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Setting a single crystal by non-equatorial X-ray reflexions.

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Normal X-ray methods of orienting a crystal to rotate accurately about a principal symmetry axis fail when no reflexions in the equatorial layer line can be identified. A review of methods hitherto published is included in a comprehensive paper by Jeffery (1949) but to meet a particular problem, not covered by methods discussed by Jeffery, a technique was developed which has a wider applicability.

It was necessary to set a crystal of a lamellar mineral to rotate accurately about the sixfold axis perpendicular to the lamellae. From the external form this could easily be done to within 5°, but as the hexagonal unit cell had dimensions $a = 9{\cdot}7$ and $c = 133$ Å it was quite impossible to identify equatorial reflexions. As the row lines were well separated the following method was used.

Three 5°-oscillation photographs were taken on the same film at exactly 120° intervals of azimuth (using a Unicam single-crystal X-ray goniometer). To enable these three superimposed photographs to be distinguished, the cassette was rotated by about 2° to each side of its normal position so that the three equivalent row lines appeared side by side. When exactly set to rotate about the hexad axis, corresponding features on the three row lines lie at the same distance from the equator of the photograph, but when mis-set their relative displacements give the corrections necessary.

Suppose α_1, α_2 and α_3 were the angular distances of three equivalent reciprocal-lattice vectors from the axis of rotation. The distances y_1, y_2 and y_3 of the corresponding reflexions from an equatorial line scribed on the film were measured as accurately as possible and ζ_1, ζ_2 and ζ_3 were obtained from $\zeta = y(r^2+y^2)^{-\frac{1}{2}}$. ξ for the particular row line used was calculated or measured and hence, from $\cot\alpha = \zeta/\xi$, α_1, α_2 and α_3 were found. As the differences of α values are small (less than 5°), and as infinitesimal rotations can be treated as vectors, the resultant of three vectors of magnitudes $(90°-\alpha_1)$, $(90°-\alpha_2)$ and $(90°-\alpha_3)$ spaced 120° apart gave the magnitude and direction of the necessary correction. The direction of this correction was known to $\pm 2\frac{1}{2}°$ from the oscillation range. The angular correction was resolved into two components parallel to the two arcs. Adding the vectors, relating them to the positions of the arcs, and resolving the resultant correction parallel to the arcs were done graphically. If the initial setting of the lower arc were far from zero, correction for the tilt of the upper arc would have to be applied, being found by solving a spherical triangle. The corrections obtained are not exact and two applications are necessary for setting to 0·1°.

The method can of course be used for other than sixfold axes if the rotation intervals are chosen appropriately.

Reference

JEFFERY, J. W. (1949). *Acta Cryst.* **2**, 15.

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The direct-inspection method in systems with a principal axis of symmetry.

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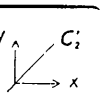
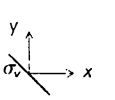
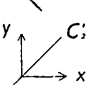
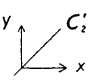
The direct-inspection method (Fumi, 1952*a*)* can be used *to obtain directly* the independent components of tensor properties of matter only for symmetry groups in which one can find Cartesian orthogonal coordinates that do not transform into linear combinations of themselves under the independent symmetry elements. The Cartesian orthogonal reference frames usually applied for groups with a principal axis $C_n(n \geq 3)$ (z||to the axis, x and $y \perp$ to it) satisfy this condition only for $n = 4$, but there are other frames which allow direct inspection in

Table 1

Finite groups with a principal axis $C_n(n \geq 3)$		Generating elements besides C_n	Possible choices of x and y		
n even	n odd				
D_n	D_n	C_2'	$x\|\|C_2'$	$y\|\|C_2'$	
C_{nv}	C_{nv}	σ_v	$yz\|\|\sigma_v$	$zx\|\|\sigma_v$	
C_{nh}	C_{nh}	σ_h		Any	
D_{nh}	D_{nh}	C_2', σ_h	$x\|\|C_2'$	$y\|\|C_2'$	
	C_{ni}	i		Any	
	D_{nd}	C_2', i	$x\|\|C_2'$	$y\|\|C_2'$	

C_2' = binary axis $\perp C_n$; $\sigma_v(\sigma_h)$ = symmetry plane||$(\perp)C_n$; i = inversion.

