result from the tension created by the drag of the melt on the seed.

We may also consider the idea that deposition of atoms around ending dislocation lines may initially occur as circular, and then may become polygonal, and in particular hexagonal as is known from many cases of crystal growth (Smakula, 1962). Superposition of all of these 'unit cells' around dislocations may then give the observed hexagonal geometry. However, it is quite unlikely that polygonal spirals grow around dislocations while the crystal is pulled from the melt. Thus, all that remains is to believe in the tendency of equilibrium to form hexagonal geometry, of which nature is known to give many examples. Several types of single crystal grown from the melt were shown to exhibit a hexagonal network the size and regularity of which were found to depend upon speed of growth, temperature gradient, and impurity content, but have nothing to do with crystal structure. Rutter & Chalmers (1952) have shown that these hexagonal cells of that network essentially consist of a particular distribution of impurities resulting from non-equilibrium during solidification. The hexagonal geometry reported in this paper, however, was found not to depend on impurities; thus, Rutter & Chalmer's concept does not apply to the present case.

The interpretation above of the acoustically formed hexagonal geometry implies that an increase in the rate of growth is expected to accompany the increase in the density of defects at the solid-liquid interface. It was quite gratifying that an increase in rate of growth, v, actually occurred during acoustic irradiation (this increase as mentioned in the preceding section amounted to as much as a factor of 1·6 to 1·8). It is still necessary to show that such an increase in v can not be achieved by much simpler effects than dislocation activation *etc.*, for instance by acoustically affected cooling of the solid phase.

For 'conventional' growth (when no sound is applied), Andrade & Roscoe (1937) correlate the rate of growth, v, with the temperature gradient G, in the form

$$v = \frac{(1+K_1/K_2)K_1}{L}\cdot G \qquad (2)$$

where K_1 and K_2 represent the thermal conductivity of the crystal and the melt, respectively, and L is the heat of crystallization per unit volume. This correlation is known to be a qualitative description rather than a quantitative one. However, an increase in v by as much as 1·6 to 1·8 requires a decrease in the temperature of the solidifying crystal by some 20° C. However, no changes greater than 8 °C were measured, and thus acoustic cooling can not account for the observed increase in v.

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The Determination of Axial Ratios from Powder Diffraction Patterns

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Accurate axial ratios of anisotropic crystalline phases can be obtained from precision powder data by computing exhaustively the axial ratios from pairs of closely spaced, non-overlapping reflections. The method has been applied successfully to the tetragonal, hexagonal, orthorhombic, and monoclinic systems.

The determination of axial ratios with the reflecting goniometer was developed into a precise technique by mineralogists of the nineteenth century. Compendia such as Dana's *System of Mineralogy* or Groth's *Chemische Krystallographie* are replete with this type of morphological information which has been of immense value to X-ray crystallographers. During the past three decades, mineralogists have shifted from the determination of axial *ratios* by optical goniometry to the determination of unit-cell *dimensions* by X-ray diffraction. Single-crystal methods, in general, have proved vastly superior to the powder methods in establishing the correct unit cell of a crystalline phase. However, in many cases, the accuracy of these cell constants is not sufficiently high to yield axial ratios comparable in accuracy to those determined by the two-circle goniometer. The reason for this limited accuracy can be attributed largely to the general use of small-radius cameras for rotation or Weissenberg photographs. Modern powder methods, on the other hand, are capable of yielding axial ratios of greater accuracy than those obtained by the best morphological measurements (Frondel, 1962). There is an abundance of published data on precision measurements of lattice parameters of polycrystalline phases (Klug & Alexander, 1954; Edmunds, Lipson & Steeple, 1955; Azaroff & Buerger, 1957; Parrish & Wilson, 1959; I.U.Cr. Stockholm meeting, 1959); unfortunately, however, the substances investigated pertain to relatively simple structures for which unequivocally indexed back-reflections can be registered. For anisotropic substances with cell dimensions exceeding 6 Å, it is rather unusual to observe in the back-reflection region unambiguous pinacoid reflections of sufficient intensity for the reliable determination of lattice parameters. To circumvent this limitation of the powder method it has been found advantageous to compute exhaustively the axial ratios from pairs of closely spaced, non-overlapping reflections.

Theory

The *ratio* of two interplanar spacings, $d_m = d(h_m k_m l_m)$ and $d_n = d(h_n k_n l_n)$, can be determined with a minimum error when these spacings form a clearly resolved 'doublet' because as θ_n approaches θ_m (without overlapping) the principal systematic errors cancel out; *e.g.* film shrinkage, effective camera radius, absorption correction, beam divergence, and refraction correction at low θ. For an orthorhombic crystal, the square of this ratio is given by the expression

$$d_m^2 d_n^{-2} \doteq \frac{h_n^2 r_1^{-2} + k_n^2 + l_n^2 r_2^{-2}}{h_m^2 r_1^{-2} + k_m^2 + l_m^2 r_2^{-2}} = \frac{\sin^2(\theta_n - \Delta\theta_n)}{\sin^2(\theta_m - \Delta\theta_m)} \simeq \frac{\sin^2\theta_n}{\sin^2\theta_m}\,, \qquad (1)$$

where $r_1 = a/b$, $r_2 = c/b$, the cell edges follow the convention $0 < c < a < b$, and $\Delta\theta_n$ is the refraction correction of the glancing angle for d_n (Wilkens, 1960). From two such pairs of closely spaced reflections one can compute the axial ratios r_1 and r_2:

$$r_1 = \frac{\begin{vmatrix} (h_n^2 - h_m^2 d_m^2 d_n^{-2}) & (l_n^2 - l_m^2 d_m^2 d_n^{-2}) \\ (h_q^2 - h_p^2 d_p^2 d_q^{-2}) & (l_q^2 - l_p^2 d_p^2 d_q^{-2}) \end{vmatrix}^{\frac{1}{2}}}{\begin{vmatrix} (k_m^2 d_m^2 d_n^{-2} - k_n^2) & (l_n^2 - l_m^2 d_m^2 d_n^{-2}) \\ (k_p^2 d_p^2 d_q^{-2} - k_q^2) & (l_q^2 - l_p^2 d_p^2 d_q^{-2}) \end{vmatrix}^{\frac{1}{2}}}\,, \qquad (2)$$

and a comparable expression for r_2. Since the lattice constants are positive quantities, it follows that the determinants in expression (2) must be of the same sign for correctly indexed reflections. Although only three separate reflections are required to evaluate r_1 and r_2, the accuracy of these calculated values depends on the magnitude of the determinants and the precision of the experimentally determined ratios $d_m d_n^{-1}$ and $d_p d_q^{-1}$. It is obvious that as the numerator of (2) approaches zero, the answers for r_1 and r_2 become indeterminate (0/0). To guard against these fluctuations, the entire powder pattern is grouped into ν pairs of closely spaced, unequivocally indexed reflections from which $\nu(\nu-1)/2$ non-redundant values of r_1 and r_2 are obtained. After eliminating the highly inaccurate cases arising from unfavorably small determinants, one averages the many remaining answers to obtain the most probable values for r_1 and r_2. Specific programs have been compiled on the Burroughs 220 digital computer to perform these computations for the tetragonal, hexagonal, orthorhombic, and monoclinic systems.

