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Simultaneous Diffraction in Anthracene*

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An analytical method is used to index the (100) simultaneous diffractions in (monoclinic) anthracene. The expected pattern of diffractions is calculated and compared with experimental observations. The computations are amenable to desk calculators. Simultaneous diffractions from 23 different pairs of planes have been identified and tabulated for anthracene using Cu $K\alpha$ radiation.

Introduction

Recently there appeared in the literature a graphical method of indexing simultaneous diffractions, with an extensive discussion of the (222) pattern of germanium (Cole, Chambers & Dunn, 1962). An alternative, although equivalent, analytical method has been in use for several years at this laboratory (Alexander, Fraenkel & Kalman, 1959). This method is capable of predicting the pattern of the expected simultaneous diffractions for a particular case and is amenable to computations on a desk calculator. It will be described in detail for the case of the (100) Cu $K\alpha$ pattern of (monoclinic) anthracene.‡

To produce the $(h_rk_rl_r)$ simultaneous diffractions the crystal is rotated about $\mathbf{h}(r)$, the reciprocal lattice vector of the $(h_rk_rl_r)$ planes, and the X-ray beam is incident at the Bragg angle appropriate for these planes. As the crystal rotates there are certain positions in which the Bragg condition will be satisfied as well for another set of planes $(h_sk_sl_s)$. These positions occur whenever the incoming beam is directed along an intersection of the Kossel cones about the vectors $\mathbf{h}(r)$ and $\mathbf{h}(s)$, where $\mathbf{h}(s)$ is the reciprocal lattice vector of the $(h_sk_sl_s)$ planes. The direction of the beam for this position is $\mathbf{S}_{rs}$ (Fig. 1). In this case both $\mathbf{h}(r)$ and $\mathbf{h}(s)$ vectors lie on the Ewald sphere in reciprocal space, and as is well known (Laue, 1960), simultaneous diffraction occurs, involving the $(h_sk_sl_s)$ and $(h_tk_tl_t)$ planes. These planes will be referred to as the 'operative' (or 'first') and the 'cooperative' (or 'second') planes, respectively (Cole *et al.*, 1962). The relation among the indices of these planes is found to be (Renninger, 1937; Laue, 1960; James, 1958):

$$h_r = h_s + h_t,\quad k_r = k_s + k_t,\quad l_r = l_s + l_t\,. \qquad (1)$$

The same relationship holds when the roles of $(h_sk_sl_s)$ and $(h_tk_tl_t)$ are interchanged.

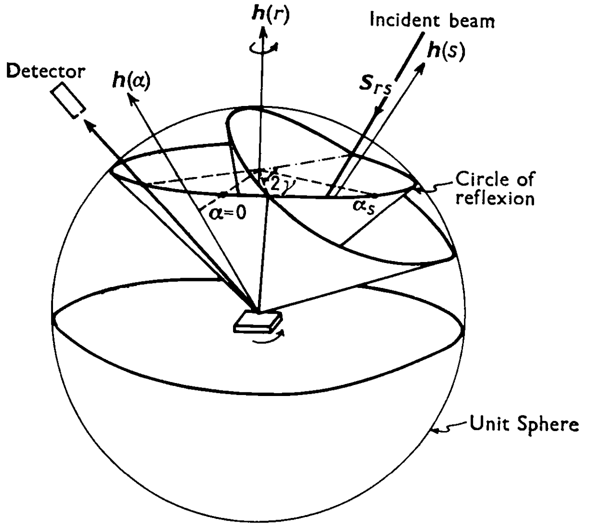

Fig. 1. The unit sphere showing the Kossel cones of the $(h_rk_rl_r)$ and the $(h_sk_sl_s)$ planes. The crystal rotates about $\mathbf{h}(r)$, the reciprocal lattice vector of the $(h_rk_rl_r)$ planes. The angular separation of the intersections of the cones, measured along the circle of reflexion, is 2γ. An arbitrary vector $\mathbf{h}(\alpha)$ determines the reference point $\alpha = 0$, as described in the text. The beam enters at the Bragg angle for the $(h_rk_rl_r)$ planes. Simultaneous diffraction occurs when the beam enters in the $\mathbf{S}_{rs}$ direction, along an intersection of the two cones, and is detected as a peak above the background.

