) of the crystal for the wavelength concerned (λ_0), then it is easily seen that the angular variation of the intensity in the reflected beam is given by

$$I_{\phi} = \exp [- \phi^2 (\log 2)/(w^2 + D^2 w_{\lambda}^2)] \quad (4)$$

where ϕ is the angle measured from that for which the intensity is a maximum. Putting $Dw_{\lambda} = l$, the half-width at half-maximum is equal to $(w^2 + l^2)^{1/2}$. Denoting this by W ,

$$W = \sqrt{w^2 + l^2} \quad (5)$$

We shall now derive an expression for the half-width a of the line on a film kept at a distance R from the source in terms of W and the width of the slit $2b$. For this, we follow a procedure analogous to that employed in a theory, first given by Allison (1931), for an arrangement slightly different from ours. If F be the centre of the line on the film (Fig. 1), and if we consider a point F_1 at a distance x from it, then the intensity at F_1 is given by

$$I_x = \int_{\frac{a}{R} - \frac{b}{R}}^{\frac{a}{R} + \frac{b}{R}} e^{-(\phi^2/w^2) \log 2} d\phi. \quad (6)$$

Put $(x/R) \div (W/\sqrt{\log 2}) = X$ and $(b/R) \div (W/\sqrt{\log 2}) = B$. Then,

$$I_x = \int_{X-B}^{X+B} e^{-\phi^2} d\phi. \quad (7)$$

This gives the intensity distribution of the line on the plate, and its half-width a can be determined by plotting the value of the integral (6) as was done by Allison. The elaborate procedure of plotting graphs can, however, be avoided, and the half-width can be determined with greater accuracy by the method described below. One has only to make use of a table of the error integral

$$Ei(z) = \int_0^z e^{-\phi^2} d\phi. \quad (8)$$

First determine $I_0 = 2Ei(B)$, and then find from the tables the value of X , for which $Ei(X+B) - Ei(X-B) = I_0/2 = Ei(B)$. This can easily be done by interpolation. In this way, the half-width of the line has been evaluated for various values of B , and the results are tabulated in Table I. The actual quantities given in the table are those that would be needed in calculations with the observed values. A is $= a/R$, D is $= b/R$, and W has the same significance as before. The various ratios of these quantities are given in Table I, since they alone come in, in the numerical computations.

Making use of this table, it is a simple matter to determine the half-width of the divergence w from the measured value of a , knowing the slit-width $2b$. One has only to find the ratio a/b , which is equal to A/D , and then find the corresponding value of A/W . The magnitude of W is then known, and from (5), w can be calculated, knowing l .

4. Technique of Measurement

In actual practice, it is not possible to apply directly the theory described in the previous section for the evaluation of the divergence of the crystal

TABLE I

D/W	A/W	A/D	D/W	A/W	A/D
0.120	1.003	8.35	1.500	1.581	1.054
0.240	1.014	4.22	1.562	1.631	1.045
0.500	1.059	2.12	1.682	1.732	1.030
0.601	1.086	1.81	1.802	1.838	1.020
0.721	1.126	1.56	1.922	1.947	1.014
0.841	1.173	1.395	2.042	2.060	1.009
0.961	1.228	1.280	2.162	2.174	1.006
1.000	1.247	1.247	2.282	2.291	1.004
1.081	1.294	1.197	2.402	2.406	1.002
1.201	1.367	1.138	2.523	2.525	1.001
1.321	1.448	1.096	2.763	2.764	1.0005
1.442	1.537	1.066	3.003	3.003	1.0002

reflection from the measured width. This is because a microphotometer has to be employed for the measurement of the half-width of the photographic line, and the microphotometric spot which scans the line has a finite width. This brings in complications, and the half-width deduced from the microphotometric trace has to be corrected for this. It is obvious that it is not possible to carry out the correction in an exact manner, since too many unknown quantities come in. In the present experiment, the following approximate method was employed.

It was assumed that the effect of the microphotometry is merely to increase the effective width of the slit. In other words, the broadening produced by the instrument could be represented as equivalent to an increase in the width of the slit. Consequently, the width $2b$ of the slit in the formulæ in section 3 should be replaced by another quantity $2b'$ which may be called the "effective width" of the slit, and which has to be determined. It was for this purpose that a number of photographs were taken with each diamond at different distances.