* In this paper § 3 (*a*) is somewhat too condensed to be completely clear. Equations (9) and (10), like equations (6) and (7), are relations between equations (3); when written fully, equation (9) reads

$$t_{xyz} = t_{yzx} = t_{zxy} = t_{xzy} = t_{yxz} = t_{zyx}.$$

The last sentence of § 3 (*a*) states the identity of the scheme of independent components of the axial and polar third-order tensors for symmetry O with the scheme of the axial third-order tensor for symmetry T_d.

Table 2. *Symmetry* C_3: $x \to -\frac{1}{2}x+\frac{1}{2}\sqrt{3}.y$, $y \to -\frac{1}{2}\sqrt{3}.x-\frac{1}{2}y$, $z \to z$

	$x^2 \to \frac{1}{4}x^2+\frac{3}{4}y^2-\frac{1}{2}\sqrt{3}.xy$	$y^2 \to \frac{3}{4}x^2+\frac{1}{4}y^2+\frac{1}{2}\sqrt{3}.xy$	$z^2 \to z^2$	$yz \to -\frac{1}{2}\sqrt{3}.zx-\frac{1}{2}yz$	$zx \to -\frac{1}{2}zx+\frac{1}{2}\sqrt{3}.yz$	$xy \to \frac{1}{4}\sqrt{3}.x^2-\frac{1}{4}\sqrt{3}.y^2-\frac{1}{2}xy$
x^2	$\frac{1}{16}x^4+\frac{9}{16}y^4+\frac{3}{4}xyxy+$ $+\frac{3}{16}x^2y^2+\frac{3}{16}y^2x^2-$ $-\frac{1}{8}\sqrt{3}.x^2xy-\frac{1}{8}\sqrt{3}.xyx^2-$ $-\frac{3}{8}\sqrt{3}.y^2xy-\frac{3}{8}\sqrt{3}.xyy^2$	$\frac{3}{16}x^4+\frac{3}{16}y^4-\frac{3}{4}xyxy+$ $+\frac{1}{16}x^2y^2+\frac{9}{16}y^2x^2+$ $+\frac{1}{8}\sqrt{3}.x^2xy-\frac{3}{8}\sqrt{3}.xyx^2+$ $+\frac{3}{8}\sqrt{3}.y^2xy-\frac{1}{8}\sqrt{3}.xyy^2$	$\frac{1}{4}x^2z^2+\frac{3}{4}y^2z^2-\frac{1}{2}\sqrt{3}.xyz^2$	$-\frac{1}{8}\sqrt{3}.x^2zx-\frac{1}{8}x^2yz-$ $-\frac{3}{8}\sqrt{3}.y^2zx-\frac{3}{8}y^2yz+$ $+\frac{3}{4}xyzx+\frac{1}{4}\sqrt{3}.xyyz$	$-\frac{1}{8}x^2zx+\frac{1}{8}\sqrt{3}.x^2yz-$ $-\frac{3}{8}y^2zx+\frac{3}{8}\sqrt{3}.y^2yz+$ $+\frac{1}{4}\sqrt{3}.xyzx-\frac{3}{4}xyyz$	$\frac{1}{16}\sqrt{3}.x^4-\frac{3}{16}\sqrt{3}.y^4+$ $+\frac{1}{4}\sqrt{3}.xyxy-\frac{1}{16}\sqrt{3}.x^2y^2+$ $+\frac{3}{16}\sqrt{3}.y^2x^2-\frac{1}{8}x^2xy-$ $-\frac{3}{8}xyx^2-\frac{3}{8}y^2xy+\frac{3}{8}xyy^2$