Our object then is to find all the real intersections between the fixed cone about $\mathbf{h}(r)$ and the cones about any other vectors $\mathbf{h}(s)$. Consider the circle of reflexion, *i.e.*, the intersection of the Kossel cone about $\mathbf{h}(r)$ and the unit sphere (Fig. 1). The cone about $\mathbf{h}(s)$ will in general have two intersections with the $\mathbf{h}(r)$ cone. Let the angular separation of these two 'equivalent' intersections, measured along the circle of reflexion, be called 2γ. This information alone is insufficient to identify unequivocally the

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‡ The existence of a (100) multiple diffraction in anthracene was first mentioned in the Ph.D thesis of one of us (B. S. F.), Jerusalem, 1954. The 'forbidden' (100) reflexion was seen on a Weissenberg photograph about the b axis with Cu $K\alpha$ radiation.

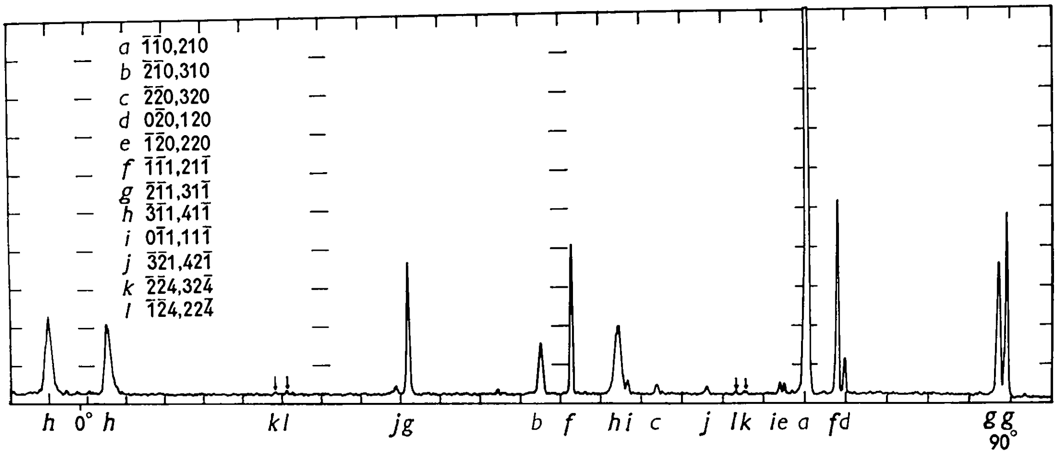

Fig. 2. Counter record of the anthracene (100) simultaneous diffraction pattern for Cu$K\alpha$ radiation, monochromatized by LiF. Full scale, 2000 c.p.s.; time constant, one second; chart speed, one inch per min; crystal rotated at 92 min per revolution; X-ray tube operated at 40 kV, 20 mA.

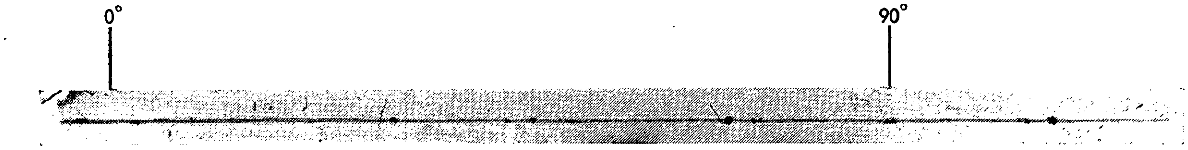

Fig. 3. Photographic record of the anthracene (100) simultaneous diffraction pattern for monochromatic Cu$K\alpha$ radiation. Crystal rotated at 92 min per revolution; X-ray tube operated at 40 kV, 20 mA; 50-hour exposure.

reflexions of an observed pattern. The pattern of simultaneous diffractions can be predicted if, in addition to knowing 2γ, the mid points of all possible pairs of equivalent reflexions are related to the same arbitrary reference point. Accordingly let us define α as the angular separation on the circle of reflexion between an arbitrary reference point and the mid point, along the circle, of two equivalent intersections. The $\alpha=0$ reference point is determined by the intersection of the reflexion circle with the plane containing $\mathbf{h}(r)$ and $\mathbf{h}(\alpha)$, an arbitrary vector.

In practice, it is possible to observe the simultaneous diffractions if the $(h_rk_rl_r)$ reflexion is weak, or forbidden, and those of $(h_sk_sl_s)$ and $(h_tk_tl_t)$ are strong. The $(h_sk_sl_s, h_tk_tl_t)$ simultaneous diffractions are then seen as peaks above the $(h_rk_rl_r)$ background (Figs. 2 and 3).