Tetragonal system

If d_m and d_n are two independent reflections of a tetragonal phase, then the axial ratio c/a is given by:

$$c/a = \left[\frac{l_m^2 d_m^2 d_n^{-2} - l_n^2}{h_n^2 + k_n^2 - (h_m^2 + k_m^2) d_m^2 d_n^{-2}}\right]^{\frac{1}{2}}. \qquad (3)$$

To test the efficacy of the described method for obtaining accurate axial ratios, formula (3) was applied to the reliable powder pattern of $AgIO_4$ published by Swanson, Cook, Isaacs & Evans (1960). Of 48 recorded reflections, 14 were excluded because of superposition; from the remaining reflections 11 pairs, shown in Table 1, were selected for the test. The value $\Delta_{m,n}$ of the numerator of (3) is also recorded in Table 1 in order to estimate the accuracy of the corresponding c/a. Averaging the 11 answers for c/a, one arrives at an axial ratio that compares as shown in Table 2 with the literature.

In general it is essential to verify the correct assignment of indices of published powder data. The following typical procedure was adopted in the case of $AgIO_4$: (1) an average value of the a translation was determined as $5{\cdot}374 \pm 0{\cdot}002$ Å from 6 unambiguous $hk0$ reflections (200, 220, 400, 420, and 600); (2) the corresponding c translation was then calculated as ($5{\cdot}374 \pm 0{\cdot}002$ Å) ($2{\cdot}2509 \pm 0{\cdot}0024$) = $12{\cdot}096 \pm 0{\cdot}019$ Å; (3) with these lattice constants all permitted reflections were computed on a Recomp III computer employing a program written by Petersen

Table 1. *Selected powder reflections of* $AgIO_4$

hkl	*d*	$\Delta_{m,n}$	*c/a*
114	2·366 Å	15·1088	2·2493
211	2·358		
204	2·007	17·8717	2·2494
220	1·899		
224	1·608	−45·9038	2·2524
008	1·512		
040	1·343	−64·0000	2·2526
028	1·318		
404	1·228	16·6997	2·2494
420	1·202		
406	1·119	20·1290	2·2595
424	1·117		
309	1·0740	45·1813	2·2431
336	1·0728		
2,0,12	0·9438	80·9198	2·2507
428	0·9408		
620	0·8496	118·4782	2·2523
4,1,11	0·8407		
4,0,12	0·8062	80·6811	2·2509
448	0·8043		
448	0·8043	33·5779	2·2505
5,1,10	0·7945		

$$\Delta_{m,n} = l_m^2 d_m^2 d_n^{-2} - l_n^2$$

arithmetic mean $(\overline{c/a}) = 2{\cdot}2509 \pm 0{\cdot}0024$

Table 2. *Lattice constants and axial ratio of* $AgIO_4$

	a (Å)	*c* (Å)	*c/a*
Birckenbach & Buschendorf (1932)*	5·379	12·037	2·2378
Swanson *et al.* (1960)	5·374	12·094	2·2505
Author			2·2509 ± 0·0024

* Å from kX for all data prior to 1948.

& McKenney (1962). Only minor revisions were required (Table 3) which did not affect the indices of Table 1, with possibly one exception — the 4,1,11 reflection.

The re-indexed spacings emphasize the importance of excluding superposed reflections from formula (3). (For the application of formula (3) the reflections $h_mk_ml_m$ and $h_nk_nl_m$ are equivalent if $h_m^2+k_m^2=h_n^2+k_n^2$). One might be tempted to equate two unresolved reflections to calculate *c/a*. This is not a valid procedure because (1) the individual intensities of the supposedly overlapping reflections are usually not known, and (2) the assumed condition, $d_m=d_n$, arbitrarily ignores the experimental $\Delta\theta$-range within which two adjacent reflections are not resolved. In every instance of the fifteen $AgIO_4$ powder reflections with multiple *hkl*'s, the calculated *c/a* is either $\sqrt{5}$ or 0/0, if equal *d*'s are assumed.

Table 3. *Re-indexed reflections of* $AgIO_4$

hkl			
NBS	Dow	d_o	d_c
118	118	1·403 Å	1·4049 Å
	217		1·4030
316	316	1·299	1·2994
	109		1·3038
	411		1·2959
503	503	1·0384	1·0385
512	512		1·0383
	433		1·0385
532	532	0·9112	0·9111
	507 437		0·9127
622		0·8425	0·8414
	1,1,14	0·8425	0·8425
1,1,14		0·8407	0·8425
	622	0·8407	0·8414
	4,1,11		0·8405

Table 4. *Selected pairs of interplanar spacings of beryl,* $Be_3Al_2(SiO_3)_6$

hkl	*d*	$\Delta_{m,n}$	*c/a*
130	2·213 Å	11·9458	0·99755
014	2·208		
014	2·208	−11·2876	0·99729
131	2·152		
222	2·060	8·9534	0·99677
114	2·056		
141	1·7110	2·2140	0·99684
232	1·7007		
233	1·5710	11·9523	0·99727
125	1·5690		
125	1·5690	−18·7500	0·99763
330	1·5349		
330	1·5349	26·8981	0·99811
006	1·5320		
006	1·5320	−20·4094	0·99769
143	1·5138		
241	1·4882	2·1240	0·99754
332	1·4566		
332	1·4566	23·8852	0·99734
116	1·4535		
152	1·3682	23·8975	0·99731
126	1·3656		
126	1·3656	−27·0000	0·99671
060	1·3306		
127	1·2041	−30·2730	0·99754
253	1·1795		
336	1·0848	−20·7900	0·99881
263	1·0405		

$(\overline{c/a}) = 0{\cdot}99746 \pm 0{\cdot}00038$

$2c' = c/a = 0.99771$, Koksharov (1853).

Table 5. *Lattice constants and axial ratio of beryl*

	a	*c*	*c/a*
1853 (Koksharov)			0·9977
1926 (Bragg & West)	9·23 Å	9·19 Å	0·9957
1935 (Schiebold) El Chivor	9·226	9·189	0·9960
Muzo	9·415	9·231	0·9804
1947 (Norrish)	9·188	9·189	1·0001
1951 (Belov & Matveeva)	9·206	9·205	0·9999
1958 (Frank-Kameneskii & Sosedko)	9·202	9·183	0·9979
	9·202	9·209	1·0001
	9·200	9·227	1·0029
1960 (Swanson *et al.*)	9·215	9·192	0·9975
1963 (Author)			0·9974

Table 6. *Indexed powder diffraction data for orthorhombic sulfur based on a=12·869, b=24·496, c=10·464 Å*