y^2		$\frac{9}{16}x^4+\frac{1}{16}y^4+\frac{3}{4}xyxy+$ $+\frac{3}{16}x^2y^2+\frac{3}{16}y^2x^2+$ $+\frac{3}{8}\sqrt{3}.x^2xy+\frac{3}{8}\sqrt{3}.xyx^2+$ $+\frac{1}{8}\sqrt{3}.y^2xy+\frac{1}{8}\sqrt{3}.xyy^2$	$\frac{3}{4}x^2z^2+\frac{1}{4}y^2z^2+\frac{1}{2}\sqrt{3}.xyz^2$	$-\frac{3}{8}\sqrt{3}.x^2zx-\frac{3}{8}x^2yz-$ $-\frac{1}{8}\sqrt{3}y^2zx-\frac{1}{8}y^2yz-$ $-\frac{3}{4}xyzx-\frac{1}{4}\sqrt{3}.xyyz$	$-\frac{3}{8}x^2zx+\frac{3}{8}\sqrt{3}.x^2yz-$ $-\frac{1}{8}y^2zx+\frac{1}{8}\sqrt{3}.y^2yz-$ $-\frac{1}{4}\sqrt{3}.xyzx+\frac{3}{4}xyyz$	$\frac{3}{16}\sqrt{3}.x^4-\frac{1}{16}\sqrt{3}.y^4-$ $-\frac{1}{4}\sqrt{3}.xyxy-\frac{3}{16}\sqrt{3}.x^2y^2+$ $+\frac{1}{16}\sqrt{3}.y^2x^2-\frac{3}{8}x^2xy+$ $+\frac{3}{8}xyx^2-\frac{1}{8}y^2xy-\frac{3}{8}xyy^2$
z^2			z^4	$-\frac{1}{2}\sqrt{3}.z^2zx-\frac{1}{2}z^2yz$	$-\frac{1}{2}z^2zx+\frac{1}{2}\sqrt{3}.z^2yz$	$\frac{1}{4}\sqrt{3}.z^2x^2-\frac{1}{4}\sqrt{3}.z^2y^2-\frac{1}{2}z^2xy$
yz	All these equations can be obtained by exchanging the two pairs of indices in the corresponding equations on the other side of the diagonal.			$\frac{3}{4}zxzx+\frac{1}{4}yzyz+$ $+\frac{1}{4}\sqrt{3}.(zxyz+yzzx)$	$\frac{1}{4}\sqrt{3}.zxzx-\frac{1}{4}\sqrt{3}.yzyz-$ $-\frac{3}{4}zxyz+\frac{1}{4}yzzx$	$-\frac{3}{8}zxx^2+\frac{3}{8}zxy^2+$ $+\frac{1}{4}\sqrt{3}.zxxy-\frac{1}{8}\sqrt{3}.yzx^2+$ $+\frac{1}{8}\sqrt{3}.yzy^2+\frac{1}{4}yzxy$
zx					$\frac{1}{4}zxzx+\frac{3}{4}yzyz-$ $-\frac{1}{4}\sqrt{3}.(zxyz+yzzx)$	$-\frac{1}{8}\sqrt{3}.zxx^2+\frac{1}{8}\sqrt{3}.zxy^2+$ $+\frac{1}{4}zxxy+\frac{3}{8}yzx^2-\frac{3}{8}yzy^2-$ $-\frac{1}{4}\sqrt{3}.yzxy$
xy						$\frac{3}{16}x^4+\frac{3}{16}y^4+\frac{1}{4}xyxy-$ $-\frac{3}{16}x^2y^2-\frac{3}{16}y^2x^2-$ $-\frac{1}{8}\sqrt{3}.x^2xy-\frac{1}{8}\sqrt{3}.xyx^2+$ $+\frac{1}{8}\sqrt{3}.y^2xy+\frac{1}{8}\sqrt{3}.xyy^2$

