PRELIMINARY STUDY OF ANOMALOUS LAUE SPOTS OF ANTHRAQUINONE

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Various workers have investigated the diffuse radial streaks which appear along with the Laue photographs and various theories have been put forward to account for the results obtained. These, however, are not consistent and are sometimes contradictory.

The present authors have made a preliminary study of the anomalous Laue spots of anthraquinone and have observed that the position of the anomalous spots varies with the orientation of the crystals but the direction of the movement of these spots are not related in any way with the direction of the movement of the Laue spots. The data obtained also do not agree with the Faxen or Zachariasen's formula.

Introduction

The appearance of extra diffuse radial streaks in Laue photographs was first observed by Friedrich,[1] and at first Faxen[2] suggested that these streaks might be due to diffuse scattering of incident continuous X-ray by Debye heat waves produced in the crystal by thermal agitation. He later showed that when a monochromatic beam of X-rays is incident on a set of lattice planes there is a maximum in the intensity of the diffuse scattering which lies in the neighbourhood of the Laue spot. So, when white radiation is used, these diffuse spots with maxima would be drawn out as streaks.

The same problem was investigated by many other workers previously, who put forward different theories to account for the results obtained. The present work was undertaken in an attempt to achieve clarification of the apparent contradictions in the experimental result and interpretations of the previous investigators.

Experimental Procedure

(*a*) *Goniometry and Mounting of the Crystal.*—Anthraquinone $C_{14}H_8O_2$ which has been studied in the present case was crystallised from benzene. It belongs to the monoclinic system. Short needle-shaped crystals were obtained, the needle length being parallel to the b-axis. The important physical data are:—Anthraquinone $C_6H_4\left\langle {CO \atop CO} \right\rangle C_6H_4$, Crystallises in holohedral class of the monoclinic system, a=15.85 Å, b=3.98Å, C=7.92 Å, β=102°7′, melting point 273°C., density 1.419. Space group, C^5_2 ($P2_1/a$). Two molecules per unit cell. Volume of the unit cell 487A°.[3] Total number of electrons per unit cell=F(000)=216. For the mounting of the crystal, a Czapski two-circle theodolite goniometer was used. A single and unstrained crystal was chosen, the angular measurements for which are given below in Table 1.

TABLE 1.—GONIOMETRIC MEASUREMENT.

Faces	Indices of the planes	Angle observed
a : c	(100) : (001)	77°19′
c : m	(001) : ($\bar{2}$01)	51°14′
m : a	($\bar{2}$01) : (100)	51°24′

It was then mounted on the goniometer head so that the 'a' face was normal to the X-ray beam. A small quantity of aluminium powder was dusted over the crystal for the measurement of the diameter of the camera and for comparing the intensity of the anomalous spots.

(*b*) *Description of the Camera and taking of Photographs.*—A cylindrical camera has been used chiefly for the following reasons: It extends the angular range of observation to a great extent, and also minimises the falling off of the intensity with the increase of the scattering angle. After first adjusting the crystal and fixing the goniometer head in the camera, with the X-ray beam passing normal to 'a', a number of photographs were taken with crystal at different orientations, the time of exposure being 7 to 8 hours (see photographs 1 and 2).

Indexing of Laue Spots

For indexing of the Laue spots the exact radius of the film was calculated by the formula ψ=2x/D,

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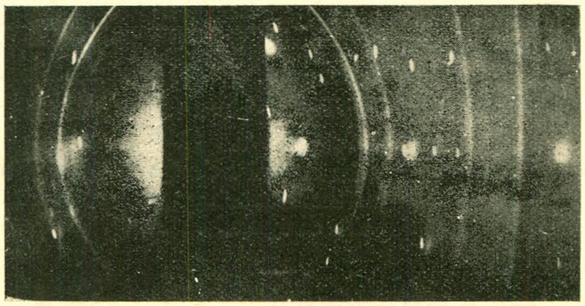
TABLE 2.—INDEXING OF THE LAUE SPOTS IN THE VICINITY OF THE ANOMALOUS SPOTS.