The method of determining the effective width was as follows. As a first approximation, the half-width measured from the microphotometric trace of the line at the shortest distance, *i.e.*, 20 cm., was taken to be equal to half the effective width. This is justified because, for this distance, a/R

was actually of the order of 2.5×10^{-5} , and the half-width W even for the most intensely fluorescent diamond was 1.1×10^{-5} , so that A/W was > 2 , and A/D was less than 1.01. Thus, the error introduced by taking the half-width of the line a to be equal to b' was less than 1%. With this value for the effective slit-width, the magnitude of W was deduced from the measurement of the line-widths at other distances as an average. For the least fluorescent diamonds, N.C. 72 and 73, the individual values varied by as much as 20%, but for the other two diamonds examined, N.C. 62 and 81, the variation was much less, being less than 10%. No systematic variation with distance occurred in any of these cases, showing that the effective width is practically a constant.

A second approximation was also worked out for one of the diamonds by using the mean value of W , and the measured half-width at 20 cm., and then evaluating the effective slit-width from these. The correction so introduced was less than 1%, and since the individual variations due to the errors of measurement far exceeded this value, it was not thought worthwhile to apply this correction. The validity of the approximation was also shown by the fact that the half-width a at 20 cm. was the same for all the four diamonds for which the value of W varied from 8 to 20 seconds, and also for both the $K\alpha_1$ and the $K\alpha_2$ lines.

The distance of the film from the source was not determined by direct measurement, but was deduced from the measured separation of the $K\alpha_1$ and $K\alpha_2$ components, the wavelength difference between which is accurately known. This had the advantage that any errors due to the shrinkage of the film, etc., were automatically corrected for. The half-width of the photographic line was obtained from the microphotometric trace after converting it into a curve showing *the intensity plotted against distance*, and then determining the width at half-maximum. This was done for both the $K\alpha_1$ and the $K\alpha_2$ lines, and incidentally, it was verified that the $K\alpha_2$ intensity was very nearly half that of the $K\alpha_1$, the mean of the measured values being 0.493 (*cf.* Williams, 1933).

The magnitude of w , the half-width of the crystal reflection was deduced by using the relation

$$W^2 = w^2 + l^2,$$

derived in section 3. The width of the X-ray line was taken from the results of Allison and Williams (1930). $2w_\lambda = 0.29$ X.U. for Mo. $K\alpha_1$ and $= 0.32$ X.U. for Mo $K\alpha_2$. The corresponding values of l for diamond are 3.58×10^{-6} and 3.95×10^{-6} .

Typical intensity curves for the line at 86.5 cm. with the four diamonds that were studied are reproduced in Fig. 2. The distance between the short vertical lines in these indicates the effective width of the slit. The mean