Table 3. *Fourth-order tensor* $pq(p, q = 1, 2, 3, 4, 5, 6)$

Polar, axial	Polar	Axial	Polar		Axial	Axial	Polar		Axial	Axial	Polar		Axial	Axial
C_1	C_3, C_{3i}	C_3	C_{3v}	D_3, D_{3d}	D_3	C_{3v}	C_{3h}, C_6, C_{6h}	C_6	C_{3h}	D_{3h}	C_{6v}	D_6, D_{6h}, D_{3h}	D_6	C_{6v}
Any	$z\|\|C_3$	$z\|\|C_3$	$z\|\|C_3$	$x\|\|C_2'$	$x\|\|C_2'$	$z\|\|C_3$	$z\|\|C_3, C_6$	$z\|\|C_6$	$z\|\|C_3$	$x\|\|C_2'$	$z\|\|C_6$	$x\|\|C_2'$	$x\|\|C_2'$	$z\|\|C_6$
			$yz\|\|\sigma_v$	$z\|\|C_3$	$z\|\|C_3$	$yz\|\|\sigma_v$				$z\|\|C_3$	$yz\|\|\sigma_v$	$z\|\|C_3, C_6$	$z\|\|C_6$	$yz\|\|\sigma_v$
11	11		11		0	11	0		0	0	11		0	
12	12		12		0	12	0		0	0	12		0	
13	13		13		0	13	0		0	0	13		0	
14	14		14		0	0	14		14	14	0		0	
15	15		0		15	0	15		0	0	0		0	
16	16		0		16	16	0		0	0	0		16	
21	12		12		0	12	0		0	0	12		0	
22	11		11		0	11	0		0	0	11		0	
23	13		13		0	13	0		0	0	13		0	
24	−14		−14		0	0	−14		−14	−14	0		0	
25	−15		0		−15	0	−15		0	0	0		0	
26	−16		0		−16	−16	0		0	0	0		−16	
31	31		31		0	31	0		0	0	31		0	
32	31		31		0	31	0		0	0	31		0	
33	33		33		0	33	0		0	0	33		0	
34	0		0		0	0	0		0	0	0		0	
35	0		0		0	0	0		0	0	0		0	
36	0		0		0	0	0		0	0	0		0	
41	41		41		0	0	41		41	41	0		0	
42	−41		−41		0	0	−41		−41	−41	0		0	
43	0		0		0	0	0		0	0	0		0	
44	44		44		0	44	0		0	0	44		0	
45	45		0		45	45	0		0	0	0		45	
46	46		0		46	0	46		0	0	0		0	
51	−46		0		−46	0	−46		0	0	0		0	
52	46		0		46	0	46		0	0	0		0	
53	0		0		0	0	0		0	0	0		0	
54	−45		0		−45	−45	0		0	0	0		−45	
55	44		44		0	44	0		0	0	44		0	
56	41		41		0	0	41		41	41	0		0	
61	−16		0		−16	−16	0		0	0	0		−16	
62	16		0		16	16	0		0	0	0		16	
63	0		0		0	0	0		0	0	0		0	
64	−15		0		−15	0	−15		0	0	0		0	
65	14		14		0	0	14		14	14	0		0	
66	$\frac{1}{2}(11-12)$		$\frac{1}{2}(11-12)$		0	$\frac{1}{2}(11-12)$	0		0	0	$\frac{1}{2}(11-12)$		0	

The axial tensor vanishes identically for symmetries C_{3i}, D_{3d}, C_{6h} and D_{6h}.

C_3, C_{3i} and C_{3v}. The remaining groups with a principal axis cannot be treated directly by this method.

Direct inspection can be used, however, *to derive* the independent tensor components in all groups with a principal axis from the independent components in the corresponding group C_n. Indeed, the usual Cartesian orthogonal coordinates with $z||C_n$ do not transform into linear combinations of themselves under the generating elements to be added to the group C_n to obtain the other groups with the same principal axis, if one fixes properly x and y (Table 1).

The independent Cartesian orthogonal components in the groups C_n can be obtained by imposing invariance on each component (Hermann, 1934), conveniently replaced by the corresponding coordinate product (Fumi 1952*a*; Juretschke 1952): in the equivalent† frames with $z||C_n$, the algebra is fairly simple since only x and y transform among each other. Ob- viously the scheme for symmetry C_6 can always be obtained by direct inspection of the scheme for symmetry C_3 since C_6 is equivalent to C_{3h} for polar properties of even order or for axial properties of odd order, and it cannot distinguish polar and axial properties.

As a simple application we treat here a (polar or axial)

† The reference frames which are not distinguishable in their relations to the symmetry elements of a given group are equivalent for it.