Theory

The conditions to be met by the incoming beam when the crystal is simultaneously diffracting are (Laue, 1960)

$$\begin{aligned} \mathbf{S}_{rs}^2 &= 1 \\ 2\mathbf{h}(r)\,.\,\mathbf{S}_{rs} &= -\lambda\mathbf{h}(r)^2 \\ 2\mathbf{h}(s)\,.\,\mathbf{S}_{rs} &= -\lambda\mathbf{h}(s)^2\,. \end{aligned} \qquad (2)$$

It can be seen from geometrical considerations (Alexander *et al.*, 1959) that

$$\cos\gamma = \frac{[\mathbf{S}_{rs}\times\mathbf{h}(r)]\,.\,[\mathbf{h}(s)\times\mathbf{h}(r)]}{|\mathbf{S}_{rs}\times\mathbf{h}(r)|\;|\mathbf{h}(s)\times\mathbf{h}(r)|}\,, \qquad (3)$$

where both the positive and negative values of γ are solutions. Combining equations (2) and (3)

$$\cos\gamma = \frac{\lambda|\mathbf{h}(r)|\,[\mathbf{h}(r)\,.\,\mathbf{h}(s)-\mathbf{h}(s)^2]}{\sqrt{(4-\lambda^2\mathbf{h}(r)^2)}\,|\mathbf{h}(s)\times\mathbf{h}(r)|}\,. \qquad (4)$$

If an arbitrary direction $\mathbf{h}(\alpha)$ is defined, similar geometrical considerations yield

$$\cos\alpha = \frac{[\mathbf{h}(r)\times\mathbf{h}(\alpha)]\,.\,[\mathbf{h}(r)\times\mathbf{h}(s)]}{|\mathbf{h}(r)\times\mathbf{h}(\alpha)|\;|\mathbf{h}(r)\times\mathbf{h}(s)|}\,. \qquad (5)$$

In addition, an expression for $\sin\alpha$ is necessary in order to determine α unambiguously. It is convenient to choose a vector of length $\sin\alpha$ as follows:

$$\frac{\mathbf{h}(r)}{|\mathbf{h}(r)|}\sin\alpha = \frac{[\mathbf{h}(r)\times\mathbf{h}(\alpha)]\times[\mathbf{h}(r)\times\mathbf{h}(s)]}{|\mathbf{h}(r)\times\mathbf{h}(\alpha)|\;|\mathbf{h}(r)\times\mathbf{h}(s)|}\,. \qquad (6)$$

This vector is either parallel or antiparallel to $\mathbf{h}(r)$, depending on the sign of $\sin\alpha$.

Anthracene (100) simultaneous diffractions

The (100) reflexion in anthracene has a zero structure factor (Mathieson, Robertson & Sinclair, 1950); therefore simultaneous diffraction peaks are expected. Thus, let $(h_rk_rl_r)$ be (100), and (hkl) be the operative

$(h_sk_sl_s)$ planes. Expressing equation (4) in terms of the monoclinic lattice constants a, b, c, and β we get

$$\cos\gamma_{100}=\frac{b^2c^2h(1-h)-a^2c^2k^2\sin^2\beta-a^2b^2l^2+l(2h-1)acb^2\cos\beta}{a^2bc\sin^2\beta\sqrt{(4\lambda^{-2}-(a\sin\beta)^{-2})}\sqrt{(c^2k^2+b^2l^2)}}\,. \tag{7}$$

With the anthracene data given by Mathieson *et al.* (1950), the expression for $\cos\gamma_{100}$ becomes for Cu $K\alpha$ radiation

$$\cos\gamma_{100}=\frac{(0\cdot0232352)[4\cdot54004h(1-h)-6\cdot17308k^2-2\cdot67022l^2-1\cdot98212l(2h-1)]}{\sqrt{(1\cdot24613k^2+0\cdot364333l^2)}} \tag{8}$$

For the reference $\alpha=0$, the reciprocal lattice vector of the (010) planes is a convenient choice for $\mathbf{h}(\alpha)$. Equation (5) becomes

$$\cos\alpha=k/\sqrt{(k^2+(b/c)^2l^2)}=k/\sqrt{(k^2+0\cdot29237l^2)}\,. \tag{9}$$

Similarly, equation (6) gives

$$\sin\alpha=l/\sqrt{(l^2+(c/b)^2k^2)}=l/\sqrt{(l^2+3\cdot4203k^2)}\,. \tag{10}$$

The positive square roots are used throughout.