hkl	d_c (Å)	NBS d_o (Å)	de Wolff d_o (Å)
111	7·7067	7·72	7·69
040	6·1239		
131	5·7573	5·78	5·76
220	5·6964	5·70	5·68
022	4·8115	4·82	4·80
151	4·1946	4·20	4·19
202	4·0595	4·062	4·06
311	3·9181	3·921	3·91
222	3·8534	3·859	3·85
331	3·5698	3·571	3·57
260	3·4473	3·450	3·44
242	3·3836	3·387	3·38
113	3·3353	3·336	3·33
062	3·2187	3·220	3·21
400	3·2174		
171	3·2136		
133	3·1124	3·115	3·11
351	3·0841	3·087	3·08
080	3·0620		3·06
262	2·8786		
440	2·8482	2·848	2·842
153	2·7746		
313	2·6900	2·690	2·688
422	2·6745	2·673	2·673
371	2·6249	2·624	2·621
004	2·6161	2·618	2·614
191	2·5806		
333	2·5689	2·570	2·569
442	2·5016	2·502	2·501
511	2·4865	2·487	
282	2·4446		
173	2·4261	2·428	2·424
044	2·4057	2·407	2·404
531	2·3899		
224	2·3773	2·379	2·375
353	2·3689	2·371	2·366
2,10,0	2·2893	2·289	2·288
462	2·2755		
244	2·2534		
391	2·2447		
551	2·2264		
0,10,2	2·2185		2·215
480	2·2181		
1,11,1	2·1476	2·146	2·146
373	2·1408		
193	2·1166	2·115	2·112
620	2·1128	2·113	
2,10,2	2·0973	2·096	2·098
264	2·0839		
513	2·0637		
115	2·0585	2·058	2·057
482	2·0421	2·042	2·041
0,12,0	2·0413		
571	2·0339		
404	2·0298		
533	2·0075	2·008	
135	2·0026	2·003	2·003
424	2·0024		
084	1·9890	1·989	1·988
602	1·9846		
622	1·9591	1·960	1·957
3,11,1	1·9421		
444	1·9267	1·926	1·926
393	1·9191		
553	1·9076	1·908	
155	1·9034	1·904	1·900
284	1·9003		
660	1·8988		
642	1·8880		
315	1·8754		
1,11,3	1·8573	1·857	1·856
591	1·8409	1·842	1·838
1,13,1	1·8355		
335	1·8329		
4,10,2	1·8264	1·823	1·823
2,12,2	1·8237		
464	1·8175		
711	1·8058		
662	1·7849	1·782	1·781
573	1·7823		
175	1·7789		
731	1·7678		
355	1·7560	1·756	1·754
026	1·7266	1·727	1·725
4,12,0	1·7237	1·723	
2,10,4	1·7228		
3,11,3	1·7196		
3,13,1	1·7022	1·698	1·698
751	1·6985		
484	1·6918		
2,14,0	1·6884		
206	1·6833		
226	1·6676	1·665	1·665
682	1·6654		
5,11,1	1·6627		
0,14,2	1·6594	1·657	1·658
375	1·6568		
593	1·6482	1·648	1·647
195	1·6455		
1,13,3	1·6443	1·644	
624	1·6437		
4,12,2	1·6371		
246	1·6231	1·623	1·622
713	1·6228		
515	1·6203	1·620	
6,10,0	1·6137		
0,12,4	1·6093	1·609	
800	1·6087		
771	1·6082	1·607	1·607
2,14,2	1·6068		
066	1·6038		
644	1·6010	1·601	1·601
1,15,1	1·6010		
733	1·5951	1·595	1·595
535	1·5926		
4,10,4	1·5629	1·563	1·563
2,12,4	1·5613		
266	1·5562		
840	1·5559		
395	1·5474		
3,13,3	1·5464		
753	1·5436	1·542	1·542
6,10,2	1·5420		
555	1·5414		
664	1·5367	1·537	
0,16,0	1·5310		1·531
822	1·5257		
426	1·5214		
5,11,3	1·5166		1·515
1,11,5	1·5145		
3,15,1	1·5102		
791	1·5076		
5,13,1	1·5046	1·504	1·504
842	1·4914	1·4914	1·490
446	1·4874	1·4875	
117	1·4822		
286	1·4751	1·4756	1·475
773	1·4749		
4,14,2	1·4748		
575	1·4730		
1,15,3	1·4693		
137	1·4609	1·4617	1·461
684	1·4584		
4,12,4	1·4393	1·4389	1·439
862	1·4390		
3,11,5	1·4370	1·4359	
466	1·4354		
2,16,2	1·4325		
880	1·4241	1·4230	1·424
6,12,2	1·4230		
157	1·4211		
0,10,6	1·4207		
1,17,1	1·4188	1·4194	1·419
2,14,4	1·4186		
911	1·4144		
317	1·4093		
7,11,1	1·4049		
3,15,3	1·3982		
793	1·3961		
931	1·3959		
595	1·3945		
5,13,3	1·3938		
1,13,5	1·3921	1·3911	1·391
337	1·3910		
2,10,6	1·3873	1·3879	
4,16,0	1·3825		
715	1·3790		
882	1·3741		
6,10,4	1·3734		
486	1·3710		
804	1·3703	1·3702	
5,15,1	1·3671		
177	1·3669		
735	1·3619	1·3620	1·362
824	1·3618		
951	1·3610		
357	1·3565	1·3561	
6,14,0	1·3558		
3,17,1	1·3544	1·3536	1·354
606	1·3532		
626	1·3450		

Hexagonal system

The axial ratio c/a of a hexagonal phase can be calculated from the expression

$$c/a = \tfrac{1}{2}\left[\frac{3(l_m^2 d_m^2 d_n^{-2} - l_n^2)}{h_n^2 + h_n k_n + k_n - (h_m^2 + h_m k_m + k_m^2) d_m^2 d_n^{-2}}\right]^{\frac{1}{2}}, \quad (4)$$

where d_m and d_n are two independent interplanar spacings. The procedure for obtaining the most probable value of c/a is analogous to that described for the tetragonal system. The NBS powder data for beryl (Swanson *et al.*, 1960) and α quartz (Swanson, Fuyat & Ugrinic, 1954) have been selected as test cases. Table 4 illustrates that, despite the rather wide fluctuations among the individual values for c/a, the average c/a for beryl is in excellent agreement with the precise goniometric determination by Koksharov (1853).

The arithmetic mean of the cell constants for 9 beryl specimens yielded a ratio of $\bar{c}/\bar{a} = 9{\cdot}202$ Å/9·232 Å = 0·9968. Compositional variation of beryl affects the c axis by only 0·32% ($9{\cdot}183 < 9.202 < 9{\cdot}231$ Å) and the a axis by as much as 2·0% ($9{\cdot}188 < 9.232 < 9{\cdot}415$ Å). This morphological information can be utilized to index the powder pattern of beryl as shown below for orthorhombic sulfur.

The test on α quartz proved equally satisfactory. Twenty-eight pairs of closely spaced reflections were used to obtain an average axial ratio of 1·10007 ± 0·00062 in favorable agreement with the value 1·1003 ± 0·0005, the average of 10 precise morphological measurements tabulated by Frondel (1962).

Orthorhombic system

The orthorhombic system (already described above) has two independent axial ratios; namely, $r_1 = a/b$ and $r_2 = c/b$, the latter being given explicitly by

$$r_2 = \frac{\begin{vmatrix} (h_n^2 - h_m^2 d_m^2 d_n^{-2}) & (l_n^2 - l_m^2 d_m^2 d_n^{-2}) \\ (h_q^2 - h_p^2 d_p^2 d_q^{-2}) & (l_q^2 - l_p^2 d_p^2 d_q^{-2} \end{vmatrix}^{\frac{1}{2}}}{\begin{vmatrix} (h_n^2 - h_m^2 d_m^2 d_n^{-2}) & (k_m^2 d_m^2 d_n^{-2} - k_n^2) \\ (h_q^2 - h_p^2 d_p^2 d_q^{-2}) & (k_p^2 d_p^2 d_q^{-2} - k_q^2) \end{vmatrix}^{\frac{1}{2}}}, \qquad (5)$$

where $d_m d_n^{-1}$ and $d_p d_q^{-1}$ are two independent ratios of interplanar spacings. It is obvious from the preceding examples that the reliability of the proposed method depends critically on the correct indexing of a given powder pattern. For large cells, valid indexing poses a serious problem for at least three reasons: (1) the relatively low absolute accuracy of most published lattice constants, (2) the limited absolute precision of conventional powder data, and (3) the inherent crowding of reflections beyond the 15 innermost reflections. If precise morphological measurements of axial ratios are available, these data can be used effectively for indexing in the manner demonstrated for orthorhombic sulfur. From measurements by Zepharovich (1869) on α sulfur, one calculates the appropriate axial ratios

$$a:b:c = (1{\cdot}9034)^{-1}:1:(0{\cdot}8131)(1{\cdot}9034)^{-1}$$
$$= 0{\cdot}52538:1:0{\cdot}42718\,.$$