fourth-order tensor $pq(p, q = 1, 2, 3, 4, 5, 6)$ in all trigonal and hexagonal groups: an higher order tensor is treated elsewhere (Fumi, 1952*b*). The equations of invariance for symmetry C_3 are obtained in Table 2: for instance, the equation for the z^2yz component reads $z^2yz = -\frac{1}{2}\sqrt{3}z^2zx - \frac{1}{2}z^2yz$. Direct inspection of the common scheme for symmetry C_3 (Table 3) gives the schemes of the polar and of the axial tensor pq for symmetries $C_{3v}(\sigma_v, x \to -x, y \to y, z \to z)$ and $C_{3h}(\sigma_h, x \to x, y \to y, z \to -z)$; for the *polar* tensor, the independent components for symmetry C_3 which are odd in x or in z vanish in C_{3v} and in C_{3h} respectively, while for the *axial* tensor these components are the only non-vanishing ones. Direct inspection of the common scheme for symmetry C_6 yields in a similar fashion the schemes for symmetry C_{6v}, and direct inspection of the common scheme for symmetry D_3 provides the scheme of the axial tensor for symmetry D_{3h}. The independent components of the axial tensor coincide with those of the polar tensor for symmetry D_6, as for the other groups which do not contain improper rotations (Fumi, 1952 a). The independent components of the polar tensor are the same in symmetry groups which differ by the inversion (Fumi, 1952 *a*).

The results for the polar tensor pq can be compared with the schemes of photoelastic constants (Szivessy, 1929; Bond, 1943; Mason, 1950; for C_3, C_{3i}, C_{3h}, C_6 and C_{6h} see, however, Bhagavantam, 1942).

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Globulite units in protein crystals?*

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It has recently been remarked (Wrinch, 1952*a*) that certain findings regarding residue numbers favor the possibility that the horse hemoglobin and myoglobin structures and the insulin and ribonuclease structures are particles made up of various complements of molecules in various arrays, all the molecules having skeletons of NCC polymers of similar type. In this note we study this hypothesis in the light of certain intensity data obtained in X-ray crystal studies which are recorded in the literature (Perutz, 1949; Boyes-Watson, Davidson & Perutz, 1947; Kendrew, 1950). In particular we look for evidence for or against the hypothesis (Wrinch, 1937) that such skeletons, if present, are globulite (and indeed cage-like) in character, not differing grossly in dimensions in various directions.

For the monoclinic horse methemoglobin crystal, the mean intensity curve as a function of distance from the origin (Perutz, 1949) and the (*h*0*l*) intensities (Boyes-Watson *et al.*, 1947) are recorded. To test the globulite hypothesis, or any other hypothesis as to shape, it is of course fruitless to study the mean intensity curve in isolation. However the (*h*0*l*) intensities throw light on the situation, when studied in conjunction with it. Perutz's (1949) mean intensity curve (small curve in Fig. 1) represents the *spherical smoothing* of all the intensities. Let us then construct, from the (*h*0*l*) intensities, the mean intensity curve as a function of distance from the origin, thus *circularly smoothing* these co-planar intensities (last curve of Fig. 1). We remark that sufficiently far from the origin there is a general resemblance between the two curves. Both descend from relatively high values to a minimum at *c.* 0·17 Å^{-1} and both subsequently develop a maximum at *c.* 0·22 Å^{-1}. So far as it goes, this situation is in accord with the hypothesis that the

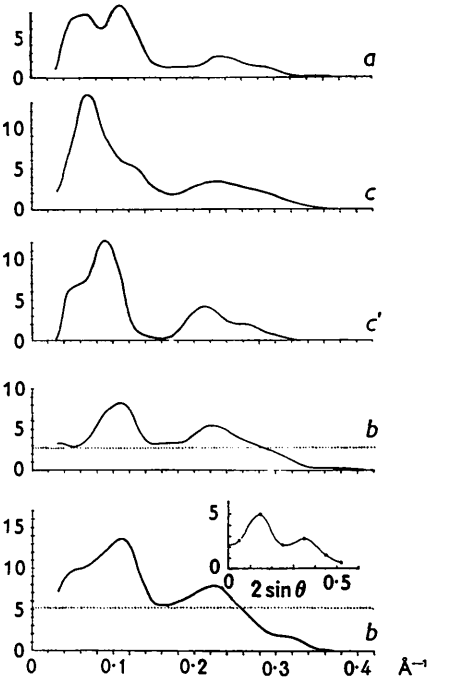

Fig. 1. Inset curve: Perutz's means intensity curve for the horse methemoglobin crystal as a function of distance from the center (Perutz, 1949). Lowest curve: the circularly smoothed intensity function for the same crystal, calculated from the given (*h*0*l*) intensities (Boyes-Watson *et al.*, 1947). Upper four curves: the circularly smoothed intensity functions for the horse myoglobin crystal calculated from the given intensities on central planes normal to *a*, *c*, *c*′ and *b* respectively (Kendrew, 1950).

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