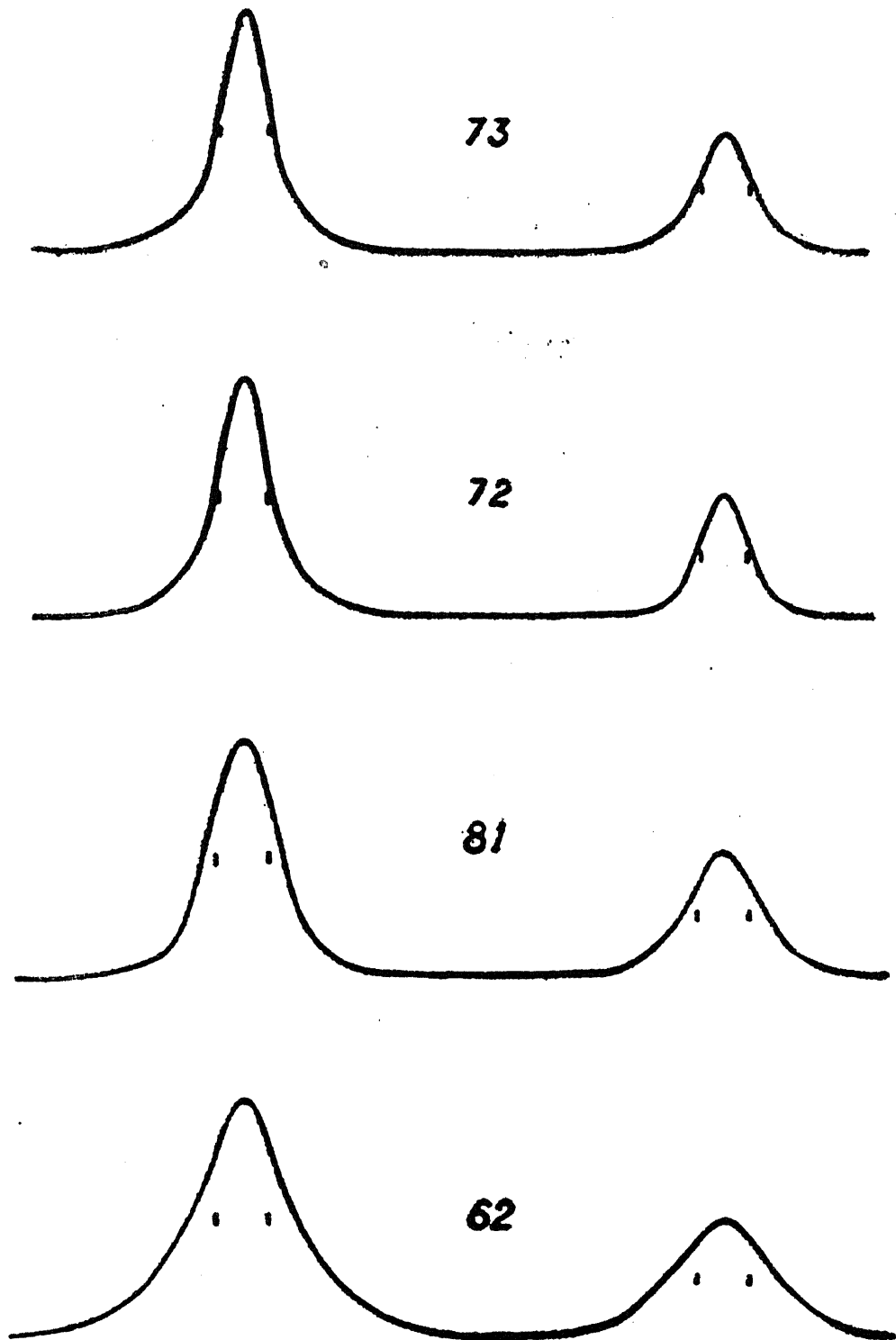


FIG. 2. Intensity Curves for Four Diamonds

values of W and w are collected in Table II below. An estimate of the relative intensity of fluorescence is also given in the last column.

TABLE II

Diamond N.C.	Mean value of W in radians		w in radians			w in seconds	m in seconds	Relative intensity of Fluores- cence
	$K\alpha_1$	$K\alpha_2$	$K\alpha_1$	$K\alpha_2$	Mean			
73	3.78×10^{-6}	4.20×10^{-6}	1.22×10^{-6}	1.43×10^{-6}	1.3×10^{-6}	2.7	1.9	1.0
72	4.26	4.62	2.31	2.39	2.35	4.8	4.3	4.1
81	7.51	7.88	6.60	6.82	6.7	13.8	13.8	23
62	11.07	11.07	10.47	10.34	10.4	21.4	21.4	990

This was obtained by photographic photometry of the fluorescence intensity. All the four diamonds were placed in a beam of ultra-violet light from a source of constant intensity, and were photographed by fluorescent light, using a filter of sodium nitrite solution to cut off the ultra-violet. A series of photographs with varying exposures from 2 seconds to 45 minutes were taken, and the density of the images on the plate was obtained by a microphotometer. By interpolation, the exposure necessary for each of the diamonds to give an image of a certain density was determined, and the reciprocal of this quantity gave a reasonable estimate of the relative intensities of fluorescence.