Angular co-ordinates of Laue spots		$h\lambda$	$k\lambda$	$l\lambda$	hkl
ψ in degrees	μ in degrees				
25°49′	0	—1.5818	0	3.539	$\bar{1}02$
54°8′	0	—6.5635	0	6.981	$\bar{4}04$
57°48′	23°27′	—8.104	1.504	6.887	$\bar{5}14$
43°54′	23°27′	—5.374	1.584	—4.314	$\bar{3}1\bar{3}$
28°2′	25°10′	—3.188	—1.692	3.636	$\bar{2}\bar{1}2$
17°24′	30°52′	—2.867	—2.042	2.297	$\bar{2}\bar{1}1$

TABLE 3.—DETERMINATION OF $\triangle$ FOR THE ANOMALOUS SPOTS OF ANTHRAQUINONE

Indices of the planes giving rise to the anomalous spots	Angular co-ordinates of anomalous spots		$2\theta_i$	$2\theta_B$	$\triangle=\theta_i-\theta_B$
	ψ	μ			
$\bar{1}02$	25°49′	0	25°49′	25°20′	0°14′
,,	26°14′	0	26°14′	,,	0°27′
,,	27°12′	0	27°12′	,,	0°56′
,,	27°54′	0	27°54′	,,	1°17′
,,	29°24′	0	29°24′	,,	2°2′
$\bar{4}04$	54°8′	0	54°8′	53°47′	0°10′
,,	54°32′	0	54°32′	,,	0°22′
,,	54°42′	0	54°42′	,,	0°22′
,,	54°56′	0	54°56′	,,	1°4′
,,	57°14′	0	57°14′	,,	1°45′
$\bar{5}14$	57°48′	23°27′	60°46′	55°13′	2°46′
,,	58°41′	24°22′	61°45′	,,	3°16′
,,	58°57′	24°22′	61°57′	,,	3°22′
,,	60°3′	24°36′	63°	,,	3°53′
,,	62°32′	25°44′	65°27′	,,	5°7′
$\bar{3}1\bar{3}$	—43°54′	23°27′	48°38′	48°31′	0°3′
,,	—42°48′	23°27′	47°42′	,,	—0°10′
,,	—42°15′	23°41′	47°13′	,,	—0°39′
,,	—42°48′	21°21′	46°53′	,,	—0°49′
,,	—41°24′	22°45′	46°15′	,,	—1°8′
$\bar{2}\bar{1}2$	28°2′	—25°10′	36°58′	32°30′	2°14′
,,	26°55′	—24°2′	35°30′	,,	1°30′
,,	27°21′	—24°2′	35°49′	,,	1°39′
,,	28°43′	—27°4′	38°39′	,,	3°4′
,,	28°43′	—25°55′	37°56′	,,	2°43′
$\bar{2}\bar{1}1$	17°24′	—30°52′	35°2′	26°36′	4°13′
,,	16°34′	—23°46′	28°42′	,,	1°3′
,,	17°16′	—29°0′	23°22′	,,	3°23′
,,	17°49′	—32°34′	36°40′	,,	5°2′
,,	17°40′	—30°2′	34°25′	,,	3°54′



Photograph 1.

where 2x is the distance between the two corresponding lines, D is the diameter of the film and ψ is the angle of diffraction (in radians). Thus with the help of radius as determined above, the angular co-ordinates ψ and μ of the Laue spots were determined from the relation,

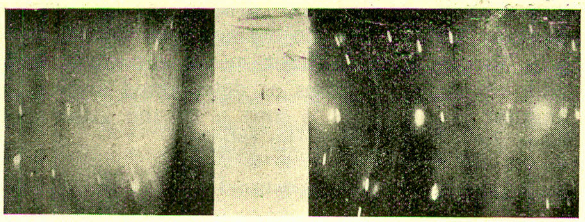
$$\psi = \frac{x}{R}\ ; \qquad \mu = \tan^{-1}\frac{e}{R}$$

where x is the horizontal distance of the film from a vertical line through the centre of the undeviated beam, e is the vertical distance from the equitorial layer lines and R is the radius of the film.

Here in the case of anthraquinone, the x-ray

TABLE 4.—DETERMINATION OF △ FOR THE LAUE SPOTS OF ANTHRAQUINONE.