To convert these ratios to lattice parameters, one needs at least one unambiguously indexed pinacoid reflection. For orthorhombic sulfur, this turns out to be the 004 reflection. Averaging the precise data of Swanson *et al.* (1960) and of de Wolff (1958), one obtains $d_{004} = 2{\cdot}616 \pm 0{\cdot}002$ Å and hence $c = 10{\cdot}464 \pm 0{\cdot}008$ Å; $b = 1{\cdot}9034c = 24{\cdot}496 \pm 0{\cdot}016$ Å; and $a = c/0{\cdot}8131 = 12{\cdot}869 \pm 0{\cdot}009$ Å. Based on these lattice constants, a complete list of *Fddd* permitted spacings $> 1{\cdot}300$ Å is calculated (Table 6) and is found to agree with the NBS data except for 11 'single' reflections to which two or more *hkl*'s are assigned. From the 22 pairs of single reflections listed in Table 7, one computes 229 separate values for a/b and c/b, a partial list of which is reproduced in Table 8. The averaged axial ratios thus obtained are bracketed by the values in bold type computed from cell measurements (Table 9).

Table 7. *Selected pairs of interplanar spacings of orthorhombic sulfur*

n	*hkl*	*d*	*n*	*hkl*	*d*
1	202	4·062 Å	23	333	2·570 Å
	311	3·921		442	2·502
3	311	3·921	25	442	2·502
	222	3·859		511	2·487
5	222	3·859	27	173	2·428
	331	3·571		044	2·407
7	331	3·571	29	224	2·379
	260	3·450		353	2·371
9	260	3·450	31	353	2·371
	242	3·387		2,10,0	2·289
11	242	3·387	33	1,11,1	2·146
	113	3·336		193	2·115
13	133	3·115	35	193	2·115
	351	3·087		620	2·113
15	440	2·848	37	620	2·113
	313	2·690		2,10,2	2·096
17	313	2·690	39	622	1·960
	422	2·673		444	1·926
19	422	2·673	41	1,11,3	1·857
	371	2·624		591	1·842
21	371	2·624	43	355	1·756
	004	2·618		026	1·727

Table 8. *Sample answers for axial ratios of orthorhombic sulfur*

The ordinal numbers n_m and n_p designate the two particular pairs of reflections selected from Table 7 for substitution in formulas (2) and (5). The symbol $\Delta_{m,p}$ refers to the determinant in the numerator of (2). In 203 instances, the absolute value of this determinant was greater than 10 and yielded sufficiently accurate axial ratios; the other 26 cases (*e.g.* values in parentheses) were not included in the averages

n_m	n_p	$\Delta_{m,p}$	a/b	c/b
1	7	−20·5447	0·52495	0·42675
1	9	16·4651	0·52583	0·42742
1	11	11·4540	0·52405	0·42606
3	19	36·6240	0·52483	0·42743
3	21	−50·6373	0·52494	0·42754
3	23	8·9782	(0·52404)	(0·42668)
7	37	−52·7924	0·52543	0·42543
7	39	−80·8500	0·52518	0·42612
7	41	65·8143	0·52530	0·42579
33	35	−270·1801	0·52585	0·427170
33	37	248·1229	0·52583	0·427170
33	39	158·7690	0·52628	0·427171
33	41	−182·4606	0·52618	0·427171
33	43	69·3951	0·52471	0·427168
21	35	−440·4261	0·52623	0·42796
13	15	−0·9702	(0·50934)	(0·41855)

$(\overline{a/b}) = 0{\cdot}5256 \pm 0{\cdot}0012$; $(\overline{c/b}) = 0{\cdot}4273 \pm 0{\cdot}0008$

Table 9. *Lattice constants and axial ratios of orthorhombic sulfur*

	a	b	c	a/b	c/b
1869 (Zepharovich)	—	—	—	0·5254	0·4272
1924 (Mark & Wigner)	12·89 Å	24·61 Å	10·63 Å	0·5238	**0.4319**
1925 (Bragg & Bragg)	12·89	24·51	10·48	0·5259	0·4276
1935 (Warren & Burwell)	12·95	24·60	10·50	0·5264	0·4268
1937 (Trillat & Oketani)	12·83	24·60	10·42	**0.5215**	**0.4236**
1951 (Ventriglia)	12·92	24·55	10·48	0·5263	0·4269
1955 (Abrahams)	12·845	24·369	10·437	**0.5271**	0·4283
1958 (de Wolff)	12·84	24·46	10·45	0·5249	0·4272
1960 (Swanson *et al.*)	12·870	24·49	10·468	0·5255	0·4274
1963 (Author)	—	—	—	0·5256	0·4273

If one lacks either precise goniometric data or precise cell constants, one is forced to resort to an iterative procedure for extending the number of unequivocally indexed reflections after each cycle of computation. The details of this method are described under the monoclinic system.

Monoclinic system

From the quadratic factors for two separate interplanar spacings of a monoclinic crystal, one derives the condition that

$$\begin{aligned}(h_n^2-h_m^2d_m^2d_n^{-2})a^{-2}b^2\sin^{-2}\beta+(l_n^2-l_m^2d_m^2d_n^{-2})c^{-2}b^2\sin^{-2}\beta\\ -2(h_nl_n-h_ml_md_m^2d_n^{-2})a^{-1}c^{-1}b^2\sin^{-2}\beta\cos\beta\\ +(k_n^2-k_m^2d_m^2d_n^{-2})=0\ ,\end{aligned}$$

where the symmetry axis is b, $c<a$, and $\beta>90°$. Substituting

$$x=\frac{a}{b}\sin\beta,\quad y=\frac{c}{b}\sin\beta,\quad z=\frac{-2b^2\cos\beta}{ac\sin^2\beta}=\frac{-2\cos\beta}{xy}\ ,$$

one can solve for x, y, and z from three non-redundant pairs of spacings (requiring at least four single reflections and at most six single reflections). The determinant form for x is given by (6); a comparable expression is valid for y.

$$x=\frac{\begin{vmatrix}(h_n^2-h_m^2d_m^2d_n^{-2}) & (l_n^2-l_m^2d_m^2d_n^{-2}) & (h_nl_n-h_ml_md_m^2d_n^{-2})\\ (h_q^2-h_p^2d_p^2d_q^{-2}) & (l_q^2-l_p^2d_p^2d_q^{-2}) & (h_ql_q-h_pl_pd_p^2d_q^{-2})\\ (h_s^2-h_r^2d_r^2d_s^{-2}) & (l_s^2-l_r^2d_r^2d_s^{-2}) & (h_sl_s-h_rl_rd_r^2d_s^{-2})\end{vmatrix}^{\frac{1}{2}}}{\begin{vmatrix}(k_m^2d_m^2d_n^2-k_n^2) & (l_n^2-l_m^2d_m^2d_n^{-2}) & (h_nl_n-h_ml_md_m^2d_n^{-2})\\ (k_p^2d_p^2d_q^{-2}-k_q^2) & (l_q^2-l_p^2d_p^2d_q^{-2}) & (h_ql_q-h_pl_pd_p^2d_q^{-2})\\ (k_r^2d_r^2d_s^{-2}-k_s^2) & (l_s^2-l_r^2d_r^2d_s^{-2}) & (h_sl_s-h_rl_rd_r^2d_s^{-2})\end{vmatrix}^{\frac{1}{2}}}\ . \tag{6}$$