5. Interpretation of the Results

The results described in the previous section make it very clear that the more intensely blue-fluorescent a diamond is, the greater is the angular divergence of the crystal reflection. Now, it is well known that even for a perfect crystal, the monochromatic reflected beam has a finite angular divergence, the half-width of which is c (Eq. 1). Any increase in the divergence must therefore be attributed to the presence of discontinuities in the lattice structure. As already said, this may be in the form of a mosaic structure *i.e.*, the crystal may consist of a large number of mosaic crystallites, which are slightly tilted with respect to one another, or there may be some irregularities in the spacing of the atomic planes, without any angular tilting, which also has the effect that the crystal reflection occurs for a range of angles larger than that for a perfect crystal. In the former case, we may consider the angular distribution of the mosaic blocks to be of the form

$$n(\alpha) = \exp [- (\log 2) (\alpha^2/m^2)], \quad (9)$$

where α is the inclination of a block to the mean orientation, and m is that value of α , for which $n(\alpha)$ is half the maximum, *i.e.*, $n(0)$. It is then easily

verified that the half-width of the crystal reflection, w , is given by

$$w^2 = c^2 + m^2 \quad (10)$$

The same result holds also in the case of a variation in lattice spacing ; but m here represents the half-width of the divergence of the reflected X-ray beam resulting from such a variation. In either case, m obviously gives one an idea of the departure from perfection of the crystal. Its magnitude is also included in Table II. This was calculated from w , making use of the theoretical value of c as calculated from Ewald's theory (see Ehrenberg *et al* 1928) *viz.*, 0.96×10^{-6} .

It is interesting to compare the magnitude of m with that of the intensity of fluorescence F . In Fig. 3, m has been plotted against $\log F$. It will be seen from the figure that the deviation from perfection is very small for small intensities of fluorescence, then increases rapidly, finally reaching a saturation value for high intensities of fluorescence.

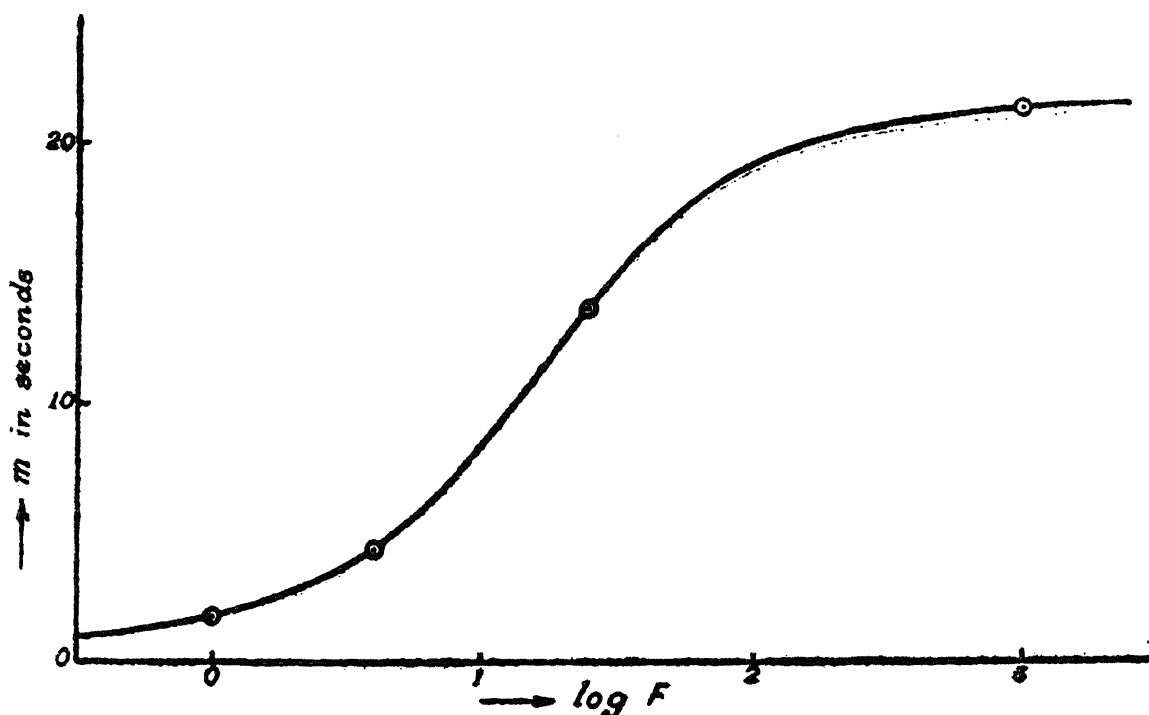


FIG. 3. Curve showing relation between fluorescence intensity and crystal perfection