Indices of the planes giving rise to the Laue spots	Angular co-ordinates of Laue spots		$2\theta_i$	$2\theta_B$	$\triangle = \theta_i - \theta_B$
	ψ	μ			
$\bar{1}02$	24°34′	0	24°34′	25°20′	—0°23′
,,	24°26′	0	24°26′	,,	—0°27′
,,	24°10′	0	24°10′	,,	—0°25′
,,	24°26′	0	24°26′	,,	—0°22′
,,	24°43′	0	24°43′	,,	—0°18′
$\bar{4}04$	53°18′	0	53°18′	25°20′	—0°14′
,,	53°26′	0	53°26′	,,	—0°10′
,,	53°18′	0	53°18′	53°18′	—0°14′
,,	55°14′	0	5o°14′	,,	—0°43′
,,	55°30′	0	55°30′	,,	0°51′
$\bar{5}14$	58°50′	23°27′	61°40′	55°13′	3°13′
,,	57°59′	24°36′	61°11′	,,	2°59′
,,	57°59′	23°27′	60°54′	,,	2°50′
,,	59°20′	24°23′	60°19′	,,	3°33′
,,	60°44′	24°36′	63°36′	,,	4°11′
$\bar{3}1\bar{3}$	—42°48′	22°52′	47°28′	48°31′	—0°31′
,,	—40°51′	23°41′	46°9′	,,	—1°11′
,,	—41°34′	23°27′	46°40′	,,	—0°55′
,,	—43°26′	22°10′	47°43′	,,	—0°24′
,,	—42°32′	23°41′	47°34′	,,	—0°29′
$\bar{2}\bar{1}2$	28°2′	—25°24′	37°8′	32°30′	2°19′
,,	27°37′	—24°29′	36°16′	,,	1°53′
,,	27°37′	—24°15′	36°7′	,,	1°48′
,,	28°19′	—26°18′	37°54′	,,	2°42′
,,	28°19′	—25°17′	37°15′	,,	2°22′
$\bar{2}\bar{1}1$	15°11′	—26°51′	30°36′	30°36′	2°
,,	14°54′	—24°50′	28°43′	,,	1°6′
,,	14°54′	—24°50′	28°43′	,,	1°6′
,,	—	—	—	—	—
,,	15°11′	—24°57′	28°55′	,,	1°9′



Photograph 2.

beam was incident on the crystal along the a-axis while b-axis was vertical. If α_0, β_0 γ_0 and α, β, γ, are the direction cosines of the incident and diffracted beam respectively, then

$$\alpha_0 = 1, \quad \beta_0 = 0, \quad \gamma_0 = \cos\delta.$$

Hence because the crystal belongs to the monoclinic system with the monoclinic angle, $\beta = 102°\ 7'$, therefore, for the diffracted beam,

$$\alpha = \cos\psi.\ \cos\mu, \quad \beta = \sin\mu$$

$$\text{and } \gamma = \beta\cos\mu.\ \cos(\beta\text{-}\psi)$$

TABLE 5.—COMPARISON OF $(2\theta_i+\psi)$ WITH $2\theta_\beta$ FOR THE PLANES $\bar{1}02$, $\bar{4}04$, $\bar{5}14$, $\bar{3}1\bar{3}$, $\bar{2}\bar{1}2$, AND $\bar{2}\bar{1}1$ AS MEASURED BY OBSERVATION AND AS CALCULATED FROM FAXEN'S FORMULA.

