

the Bragg angle. This result, however, has to be modified for actual crystals having finite absorption. For mosaic crystals, the ratio is $\cos^2 2\theta:1$, independent of absorption, and it can be shown that for perfect crystals, the value of the ratio (α) progressively deviates from $|\cos 2\theta|$ towards $\cos^2 2\theta$ with increasing absorption. The value of α depends in a complex way on the structure factor, Bragg angle, linear absorption coefficient and other constants of the crystal, and could be calculated for any particular case from the semi-empirical formulae derived by Hirsch & Ramachandran (1950).

The change of the ratio with the degree of perfection was observed by Ramaseshan & Ramachandran (1953, 1954), using natural and ground surfaces of a crystal of sodium nitrate. Measurements made with polarized X-rays, on a natural cleavage of a perfect crystal of calcite are reported here. The investigation was undertaken to see whether, for a perfect crystal, the theoretically predicted value different from $|\cos 2\theta|$ is actually found. The natural surface used by Ramaseshan & Ramachandran was not perfect and they obtained a value less than that given by theory, even taking absorption into account. Calcite can be obtained in a highly perfect condition and, further, it has a fairly large linear absorption coefficient (190 cm.^{-1} , for $\text{Cu } K\alpha$ radiation). Consequently, the theoretical values for the perfect crystal in this case are appreciably different according as to whether absorption is taken into account or not.

The second- and third-order reflexions from a cleavage face of calcite were studied. The integrated intensities at various azimuths of polarization were obtained by a Geiger-counter spectrometer, similar to that adopted by Ramaseshan & Ramachandran (1954) for the study of the degree of perfection of NaNO_3 . However, the following improvements were incorporated: (a) The monochromatic polarized beam of $\text{Cu } K\alpha$ radiation was obtained by using a 311 reflexion from a single crystal of copper, which occurs at $\theta = 45^\circ 6'$; thus the beam was almost completely polarized. (b) For each azimuthal setting the crystal was oscillated at a slow uniform rate through 3° on either side of the Bragg angle, by means of a synchronous motor, and the integrated intensity was found from the total number of counts recorded by the Geiger counter during this period, a correction being made for the background. The measured integrated intensities had an accuracy of 5%.

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A simplified computation technique for structure refinement by means of two-dimensional $F_o - F_c$ synthesis. By E. HARNIK, *Physics Department, Hebrew University, Jerusalem, Israel*

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In the course of a refinement cycle of a centrosymmetric projection by means of two-dimensional $F_o - F_c$ synthesis each atom is shifted along the gradient, at the same atomic coordinates, of the function

$$D(u, w) + D(x/a, z/c) + \sum_h \sum_l (F_o - F_c)_{hl} \cos 2\pi(hx/a + lz/c).$$

It follows that the only use one makes of the figure field is the determination of the magnitude and direction of these gradients, and, therefore, one may be interested

The results for the two reflexions are given in Table 1. The theoretical values of $r(\varphi)$ were calculated from the formula $r(\varphi) = \cos^2 \varphi + \alpha \sin^2 \varphi$.

It is seen from the table that within the limits of accuracy of the measurements, the data agree with the values calculated from the dynamical theory, taking absorption into account. It is also interesting to note that when the absorption coefficient is large the range of variation of α from a perfect to a mosaic crystal is appreciably less than the difference between $|\cos 2\theta|$ and $\cos^2 2\theta$.

Table 1. *Variation of integrated intensity with the azimuth of polarization for calcite.*

$r(\varphi)$ is the ratio of the value at azimuth φ to that for azimuth zero. The subscripts PN , PA and M respectively stand for perfect non-absorbing, perfect absorbing and ideally mosaic.

Reflection* and Bragg angle	φ ($^\circ$)	30	45	60	75	90
422 30° 30'	$r_{PN}(\varphi)$	0.871	0.742	0.614	0.519	0.485
	$r_{PA}(\varphi)$	0.844	0.687	0.531	0.416	0.374
	$r(\varphi)$	—	0.676	0.518	0.400	0.352
	$r_M(\varphi)$	0.809	0.618	0.426	0.286	0.235
633 49° 39'	$r_{PN}(\varphi)$	0.790	0.581	0.371	0.218	0.162
	$r_{PA}(\varphi)$	0.767	0.535	0.324	0.132	0.070
	$r(\varphi)$	0.777	0.597	0.324	0.139	0.069
	$r_M(\varphi)$	0.756	0.513	0.280	0.091	0.026

* The indices are referred to the X-ray unit cell with $a = 6.361 \text{ \AA}$, $\alpha = 46^\circ 7'$ (Wyckoff, 1948).

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References

- HIRSCH, P. B. & RAMACHANDRAN, G. N. (1950). *Acta Cryst.* **3**, 187.
 RAMASESHAN, S. & RAMACHANDRAN, G. N. (1953). *Acta Cryst.* **6**, 364.
 RAMASESHAN, S. & RAMACHANDRAN, G. N. (1954). *Proc. Indian Acad. Sci. A*, **39**, 20.
 WYCKOFF, R. W. G. (1948). *Crystal Structures*, vol. 1, chap. 7, p. 7. New York: Interscience Publishers.

in computing the figure field only in the immediate neighbourhood of the atomic positions. This, however, cannot be done conveniently with the Bevers-Lipson strips when used in the conventional way, but it can be performed quite easily and rapidly if the strips are given a different interpretation.