The solution for z is stated by

$$\begin{aligned}z=1/\Delta_{m,p,r}&\\ \times&\begin{vmatrix}(h_n^2-h_m^2d_m^2d_n^{-2}) & (l_n^2-l_m^2d_m^2d_n^{-2}) & (k_m^2d_m^2d_n^{-2}-k_n^2)\\ (h_q^2-h_p^2d_p^2d_q^{-2}) & (l_q^2-l_p^2d_p^2d_q^{-2}) & (k_p^2d_p^2d_q^{-2}-k_q^2)\\ (h_s^2-h_r^2d_r^2d_s^{-2}) & (l_s^2-l_r^2d_r^2d_s^{-2}) & (k_r^2d_r^2d_s^{-2}-k_s^2)\end{vmatrix}\ ,\end{aligned} \tag{7}$$

where $d_md_n^{-1}$, $d_pd_q^{-1}$, $d_rd_s^{-1}$ are three non-equivalent ratios of interplanar spacings and $\Delta_{m,p,r}$ is the determinant in the numerator of (6). Since x is a positive quantity, it follows that the determinants in (6) must be of the same sign for correctly indexed reflections. The same argument applies to the vari-

Table 10. *Comparison of calculated interplanar spacings of* Ag_2CO_3 *with NBS-indexed data based on*

$a=4·836,\ b=9·555,\ c=3·235$ Å; $\beta=92·64°$

$(hkl)_{\text{NBS}}$	d_o	d_c	$\frac{(d_c-d_o)}{d_c}10^3$
100	4·85 Å	4·8309 Å	−3·95*
020	4·78	4·7775	−0·52
110	4·32	4·3112	−2·04
120	3·41	3·3969	−3·86*
001	3·25	3·2316	−5·69*
011	3·08	3·0612	−6·14*
$\bar{1}01$	2·74	2·7451	1·86
130	2·66	2·6591	−0·34
111	2·56	2·5362	−9·38*
200	2·42	2·4154	−1·90
040	2·39	2·3888	−0·50
$\bar{1}21$	2·38	2·3801	0·04
210	2·35	2·3418	−3·50
121	2·32	2·3044	−6·77*
031	2·27	2·2684	−0·71
220	2·16	2·1556	−2·04
131	2·04	2·0282	−5·82*
$\bar{2}01$	1·976	1·9789	1·47
$\bar{2}11$	1·934	1·9378	1·96
230	1·929	1·9246	−2·29
041	1·912	1·9209	4·63*
201	1·875	1·8933	9·67*
211		1·8572	−9·58*
$\bar{1}41$	1·801	1·8020	0·55
150	1·777	1·7770	0·00
240	1·700	1·6985	−0·88
$\bar{2}31$	1·678	1·6809	1·73
051	1·639	1·6449	3·59*
231	1·626	1·6275	0·92
002	1·616	1·6158	−0·12
012	1·591	1·5932	1·38
060		1·5925	0·94
310	1·587	1·5879	0·57
$\bar{1}12$	1·538	1·5339	−2·67*
022	1·530	1·5306	0·39
$\bar{2}41$	1·526	1·5239	−1·38
160	1·511	1·5124	0·93
102	1·507	1·5115	2·98*
$\bar{3}01$	1·468	1·4685	0·34
$\bar{3}11$	1·450	1·4515	1·03
122	1·441	1·4411	0·07
032		1·4410	0·00
061	1·428	1·4285	0·35
$\bar{3}21$	1·411	1·4037	−5·20*
311	1·400	1·4002	0·14
$\bar{1}32$	1·398	1·3966	−1·00
$\bar{2}51$	1·3747	1·3747	0·00
$\bar{2}02$	1·3723	1·3725	0·15
132	1·3654	1·3656	0·15
260	1·3299	1·3295	−0·30
$\bar{2}22$	1·3192	1·3192	0·00
$\bar{1}42$	1·3023	1·3026	0·23

able y. For each solution of (x, y, and z), one can compute $\cos\beta$, a/b, and c/b by substituting in the following formulas:

$$\cos\beta = \frac{-xyz}{2},\ \frac{a}{b} = \frac{x}{(1-\cos^2\beta)^{\frac{1}{2}}},\ \frac{c}{b} = \frac{y}{(1-\cos^2\beta)^{\frac{1}{2}}}\ .$$

From ν pairs of correctly indexed reflections $\nu(\nu-1)(\nu-2)/6$ sets of answers are possible.

Great caution must be exercised in properly indexing powder patterns of monoclinic substances. Starting with the reported lattice constants one applies an internal consistency test involving the relative differences between calculated and observed spacings. Column 4 of Table 10 illustrates this test applied to the published powder data of Ag_2CO_3 (Swanson, Morris, Stinchfield & Evans, 1962). The 14 starred reflections show an unexpectedly large deviation from the calculated values. Since the single-crystal data by Eldridge (1942) yield the same indices for the first 11 reflections, one is led to the conclusion that the stated lattice constants are probably in error because the NBS d data are accurate to at least 0·3%. The first attempt to recalculate the lattice constants is based on the innermost identified pinacoid reflections; namely, 020 and 040 yielding $b=9{\cdot}56$ Å; 100 and 200 yielding $a\sin\beta=4{\cdot}845\pm0{\cdot}015$ Å; 001 yielding $c\sin\beta=3{\cdot}25$ Å. From the relation

$$d_{\bar{1}01}^{-2}=a^{-2}\sin^{-2}\beta+c^{-2}\sin^{-2}\beta+2a^{-1}c^{-1}\sin^{-2}\beta\cos\beta\ ,$$

one calculates $\beta=91{\cdot}83°$ and consequently $a=4{\cdot}847\pm0{\cdot}016$, $c=3{\cdot}253\pm0{\cdot}011$ Å. Likewise, from d_{111} and d_{121} one computes $\beta=91{\cdot}97°$ and 92·13° respectively; and from d_{031}, $b=9{\cdot}541$ Å. Using the averaged lattice constants $a=4{\cdot}848$, $b=9{\cdot}55\pm0{\cdot}01$, $c=3{\cdot}252$ Å, and $\beta=91{\cdot}98\pm0{\cdot}15°$ to index the Ag_2CO_3 pattern, one notices immediately that after the first 20 reflections in Table 10, most of the assigned indices are incorrect. From 10 pairs of correctly indexed reflections, the computer program furnished new values for a/b, c/b and $\sin\beta$ from which a new set of lattice constants was calculated. A third iteration (coupled with new, precise powder-data for the first 17 reflections of Ag_2CO_3) produced the final set of indices from which 13 pairs of properly indexed reflections (Table 11) were selected for the computer program which printed 281 answers and 5 indeterminate (0/0) cases. Table 12 reproduces the first 48 of these answers. Finally, the correctly indexed powder pattern for Ag_2CO_3 is given in Table 13. Single-crystal intensity data can furnish supplemental information to substantiate the

Table 11. *Selected pairs of interplanar spacings of* Ag_2CO_3

The values for the spacings are the averages of the corresponding d_o's in Table 13

n	*hkl*	*d*	*n*	*hkl*	*d*
1	200	2·425 Å	15	211	1·875 Å
	040	$2{\cdot}384_5$		$\bar{1}41$	1·801
3	210	2·349	17	240	$1{\cdot}700_5$
	121	2·322		$\bar{2}31$	$1{\cdot}678_5$
5	121	2·322	19	231	1·639
	031	2·274		002	1·626
7	131	2·041	21	002	1·626
	$\bar{2}01$	1·976		300	1·616
9	$\bar{2}01$	1·976	23	160	1·512
	$\bar{2}11$	1·935		112	1·508
11	$\bar{2}11$	1·935	25	$\bar{3}01$	1·468
	230	$1{\cdot}929_5$		330	1·441
13	201	1·912			
	211	1·875			