Indices of the planes giving rise to anomalous spot	$\triangle=\theta_i\text{-}\theta_B$	$2\theta_B$	$(\theta_i+\varphi)$ observed	$(\theta_i+\varphi)$ as calculated from Faxen's formula	Difference Obs.-Cal.
$\bar{1}02$	0°14′	25°11′	25°11′	23°46′	1°25′
,,	0°27′	,,	25°20′	23°47′	1°33′
,,	0°56′	,,	25°41′	23°50′	1°51′
,,	1°17′	,,	26°10′	23°51′	2°19′
,,	2°2′	,,	27°7′	23°54′	3°13′
$\bar{4}04$	°010′	53°47′	53°43′	51°14′	2°29′
,,	0°22′	,,	53°59′	51°17′	2°42′
,,	0°22′	,,	54° ′	51°19′	2°41′
,,	1°4′	,,	55°35′	51°32′	4°3′
,,	1°45′	,,	56°24′	51°46′	4°38′
$\bar{4}14$	2°46′	55°13′	61°14′	57°35′	3°39′
,,	3°16′	,,	61°27′	57°47′	3°4′
,,	3°22′	,,	61°25′	57°49′	3°36′
,,	3°53′	,,	62°39′	58°8′	4°31′
,,	—	—	—	—	—
$\bar{3}1\bar{3}$	0°3′	48°31′	38°3′	46°55′	1°8′
,,	—0°10′	,,	46°56′	46°45′	0°10′
,,	—0°39′	,,	46°56′	46°41′	0°15′
,,	—0°49′	,,	47°17′	46°37′	0°40′
,,	—1°8′	,,	46°54′	46°20′	0°34′
$\bar{2}\bar{1}2$	2°14′	32°30′	37°3′	33°41′	3°22′
,,	1°30′	,,	35°53′	33°34′	2°19′
,,	1°39′	,,	35°53′	35°35′	0°22′
,,	3°4′	,,	38°16′	33°48′	4°30′
,,	2°43′	,,	37°35′	33°45′	3°50′
$\bar{2}\bar{1}1$	4°13′	26°36′	32°49′	27°43′	5°6′
,,	1°3′	,,	28°42′	27°32′	1°10′
,,	3°23′	,,	31°2′	27°37′	3°25′
,,	5°2′	,,	—	—	—
,,	3°55′	,,	31°39′	27°41′	3°58′

Thus from the Laue equations, we have,

$$\frac{a(\cos\psi\ \cos\mu - 1)}{b(\sin\mu)} = \frac{h}{k},$$

$$\frac{b(\sin\mu)}{c[\cos\mu\{\cos\ (\delta\text{-}\psi)\}\text{-}\cos\delta]} = \frac{K}{L}$$

Thus we can find h/k and k/l (axial length of the crystal being known). Laue spots of other photographs rotated to different orientations could be followed and indexed in the same manner. See photograph No. 2 where Miller indices of six spots calculated in the above described manner are shown.

Study of the Anomalous Spots

The study of the anomalous spots, the measurement of their exact positions and their comparison

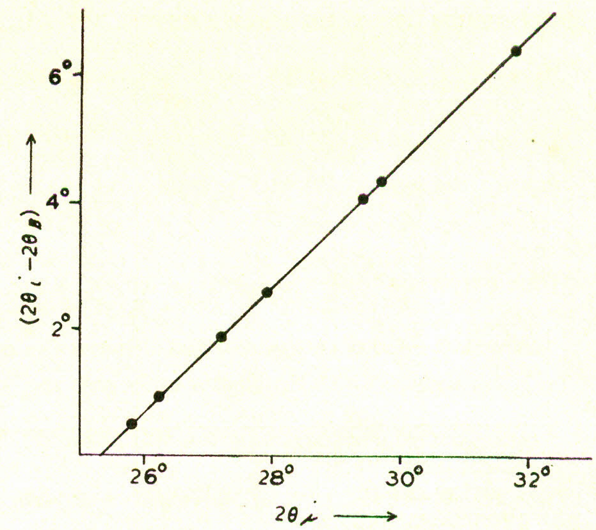
TABLE 6.—COMPARISON OF $(2\theta_i+\varphi)$ WITH $2\theta_B$ FOR THE PLANES $\bar{1}02$, $\bar{4}04$, $\bar{5}14$, $\bar{3}1\bar{3}$, $\bar{2}1\bar{2}$, AND $\bar{2}1\bar{1}$ AS MEASURED BY OBSERVATION AND AS CALCULATED FROM ZACHARIASEN'S FORMULA.