Consider now a particular set of planes $(h_sk_sl_s)$ operative. Equations (9) and (10) yield a single value α_s for these indices; equation (8) gives us γ_s. Hence, there will be two reflexions for this case, at $\alpha_s\pm\gamma_s$. Alternatively consider the $(h_tk_tl_t)$ planes operative. By equation (1) these can be re-expressed as $(1-h_s, \bar{k}_s, \bar{l}_s)$ when $(h_rk_rl_r)$ is (100). The same value γ_s results, as expected, whereas $\alpha_t=\alpha_s+\pi$. Thus for $(h_tk_tl_t)$ operative, two more reflexions are obtained, at $\pi+\alpha_s\pm\gamma_s$. Similarly, the $(h_s\bar{k}_sl_s)$ planes lead to two reflexions, at $\pi-\alpha_s\pm\gamma_s$; the $(h_t\bar{k}_tl_t)$ or $(1-h_s, k_s, \bar{l}_s)$ planes also give two, at $-\alpha_s\pm\gamma_s$ (with the same numerical values of γ_s and α_s throughout).

Thus for the anthracene (100) case each pair of planes $(h_sk_sl_s, h_tk_tl_t)$ satisfying equation (1) gives rise to four reflexions, two from each set of planes considered in turn as operative. Four more reflexions arise from the symmetrically related pair of planes $(h_s\bar{k}_sl_s, h_t\bar{k}_tl_t)$. If the incoming beam is unpolarized these four pairs of reflexions are of equal intensity. (For a polarized beam this is in general not true.) Therefore, eight reflexions appear, in general, at $\pm\alpha_s\pm\gamma_s$ and $\pi\pm\alpha_s\pm\gamma_s$.

If α is 0 or π, as it is if the pair of planes is of the type (h_sk_s0, h_tk_t0), only four reflexions appear. Since α is independent of h, different pairs of planes with different values of h, but the same values of k and l, show a symmetrical distribution about the same points $\pm\alpha$, and $\pi\pm\alpha$.

The convenience of $\mathbf{h}(010)$ as $\mathbf{h}(\alpha)$ results from the symmetry properties it has for the (100) simultaneous diffraction case. (An alternative and equally convenient choice for $\mathbf{h}(\alpha)$ would be $\mathbf{h}(001)$). Had $\mathbf{h}(\alpha)$ been chosen less conveniently, the expressions for $\cos\alpha$ and $\sin\alpha$ would have been somewhat more complicated.

When one considers the (100) anthracene case, one is struck by the large number of possible combinations of planes which satisfy equation (1). There are over a thousand possibilities of simultaneous diffractions in the (100) case for Cu $K\alpha$, as can easily be seen from the list of planes whose structure factors are reported by Mathieson *et al.* (1950). Many of these pairs are forbidden because by equation (8) $\cos\gamma>1$. Most, however, are pairs of planes with small structure factors which contribute in an undetermined way to the background. In practice we have observed about 76 peaks standing out from a more or less homogeneous background. These reflexions are labelled *a* to *l* in Fig. 2. Many other possible but weak reflexions can be made out along the recorder chart, distinguishable from the background only by careful comparison of several runs over the same or equivalent range. These are not marked on the chart, but are included in Table 1. Owing to the symmetrical distribution of reflexions only a $\pi/2$ range need be examined at a time.

To minimize the amount of calculation necessary to effect the complete identification, we chose only those possible pairs of planes whose products of structure factors are larger than 200. There are 26 different pairs of planes, and they are sufficient to account for all observed peaks. That this procedure is justified can be seen from the table. The strongest reflexions observed did indeed originate from pairs of planes with large structure factors. Had complete identification been impossible using this first selection, the calculation would have been extended to those planes whose products of structure factors are, say, between 150 and 200, and so on, until all observations were accounted for. Any remaining ambiguities, due possibly to overlapping reflexions, can often be resolved by changing the wavelength used, and hence changing the appearance of the pattern. Conversion of the set of $\cos\gamma$ values for the new wavelength is effected simply by multiplication by a constant (equation (4)). The value of α is independent of the wavelength.

We found the commercially available anthracene crystals of scintillation grade to be inadequate for our purpose; only a few reflexions were observed (those labelled *a*, *g*, *f*, *h*), and these were observed on the film as clusters of spots, making difficult the identification of any weak, closely situated reflexions. To obtain better crystals we dissolved purified anthracene in alcohol and set the container in a place free from vibrations for several weeks. As the alcohol evaporated, the anthracene crystallized out. Most of the crystals thus obtained were thin irregular hexagons, several tenths of a millimeter in diameter, several hundredths of a millimeter in thickness. Occasionally crystals grew that were thicker than most, although no larger in diameter. More reflexions were

Table 1. (100) *Simultaneous diffractions in anthracene with* Cu $K\alpha$ *radiation*