Table 12. *The first* 48 *computations of* $\sin\beta$, a/b, *and* c/b *for* Ag_2CO_3

The ordinal numbers n_m, n_p, and n_r designate the three pairs of reflections from Table 11 for substitution in formulas (6) and (7). The symbol $\Delta_{m;p;r}$ refers to the determinant in the numerator of (6). The averages include only those cases (88) for which $|\Delta_{m;p;r}| \geq 10$

n_m	n_p	n_r	$\Delta_{m;p;r}$	$\sin\beta$	a/b	c/b
1	3	5	−3·7486	0·99936	0·50882	0·34173
1	3	7	−10·9908	0·99946	0·50877	0·34104
1	3	9	0·4815	0·99949	0·50875	0·34080
1	3	11	11·7257	0·99947	0·50876	0·34094
1	3	13	−0·1498	0·99845	0·50928	0·34649
1	3	15	−11·1209	0·99937	0·50881	0·34164
1	3	17	−11·4243	0·99944	0·50878	0·34115
1	3	19	−19·2958	0·99943	0·50878	0·34124
1	3	21	15·6343	0·99942	0·50879	0·34129
1	3	23	−7·7758	0·99949	0·50875	0·34081
1	3	25	15·6343	0·99941	0·50879	0·34136
1	5	7	0·2197	0·99963	0·50868	0·31220
1	5	9	−0·1777	0·99938	0·50881	0·33930
1	5	11	−4·3273	0·99938	0·50881	0·33965
1	5	13	−0·1407	0·99940	0·50880	0·33705
1	5	15	0·1688	0·99941	0·50879	0·33641
1	5	17	4·2161	0·99937	0·50881	0·34021
1	5	19	12·0745	0·99936	0·50882	0·34096
1	5	21	−16·0000	0·99936	0·50882	0·34131
1	5	23	15·5899	0·99936	0·50882	0·34128
1	5	25	−4·4910	0·99937	0·50881	0·34050
1	7	9	−0·4928	0·99946	0·50877	0·34040
1	7	11	−12·0000	0·99946	0·50877	0·34076
1	7	13	−0·4215	0·99949	0·50875	0·33592
1	7	15	−0·1569	0·99986	0·50856	0·26121
1	7	17	11·6915	0·99945	0·50877	0·34135
1	7	19	34·2704	0·99945	0·50877	0·34135
1	7	21	−45·9942	0·99946	0·50877	0·34128
1	7	23	45·2524	0·99946	0·50877	0·34093
1	7	25	−12·2507	0·99945	0·50877	0·34222
1	9	11	0	0/0	0/0	0/0
1	9	13	0·0251	0·99930	0·50885	0·33829
1	9	15	0·5055	0·99939	0·50880	0·33938
1	9	17	−0·0000			
1	9	19	−0·6363	0·99956	0·50872	0·34183
1	9	21	1·3142	0·99952	0·50874	0·34126
1	9	23	−1·6340	0·99949	0·50875	0·34081
1	9	25	−0·1642	0·99917	0·50892	0·33674
1	11	13	0·6132	0·99928	0·50886	0·33848
1	11	15	12·3095	0·99938	0·50881	0·33973
1	11	17	0	0/0	0/0	0/0
1	11	19	−15·4944	0·99952	0·50874	0·34165
1	11	21	32·0000	0·99949	0·50875	0·34127
1	11	23	−39·7886	0·99947	0·50876	0·34089
1	11	25	−4·0000	0·99923	0·50889	0·33781
1	13	15	0·4243	0·99940	0·50880	0·33703
1	13	17	0·5974	0·99926	0·50887	0·33879
1	13	19	1·2071	0·99914	0·50893	0·34012

$$\overline{\sin\beta}=0{\cdot}99942\pm0{\cdot}00002;\ \overline{(a/b)}=0{\cdot}5083_8\pm0{\cdot}00039;$$

$$\overline{(c/b)}=0{\cdot}3410_1\pm0{\cdot}00024$$

Table 13. *Indexed powder pattern of* Ag_2CO_3 *with lattice constants* $a = 4{\cdot}850_5 \pm 0{\cdot}005$, $b = 9{\cdot}541 \pm 0{\cdot}002$, $c = 3{\cdot}253_4 \pm 0{\cdot}004$ Å, $\beta = 91{\cdot}95° \pm 0{\cdot}04°$

The counter data of Ag_2CO_3 were recorded on a Norelco diffractometer with filtered Cu $K\alpha$ radiation, 35 kV, 20 mA; 1° slits; ¼°/min (2θ); time constant 2. Silicon powder was used as internal standard. The film data were obtained in an AEG Guinier double cylinder camera (114·7 mm diameter) with monochromatic Cu $K\alpha_1$ radiation. Aluminum foil served as internal standard. $I_{hkl} \propto [(1+\cos^2 2\theta)/\sin^2\theta \cos\theta] j_{hkl} F^2_{hkl}$, where the experimental F_{hkl}'s are obtained from the single-crystal data of Eldridge (1942). The silver carbonate was prepared in a high-pressure glass ampoule by reacting pure dry AgO and liquid CO_2 at room temperature (23–30 °C) for 2½ years. ($2AgO + CO_2 \rightarrow Ag_2CO_3 + \tfrac{1}{2}O_2$). An infrared spectrum by the mull technique revealed none of the trace impurities encountered in commercial Ag_2CO_3

hkl	d_c	d_o Counter	d_o Film	$I_{hkl}/I_{\bar{1}01}$
100	4·8476 Å	4·845 Å	4·840 Å	
020	4·7705	4·773	4·770	
110	4·3218	4·323	4·322	
120	3·4002	3·401		
001	3·2516	3·252		
011	3·0778	3·077		
$\bar{1}01$	2·7439	2·745	2·745	1·000
021	2·6868			0·015
130	2·6591	2·660	2·657	0·855
101	2·6589			0·714
$\bar{1}11$	2·6370			absent
111	2·5613	2·562		
200	2·4238	2·424	2·426	
040	2·3853	2·385	2·384	
$\bar{1}21$	2·3785	2·379		
210	2·3492	2·349		
121	2·3225	2·322		
031	2·2736	2·274		
220	2·1609	2·161		
140	2·1402			0·027
$\bar{1}31$	2·0775		NBS	0·028
131	2·0399	2·041	(counter)	
$\bar{2}01$	1·9758		1·976	
$\bar{2}11$	1·9347	1·936	1·934	
230	1·9277	1·930	1·929	
041	1·9233			absent
201	1·9124	1·912	1·912	
211	1·8751	1·875	1·875	
$\bar{2}21$	1·8254			0·027
$\bar{1}41$	1·8002	1·801	1·801	
150	1·7756	1·776	1·777	0·125
141	1·7755			0·110
221	1·7751			0·139
240	1·7001	1·701	1·700	
$\bar{2}31$	1·6783	1·679	1·678	
051	1·6457			0·138
231	1·6389	1·639	1·639	0·212
002	1·6258	1·626	1·626	
300	1·6159		1·616	
012	1·6027			
310	1·5932	1·592	1·591	
060	1·5902		1·587	