Indices of the planes giving rise to anomalous spots	$\triangle=\theta_i\text{-}\theta_B$	$2\theta_B$	$(\theta_i+\varphi)$ observed	$(\theta_i+\varphi)$ as calculated from Zachariasen's formula	Difference Obs.-Cal.
$\bar{1}02$	0°14′	25°20′	25°11′	25°21′	0°10′
,,	0°27′	,,	25°20′	25°22′	—0°2′
,,	0°56′	,,	25°41′	25°25′	0°16′
,,	1°17′	,,	26°10′	25°27′	0°43′
,,	2°2′	,,	27°7′	25°31′	1°36′
$\bar{4}04$	0°10′	53°47′	53°43′	53°51′	—0°8′
,,	0°22′	,,	53°59′	53°56′	0°3′
,,	0°22′	,,	54°′	53°56′	0°4′
,,	1°4′	,,	55°35′	54°12′	1°23′
,,	1°45′	,,	56°24′	54°29′	1°55′
$\bar{5}14$	2°46′	55°13′	61°14′	56°23′	4°51′
,,	3°16′	,,	61°27′	56°31′	4°56′
,,	3°22′	,,	61°25′	56°33′	4°52′
,,	3°53′	,,	62°39′	56°50′	5°49′
,,	—	—	—	—	—
$\bar{3}1\bar{3}$	0°3′	48°31′	48°3′	48°32′	0°29′
,,	—0°10′	,,	46°55′	48°28′	—1°13′
,,	—0°39′	,,	46°56′	48°18′	—1°12′
,,	—0°49′	,,	47°17′	48°15′	—0°58′
,,	—1°8′	,,	46°54′	48°9′	—1°15′
$\bar{2}1\bar{2}$	2°14′	2°330′	37°3′	32°50′	4°13′
,,	1°30′	,,	35°53′	32°44′	3°9′
,,	1°39′	,,	35°57′	32°45′	3°12′
,,	—	,,	—	—	—
,,	2°43′	,,	37°35′	32°55′	4°40′
$\bar{2}1\bar{1}$	1°3′	26°36′	28°42′	26°42′	2°
,,	3°23′	,,	31°2′	26°57′	4°5′
,,	5°2′	,,	—	—	—
,,	3°54′	,,	31°39′	27°′	4°39′
,,	4°16′	,,	32°22′	27°3′	5°9′

with those of the corresponding Laue spots is first required. For the anomalous spots in the central layer, the distance of the spot was measured from the nearest aluminium line so that the angular separation from the aluminium line was easily calculated from the actual radius of the camera. The scattering angle of aluminium being known, the angle between the direct ray and the direction of the anomalous spot was thus accurately known. For the spots above or below the central layer, the co-ordinates ψ_a and μ_a were evaluated and $2\theta_a$ the total scattering angle of the anomalous spot was obtained from the relation $2\theta_a = \cos\psi_a . \cos\mu_a$. In this way the spots corresponding to $(\bar{1}02)$, $(\bar{4}04)$, $(\bar{5}14)$, $(\bar{3}1\bar{3})$, $(\bar{2}12)$ and $(\bar{2}11)$ have been studied in different photographs. It was observed from these measurements that the position of the anomalous spot, varied with the orientation of the crystal, i.e. the Laue spots. It was also observed that the direction of movements of the anomalous spots were not related in any way with the direction in which the Laue spots moved.

Table 2 gives some details of the indexing of the Laue spots while Table 3 gives the angular co-ordinates of the anomalous spots associated with the $\bar{1}02$, $\bar{4}04$, $\bar{5}14$, $\bar{3}1\bar{3}$, $\bar{2}12$ and $\bar{2}11$ reflection together with the calculated value of $\triangle$, for various settings of the crystal.

The variations of $(2\theta_i - 2\theta_a)$ with $2\theta_i$ were studied to identify the association of anomalous spot with a given Laue spot. The values of $(2\theta_i - 2\theta_a)$ were plotted against the values of $2\theta_i$ in a graph. The most interesting and important result was that observed from this graph was that all the curves were straight lines. This shows that the variation of $(2\theta_i - 2\theta_a)$ with $2\theta_i$ are regular and directly proportional to each other. This was not predicted in any of the existing theories. Moreover, this straight line intersects the $2\theta_i$ axis at a point whose value is equal to $2\theta_b$ for that spot for Cu $K\alpha$ well within the limits of experimental error. It means that when the difference is zero, the anomalous spot coincides with the Laue spot and the scattering angle for the combined spot is equal to $2\theta_B$ (see Graph 1).



Graph 1.

Discussion

In course of the present studies the following facts have been observed.

The position of the anomalous spot varies with the orientation of the crystal. However, Table 3 shows that the directions of movement of the anomalous spots are not related in any way with the direction in which the Laue spots move. A comparison with theory is made in Table 5 and Table 6 below, but it is seen that the agreement with either Faxen's or Zachariasen's formula is poor. The differences between the observed and the calculated values of $(\theta_i + \varphi)$ are considerably greater than the limits of experimental error in this experiment for the larger values of $\triangle$, i.e. greater than 2°.

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