We shall now consider the relation between the divergence of crystal reflection and the integrated intensity of the Bragg reflection. Considering a monochromatic X-ray, it is clear that with a perfect crystal the reflected beam would have a half-width equal to c . In an imperfect crystal, however, the reflection would occur over a wider range of angles, and the reflected beam would have a half-width w , greater than c . The integrated intensity

would consequently be proportional to

$$\int_{-\infty}^{+\infty} e^{-(\log 2) (\phi^2/w^2)} d\phi = w\sqrt{\pi} \quad (11)$$

This is true for every monochromatic component of the X-ray, so that the integrated reflection is directly proportional to w . Now, from Table II, the ratio of the values of w for the two diamonds N.C. 81 and 72 is 2.85. Hariharan (*loc. cit.*) who studied the integrated intensity of the Bragg reflection, finds that the ratio for the same two diamonds, D 41 and D 45 respectively, is 3.2. The two are in satisfactory agreement, considering the limits of experimental error. As far as the author is aware, this relation between the integrated intensity and the width of X-ray reflection does not seem to have been verified by anybody previously.

It is interesting to note that in N.C. 73, the most perfect of the diamonds examined, the half-width of the divergence is very nearly the same as the theoretical value, being equal to 1.3×10^{-6} , as compared with 0.96×10^{-6} , given by Ewald's theory.

A remark is here necessary on the statement made by Allison (1931) on Valasek's (1930) determination of the width of X-ray lines by the photographic method, employing an experimental arrangement similar to the author's. Commenting on the fact that Valasek's value is appreciably greater than that obtained by the double spectrometer method, Allison remarks that the photographic method is unreliable since a lateral spreading of the image occurs owing to the scattering in the photographic film. That such an effect, if it exists, can be reduced to negligible proportions is shown by the present experiment. Here, special care was taken to obtain the photograph with the least density necessary to obtain measurable microphotometric traces. It is obvious that, if spreading had occurred, the values obtained with increasing distances (R) would not be a constant. The large value obtained by Valasek is most probably to be attributed to *the effect of the finite width of the microphotometric spot*, for which he has not corrected, and not to the spreading of the photographic image.

In conclusion, I wish to express my grateful thanks to Prof. Sir C. V. Raman for the suggestion of the problem, and for the kind interest he took in the investigation.

6. Summary

The angular divergence of the monochromatic X-ray reflection given by four blue-fluorescent diamonds has been measured. The diamonds were chosen to have widely different intensities of fluorescence, the intensities

being in the ratio of 1:4·1:23:990. The divergence of crystal reflection was measured by means of a stationary crystal, using a narrow slit as the source of X-rays, the characteristic $\text{MoK}\alpha_1$ and $\text{K}\alpha_2$ reflected beams being photographed at a large distance from the crystal. Correcting for the lack of monochromatism of the X-rays, the half-widths of the divergence for the four specimens were found to be respectively 2·7, 4·8, 13·8 and 21·4 seconds of arc, as compared with the theoretical value 2·0 for a perfect crystal, showing clearly that the more intensely blue-fluorescent a diamond is, the larger is the divergence of the reflection given by it. It is pointed out that the integrated intensity of the Bragg reflection should be proportional to the half-width of the divergence, and this has been verified to be the case for two of the diamonds studied.

REFERENCES

1. Allison, S. K. .. *Phys. Rev.*, 1931, **38**, 203.
2. ——— and Williams, J. H. *Ibid.*, 1930, **35**, 1476.
3. Ehrenberg, W. Ewald, P. P. *Zeits. f. Krist.*, 1928, **66**, 547.
and Mark, H.
4. Hariharan, P. S. .. *Proc. Ind. Acad. Sci., A*, 1944, **19**, 261.
5. Krishnan, R. S. .. *Ibid.*, 1944, **19**, 298.
6. Lonsdale, K. .. *Nature*, 1942, **148**, 112.
7. Mark, H. .. *Naturwiss.*, 1925, **13**, 1042.
8. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci., A*, 1944, **19**, 280.
9. Raman, Sir C. V. .. *Ibid.*, 1944, **19**, 189.
10. Valsek, J. .. *Phys. Rev.*, 1930, **36**, 1523.
11. Williams, J. H. .. *Ibid.*, 1933, **44**, 146.