hkl	d_c	d_o Counter	d_o NBS	$I_{hkl}/I_{\bar{1}01}$
$\bar{1}51$	1·5666			absent
$\bar{1}02$	1·5575			
151	1·5503			absent
022	1·5389	1·539	1·538	
$\bar{1}12$	1·5371			
320	1·5305	1·531		
102	1·5259		1·526	
$\bar{2}41$	1·5216			absent
160	1·5110	1·513	1·511	
112	1·5067	1·509	1·507	
250	1·4993			0·030
241	1·4920			
$\bar{1}22$	1·4806			
$\bar{3}01$	1·4671	1·468	1·468	
122	1·4533			
$\bar{3}11$	1·4500		1·450	
032	1·4476			
330	1·4406		1·441	
061	1·4285	1·428	1·428	0·015
301	1·4278			0·050
311	1·4121	1·412	1·411	
$\bar{3}21$	1·4023	1·4005	1·400	
$\bar{1}32$	1·3988		1·398	
$\bar{1}61$	1·3758		1·3747	0·125
132	1·3757			
$\bar{2}51$	1·3726		1·3723	0·085
$\bar{2}02$	1·3720			
321	1·3679		1·3654	0·051
161	1·3647			0·116
$\bar{2}12$	1·3580			
251	1·3508			0·034
042	1·3434			
340	1·3378			0·013
$\bar{3}31$	1·3322	1·3308	1·3299	0·083
260	1·3296			0·109
202	1·3294			
$\bar{2}22$	1·3185		1·3192	
212	1·3167			
170	1·3121			absent
$\bar{1}42$	1·3041	1·3028	1·3023	
331	1·3026			0·148

Table 14. *Lattice constants and axial ratios of the ε isomer of* 1, 2, 3, 4, 5, 6-*hexachlorocyclohexane*

	a	*b*	*c*	*β*	*a/b*	*c/b*
1947 (Kauer, DuVall & Alquist)	6·94 Å	11·66 Å	6·77 Å	111°	0·5952	0·5806
1950 (Norman)	7·02 Å	11·79 Å	6·80 Å	112°	0·5954	0·5768
1963 (Author)		11·77 Å		112° 6′	0·5953	0·5765
		±		±	±	±
		0·005		10′	0·0006	0·0006

correct assignment of indices: firstly, by excluding those permitted reflections not observed from single crystals; and secondly, by evaluating the relative intensity of each reflection contributing to the total intensity of an unresolved powder line. Column 5 of Table 13 reveals clearly that reflections 041 and $\bar{2}41$ should have negligible intensities and that powder lines 2·66, 1·777, and 1·428 Å are not single reflections (see Table 10). The data by Eldridge would exclude also the 1·639 Å line as a single reflection.

A somewhat more difficult case was encountered in the determination of the axial ratios of the ε isomer of 1,2,3,4,5,6-hexachlorocyclohexane because spacings no larger than 2·2 Å were used in the computation. Three cycles of indexing were required to verify the unequivocal assignments of 9 pairs of single reflections. The resultant data indicate the accuracy attainable by the described method (Table 14).

Triclinic system

In the triclinic system the cell edges are the shortest three non-coplanar translations labeled according to the convention $0<c<a<b$, and oriented so that angles α and β are both greater than 90°. From the ratio of the quadratic factors of two separate interplanar spacings d_n and d_m, one obtains the condition that

$$\begin{aligned}&(h_n^2-h_m^2d_m^2d_n^{-2})(a^{*2}/b^{*2})+(l_n^2-l_m^2d_m^2d_n^{-2})(c^{*2}/b^{*2})\\&\quad+2(k_nl_n-k_ml_md_m^2d_n^{-2})(c^*/b^*)\cos\alpha^*\\&\quad+2(h_nl_n-h_ml_md_m^2d_n^{-2})(a^*c^*/b^{*2})\cos\beta^*\\&\quad+2(h_nk_n-h_mk_md_m^2d_n^{-2})(a^*/b^*)\cos\gamma^*\\&\quad+(k_n^2-k_m^2d_m^2d_n^{-2})=0\,,\end{aligned}$$

where a^*, b^*, c^*; α^*, β^*, and γ^* are the reciprocal cell constants. Substituting

$$x_1=(a^{*2}/b^{*2}),\ x_2=(c^{*2}/b^{*2}),\ x_3=(2c^*/b^*)\cos\alpha^*,$$
$$x_4=(2a^*c^*/b^{*2})\cos\beta^*,\ x_5=(2a^*/b^*)\cos\gamma^*,$$

one can solve for these x's from five non-redundant pairs of spacings (requiring at least six single reflections and at most ten single reflections). From these solutions one can compute

$$\cos\alpha^*=\frac{x_3}{2x_2^{\frac12}},\quad \cos\beta^*=\frac{x_4}{2x_1^{\frac12}x_2^{\frac12}},\quad \cos\gamma^*=\frac{x_5}{2x_1^{\frac12}}\,;$$

$$\cos\alpha=\frac{\cos\beta^*\cos\gamma^*-\cos\alpha^*}{\sin\beta^*\sin\gamma^*}\,,$$

$$\cos\beta=\frac{\cos\gamma^*\cos\alpha^*-\cos\beta^*}{\sin\gamma^*\sin\alpha^*}\,,$$

$$\cos\gamma=\frac{\cos\alpha^*\cos\beta^*-\cos\gamma^*}{\sin\alpha^*\sin\beta^*}\,.$$

Hence, the axial ratios follow

$$\frac{a}{b}=\frac{\sin\alpha}{x_1^{\frac12}\sin\beta}\quad\text{and}\quad\frac{c}{b}=\frac{\sin\gamma}{x_2^{\frac12}\sin\beta}\,.$$

From ν pairs of correctly indexed reflections, an upper limit of $\binom{\nu}{5}$ sets of answers are obtainable. No program has been written for this general case because of limited demand.

Comparison with least-squares methods

The mathematics pertaining to the least-squares method (developed by Gauss in 1821) has been applied in recent years to the refinement of lattice constants and in turn to the refinement of axial ratios. To define the problem let v_j, given by

$$\begin{aligned}v_j=d_j^{*2}-(d^*_{\rm obs})_j^2&=h_j^2a^{*2}+k_j^2b^{*2}+l_j^2c^{*2}+2k_jl_jb^*c^*\cos\alpha^*\\&\quad+2l_jh_jc^*a^*\cos\beta^*+2h_jk_ja^*b^*\cos\gamma^*-(d^*_{\rm obs})_j^2\,,\end{aligned}$$

be the residuals, or deviations of the computed quadratic factors, d_j^{*2}, from the corresponding observed values, $(d^*_{obs})_j^2$, where j ranges from 1 to n. The task is to find those values of a^*, b^*, c^*, $\cos\alpha^*$, $\cos\beta^*$, $\cos\gamma^*$ which yield the best overall agreement between the computed and observed values of all the observed interplanar spacings. In the least-squares approach this implies that $\sum_{j=1}^{n} v_j^2$ be a *minimum.* The necessary but not sufficient conditions for a minimum to obtain are

$$\frac{\partial}{\partial a^*}\left(\sum_{j=1}^{n}v_j^2\right)=0,\ \frac{\partial}{\partial b^*}\left(\sum_{j=1}^{n}v_j^2\right)=0,\ \ldots,$$
$$\frac{\partial}{\partial(\cos\gamma^*)}\left(\sum_{j=1}^{n}v_j^2\right)=0\,.$$