The Bevers-Lipson strips present the function $A \cos 2\pi hu$ or $A \sin 2\pi hu$; for any given value of A and of h there is a strip on which the values of the function

are given at the points $u = n/120$, on the one side for $n = 0, 2, \dots, 30$, and on the other for $n = 1, 3, \dots, 29$. Now any strip, $A \cos 2\pi h_1 u$ for instance, can be looked upon as presenting the values of the function at the point $u_1 = h_1/120$, for the values of $h = n = 0, 2, \dots, 30$ and $h = n = 1, 3, \dots, 29$ respectively, (or at $u_1 = h_1/60$ for $h = 1, 2, \dots, 15$, on the even side of the strip). Consequently the value of the function

$$C(u, w) = \sum_h \sum_l D_{hl} \cos 2\pi hu \cdot \cos 2\pi lz = \sum_h B_h(w) \cos 2\pi hu,$$

at points (u_i, w_j) , at intervals of $1/60$, can be calculated in the following way. First one prepares, in the conventional way, the figure table $B_h(w) = \sum_l D_{hl} \cos 2\pi lw$, then, laying the strip $A = 10$ (or 100, according to the accuracy needed) and $h = 60u_i$ of the cos function under the line of figures corresponding to w_j on the $B_h(w)$ table, one multiplies the two lines of figures additively, as can be conveniently done with most business computing machines. When the figure field is desired at point intervals of $1/120$, a set of strips with $A = 10$ (or 100) and the values of the function for $n = 1, 2, \dots, 30$ all written on the same side, should be prepared. The sine term

$$S(u, w) = \sum_h \sum_l D_{hl} \sin 2\pi hu \cdot \sin 2\pi lw$$

can be calculated in exactly the same way, using the sin strips. To obtain the value of $D(u_i, w_j)$, the tables for the different terms, with the respective strips on them, are laid side by side and the additive multiplication is carried through the lines $w = w_j$, on the different tables. The results can be copied from the computing machine right to the figure map, this being also facilitated by the fact that the indices (i, j) on the tables and strips coincide with those of the points on the map.

This technique was applied, with considerable success, to the refinement of the atomic coordinates in the structure analysis of dianthrone (Harnik & Schmidt, 1954). It is fairly rapid and, as one gets accustomed, can be performed almost automatically. Compared to the conventional technique the time needed to perform a cycle of refinement is reduced by approximately 50%.

Reference

- HARNIK, E. & SCHMIDT, G. M. J. (1954). *J. Chem. Soc.* p. 3295.

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The X-ray crystallography of 2,6-dimethyl- γ -pyrone. By GEORGE M. BROWN and HILLYER G. NORMENT, *Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.*

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The unusual chemical behavior of the γ -pyrones (reviewed by Fried, 1950) has prompted an investigation in this laboratory of the structure of 2,6-dimethyl- γ -pyrone by single-crystal X-ray methods. Rotation, Weissenberg, and precession photographs have been taken using $\text{Cu K}\alpha$ radiation. Analysis of the films yields the following data:

$$a = 7.672 \pm 0.007, \quad b = 7.212 \pm 0.007, \quad c = 13.92 \pm 0.01 \text{ \AA}, \\ \beta = 120^\circ 59' \pm 2';$$

axial ratios: 1.0638:1:1.9301; space group: $C_{2h}^5-P2_1/c$.

The transformation $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{a} - \mathbf{c}$ gives a cell with axial ratios 1.0638:1:1.6563 and $\beta = 92^\circ 28'$ (space group $P2_1/n$), in fair agreement with the ratios 1.0599:1:1.6441 and angle $\beta = 92^\circ 30'$ determined goniometrically by Wyrouboff (1909) and recorded by Groth (1919).

The space group $P2_1/c$ is uniquely established by the extinction of reflections $0k0$ for odd values of k and of reflections $h0l$ for odd values of l . The absence of centrosymmetry in the molecules of 2,6-dimethyl- γ -pyrone requires that there be at least four molecules in the unit cell. The calculated density for four molecules is 1.249 g.cm.^{-3} ; the observed density by the flotation method is 1.254 g.cm.^{-3} .

The equi-inclination, multiple-film Weissenberg method has been used to collect intensity data. The crystal specimens used were approximately cylindrical, about 0.4 mm. in diameter, enclosed in thin-wall glass capillaries

to prevent evaporation. Of the 1450 reflections theoretically accessible, using $\text{Cu K}\alpha$ radiation, about 1200 have been recorded, and their intensities have been estimated visually. After correction for the Lorentz and polarization factors, the data have been put on an absolute basis by the Wilson (1942) method; and the B value of the temperature factor has been established as $4.15 \times 10^{-16} \text{ cm.}^2$. Preliminary calculations are in progress for application of the Hauptman-Karle (1953) method of solution.

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References

- FRIED, J. (1950). 'Monocyclic Pyrans, Pyrones, Thiapyrans, and Thiapyrones', chap. 7 in *Heterocyclic Compounds*, vol. I (R. C. Elderfield, Editor). New York: Wiley.
- GROTH, P. (1919). *Chemische Kristallographie*, vol. 5, p. 641. Leipzig: Engelmann.
- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A. C. A. Monograph No. 3. Wilmington: The Letter Shop.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
- WYROUBOFF, G. (1909). *Bull. Soc. franç. Minér.* **32**, 336.