	Planes	Measured(1) $(F_1F_2)^2$	Measured Peak intensity	γ	α	Predicted positions in first quadrant	
a	$(\bar{1}\bar{1}0, 210)$	7728×10^3	~ 3100 c.p.s.	71·48°	0·0°	71·48°	71·48°
g	$(\bar{2}\bar{1}1, 31\bar{1})$	1625	760	61·37	28·40	89·77	32·97
f	$(\bar{1}\bar{1}1, 21\bar{1})$	1210	870	77·33	28·40	48·93	74·27
h	$(\bar{3}\bar{1}1, 41\bar{1})$	1088	370	25·13	28·40	3·27	53·53
b	$(\bar{2}\bar{1}0, 310)$	370	260	45·93	0·0	45·93	45·93
—	$(\bar{4}\bar{2}1, 52\bar{1})$	308	—	(2)	15·13	—	—
j	$(\bar{3}\bar{2}1, 42\bar{1})$	264	43	46·93	15·13	31·80	62·06
d	$(0\bar{2}0, 120)$	216	170	75·11	0·0	75·11	75·11
c	$(\bar{2}\bar{2}0, 320)$	135	50	57·28	0·0	57·28	57·28
—	$(\bar{5}\bar{2}1, 62\bar{1})$	128	—	(2)	15·13	—	—
m	$(\bar{2}\bar{1}5, 31\bar{5})$	116	20	68·57	69·70	1·13	41·73
—	$(\bar{3}\bar{1}0, 410)$	110	—	(2)	0·0	—	—
l	$(\bar{1}\bar{2}4, 22\bar{4})$	103	20	68·13	47·24	20·89	64·63
n	$(0\bar{1}5, 11\bar{5})$	97	16	62·93	69·70	6·77	47·37
i	$(0\bar{1}1, 11\bar{1})$	83	63	82·78	28·40	54·38	68·82
r	$(0\bar{3}1, 13\bar{1})$	73	10	67·42	10·22	57·20(3)	77·64
e	$(\bar{1}\bar{2}0, 220)$	72	50	69·42	0·0	69·42	69·42
p	$(0\bar{3}\bar{5}, 135)$	70	16	47·03	42·02	5·01	89·05(4)
q	$(\bar{3}\bar{1}5, 41\bar{5})$	69	16	65·22	69·70	4·48	45·08
t	$(\bar{1}\bar{1}5, 21\bar{5})$	66	< 10	67·82	69·70	1·88	42·48
k	$(\bar{2}\bar{2}4, 32\bar{4})$	64	16	67·13	47·24	19·89	65·63
s	$(0\bar{1}4, 11\bar{4})$	63	10	69·03	65·19	3·84	45·78(5)
u	$(0\bar{2}4, 12\bar{4})$	59	12	65·15	47·24	17·91	67·61
v	$(\bar{3}\bar{1}4, 41\bar{4})$	55	< 10	65·28	65·19	0·09	49·53
w	$(\bar{3}\bar{4}4, 44\bar{4})$	54	10	49·98	28·40	21·58	78·38
x	$(\bar{2}\bar{1}9, 31\bar{9})$	51	< 10	47·74	78·38	30·64(6)	53·88
—	$(\bar{4}\bar{1}1, 51\bar{1})$	39	—	(2)	28·40	—	—

(1) Mathieson *et al.* (1950). (2) $\cos\gamma > 1$. (3) Overlaps *c*. (4) Overlaps *g*. (5) Overlaps *b*. (6) Unobserved.

seen in these than in the thin samples. There was considerable advantage in using counter rather than film techniques. The extremely weak reflexions were not observed on the films; on the recorder charts, the weakest reflexions had peaks about 5–10 cps above a background of about 30 ± 5 cps, still discernible (Figs. 2 and 3). The tabulated reflexions labelled *m* to *x* are of this weak intensity, and only by comparing with other runs was it possible to verify their presence. With any slight misorientation of the crystal they disappear. For instance, reflexions $m(\bar{2}\bar{1}5, 31\bar{5})$ appear in Fig. 2 at ±1·13°, and at ±41·73°. The former can be seen in the structure between reflexions *h* on either side of the zero mark on the chart; the latter, at 41·73°, is the small pip about one-third of the way between *b* and *g*, near the center of the chart. This illustration is typical of very weak reflexions.

A General Electric XRD-3 source was used, operated at 40 kV, 20 mA. The beam was monochromatized by reflexion from lithium fluoride. A General Electric No. 3 detector unit was employed with the Geiger tube and preamplifier interchangeable with the film holder of the multiple diffraction spectrometer (Fraenkel, 1958).

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