Since approximate values for the reciprocal cell constants are assumed to be known, one makes the transformation $a^*=(a^*)_0+\Delta a^*$, *etc.*, and reduces d_j^{*2} to a linear form by a Taylor expansion neglecting terms higher than the first order in the increments. Imposing the above conditions on the resultant expression of $\sum_{j=1}^{n} v_j^2$, one arrives at the *normal* equations which can be solved for the six unknown increments by various schemes (Mueller, Heaton & Miller, 1960; Plackett, 1960; Caron & Donohue, 1961; Kempter & Vogel, 1962; Mozzi & Newell, 1962; Evans, Appleman & Handwerker, 1963). Two important assumptions are involved in the least-squares method: (1) the *correct* assignment of $h_jk_jl_j$ is assumed for each observed reflection and (2) the residuals, v_j, are assumed to follow the Gaussian law of error (Fig. 1). The first assumption is difficult to meet because unique indexing of a powder pattern of moderate complexity is seldom achieved in practice. Most least-squares programs proceed from an initially indexed pattern to obtain refined lattice constants. For uniaxial

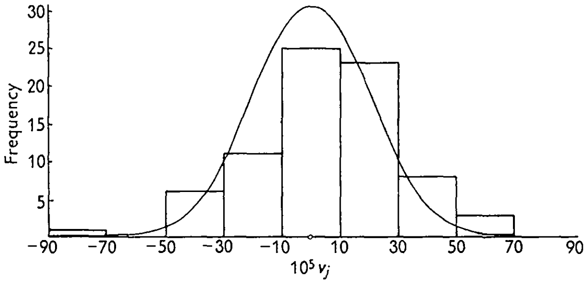

Fig. 1. Histogram: frequency distribution of v_j pertaining to the d data of α-S_8 shown in Table 6, columns 2 and 3. Comparison with the normal curve of error reveals a definite skewness of the v_j distribution. This asymmetry has a negligible effect on the least-squares method provided the v_j's become sufficiently small.

Table 15. *Comparison of cell refinements*

The lattice constants in italic are the reference data to convert from axial ratios to cell dimensions

Substance	a (Å)	b (Å)	c (Å)	β (°)	Cell	Method	Reference
Ag_2CO_3	4·84	9·54	3·24	92·7	initial		Eldridge (1942)
	4·836	9·555	3·235	92·64	refined	Least squares	Swanson *et al.* (1960)
	4·851	*9.541*	3·253	91·95	refined	Axial ratios	
α-S_8	12·84	24·46	10·45		initial		de Wolff (1958)
	12·870	24·49	10·468		refined	Least squares	Swanson *et al.* (1960)
α-S_8	12·870	24·49	10·468		initial		
	12·870	24·493	10·467		refined	Least squares	Caron & Donohue (1961)
	±0·001	±0·003	±0·001				
α-S_8	c/ 0·8131	1·9034c	*10.464*		initial		
	12·870	24·485	10·469		refined	Axial ratios	
	±0·001	±0·006	±0·003				
ε isomer of 1,2,3,4,5,6-$C_6H_6Cl_6$	6·94	11·66	6·77	111	initial		Kauer *et al.* (1947)
	7·012	11·769	6·786	112·07	refined	Least squares	Evans* (1963)
	±0·001	±0·002	±0·001	±0·02			
	7·007	*11.770*	6·785	112·1	refined	Axial ratios	
	±0·009	±0·005	±0·009	±0·17			

* Private communication.

substances, biaxial crystals with small lattice constants, or crystals with accurately known large cells, the least-squares method does yield satisfactory refinements. To reduce the probability of incorrect indexing Evans *et al.* (1963) have programmed an iterative procedure for automatic computer indexing. A match between d_c and d_o is accepted 'if and only if there is no other observed reflection and no other calculated reflection with a Bragg angle less than a specified tolerance T different from that of the given reflection.' Through the courtesy of Dr Howard T. Evans, Jr. (U.S. Geological Survey) the unindexed powder data of the ε isomer of 1,2,3,4,5,6-hexachlorocyclohexane were processed by this program yielding cell constants in excellent agreement with those from the axial ratios procedure (Table 15). It must be pointed out, however, that the least-squares refinement even with automatic iterative indexing does not guarantee unique or correct indexing. For example in the case of the ε isomer of $C_6H_6Cl_6$, after nine cycles of refinement, 22 reflections out of 28 observed reflections were indexed as single of which three were designated ambiguous by the axial ratios method. Moreover, the single reflections 100, $\bar{2}02$, 220, and $\bar{2}41$ were not accepted by the program either because of poor agreement or of ambiguous indexing (Table 16).

The axial ratios method required three cycles for refinement involving 14 distinct reflections. By testing each unambiguous reflection crystallographically against all other uniquely indexed reflections, one notes that the calculated axial ratios are sensitive to incorrect indexing, to extraneous lines, or to faulty d measurements — as evidenced by excessive deviations from the arithmetic mean of a particular axial ratio or by the appearance of imaginary values for a/b or c/b. Regrettably, the axial ratios method requires the discriminating judgment of an experienced X-ray crystallographer. Ambiguous reflections are not ignored. Relative intensities of these reflections are calculated either from intensity data on single crystals or from known atom-coordinates (the program by Smith (1963) is very useful in this connection). Appropriate weighting factors are then applied to estimate the effective d values for the superposed reflections.

Table 16. *Comparison of indexed reflections of ε isomer of* 1,2,3,4,5,6-*hexachlorocyclohexane*

d_o	d_c	hkl USGS	hkl Dow	$(I_{hkl}/I_{021})_c$
6·50 Å	6·498 Å	R	100	0·078
3·327	3·3285	031	031	0·274
	3·3248		$\bar{2}11$	0·482
3·223	3·2236	121	121	0·387
	3·2350		$\bar{1}31$	0·002
2·856	2·8591	R	$\bar{2}02$	0·161
2·849	2·8443	R	220	0·097
2·776	2·7783	$\bar{2}12$	$\bar{2}12$	0·118
	2·7732		022	0·004
2·336	2·3359	$\bar{3}01$*		0·000
	2·3385		141	0·155
2·241	2·2431	R	$\bar{2}41$	0·104

R = rejected by program.

* Space group limitations on possible reflections intentionally omitted.

For computing cell constants from accurate axial ratios two approaches are pursued. The first has been described in the case of orthorhombic sulfur and requires the d value of at least one unambiguous pinacoid reflection. To avoid tying all lattice constants to one pinacoid, the second and preferred approach utilizes reflections dominant in one particular index. For example the value of $b = 24{\cdot}485 \pm 0{\cdot}006$ Å for α-S_8 in Table 15 was calculated from the set of reflections 2,10,0, 1,11,1, 1,11,3, 5,13,1 by substitution in the convenient expression

$$b = d_{hkl}\sqrt{(k^2 + h^2 r_1^{-2} + l^2 r_2^{-2})} \; .$$

Likewise the value of $a = 12{\cdot}870 \pm 0{\cdot}001$ Å was computed from the selected unambiguous reflections 440, 620, 842, and 804. The results from the two approaches compare as follows in the case of α-S_8:

	a	b	c
Method 1	12·871 Å	24·489 Å	10.464 Å
Method 2	12·870	24·485	10·469
	±0·001	±0·006	±0·003

From the limited comparison in Table 15 it appears that the axial ratios procedure for cell refinement is a valid referee method for the least-squares refinements. The reader should be cautioned, however, that the described method is no panacea for run-of-the-mill powder patterns; on the contrary, it tends to expose their inherent limitations. In the process of tabulating diffraction data on isomorphous substances the author has examined in detail several hundred indexed powder patterns (both from the literature and from the Dow files) and has come to the conclusion that many of these patterns, while satisfactory for 'fingerprint' systems of chemical identification, are not of sufficient resolution and absolute accuracy for the precise determinations of lattice constants and usually are not reliable in the assignment and value of relative integrated intensities. The general utility of the powder method would be markedly enhanced by greater absolute accuracy in the measurement of interplanar spacings greater than 4 Å.

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