ACTA CHEMICA SCANDINAVICA 11 (1957) 1587—1593

Determination of Accurate Interplanar Spacings and Lattice Parameters from Guinier Powder Photographs

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X-Ray powder photographs obtained in a Guinier type focusing camera of 80 mm diameter (transmission position) often permit the calculation of interplanar spacings and unit cell dimensions with considerable accuracy provided that an internal standard is admixed with the powder specimens. The procedure is rapid and simple. The high accuracy obtained in the low-angle region is particularly valuable when applying analytical methods for indexing powder patterns.

Accuracy in powder data is of great importance in many instances of X-ray diffraction studies, *e. g.* when indexing complicated patterns by analytical methods [1,2]. Access to accurate interplanar spacings and unit cell dimensions has been essential also in connection with studies carried out by members of the present research team on some series of closely related, discrete phases giving very similar X-ray patterns (homologous series of oxides of transition elements) [3,4]. The information thus needed has to a large extent been obtained from powder photographs.

The determination of interplanar spacings and unit cell dimensions with the highest degree of accuracy is a complicated task [1,2]. Quite often, however, a more modest degree of accuracy in the interplanar spacings values is required and for such cases the employment of a Guinier focusing camera[5] has been found to give, by a simple and rapid procedure, results satisfactory for most needs.

The two Guinier camera sets used in the present investigation were built according to a design by Professor G. Hägg, Uppsala, at the workshop of the Chemistry Department, Research Institute of National Defence (FOA 1) through the kind permission of the head of the Department, Professor G. Ljunggren. The delicate adjustment of the camera sets, which were designed for taking transmission photographs with Cu$K\alpha$ radiation, was carried out by Dr. J. Österlöf of this Institute. One of the cameras, intended for precision measurements, utilizes strictly monochromatized Cu$K\alpha_1$ radiation, while the

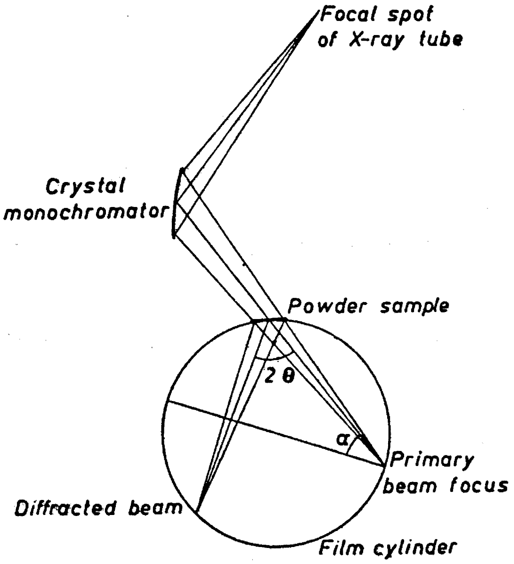

Fig. 1. Guinier focusing camera (transmission position).

other, used for ordinary work and with somewhat higher intensity, employs the Cu$K(\alpha_1 + \alpha_2)$ doublet. The diameter of the film cylinder is 80 mm. The exposure times are generally rather short, being about 30 min for substances of high symmetry and simple structure.

A condition for the camera to give sharp interference lines on the film is that the powder sample is situated on the cylinder defined by the film (*cf.* Fig. 1). In the actual procedure, the sample is stuck to a piece of thin Scotch tape which is attached to a flat metal ring rotated in a plane tangent to the focusing cylinder. A minor deviation of the sample from the correct site causes a slight broadening of the interference lines and considerable displacements of their positions on the film. Thus, if the sample is moved outwards Δa at right angles to the tangent plane, the position (s) of the interference line on the film will shift towards increasing s by an amount $\Delta s = \mathrm{F}(\Theta,\alpha) \cdot \Delta a$, where Θ is the Bragg angle and α the angle between the incident beam and the normal to the powder specimen. Fig. 2 gives a representation of the quotient $\Delta s/\Delta a$ as a function of Θ when α is given the value, 35°, of the actual camera sets. It is obvious that, with this method of mounting the specimen, accurate Θ values for the reflexions cannot be obtained by straight-forward measurements of the distances s_{obs} between the positions on the film of the primary beam and the reflexions.

Admixture of an internal standard with accurately known lattice dimensions makes it possible to correlate for each individual exposure the readings on the film s_{obs} with the Θ values of the standard. This is advantageously done by determining for every reflexion of the standard substance the difference

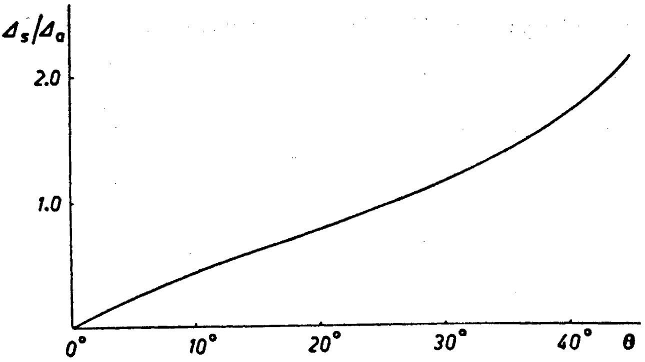

Fig. 2. Relation between line displacement (Δs) and sample displacement (Δa) as a function of diffraction angle (Θ).

$\Delta s = s^\circ - s_{obs}$, where s° represents the value calculated for a nominal value r° chosen for the camera radius. By plotting Δs against s_{obs}, a correction curve is obtained which is of a form analogous to that given in Fig. 2 if the camera is truly cylindrical and correctly adjusted. Within the limits given by the accuracy of the readings, this function corresponds to a line $\Delta s = \text{const} \times s_{obs}$.

The use of admixed standard substances in X-ray powder work has been discussed by Bacon [6], Andrews [7] and Parrish [8]. For the present investigation, use was generally made of a potassium chloride standard (Analar, British Drug Houses) the lattice parameter and linear expansion coefficient of which have been determined by Hambling [9], $a = 6.2930$ Å (25°C) and $\beta = 3.37 \times 10^{-5}/°C$. After grinding and recrystallization at 600°C for one hour, this substance gave powder interferences of good quality. Seven reflexions of suitable intensity and distribution appear within the diffraction range of the Guinier cameras used.

Other standard substances may be preferable for special purposes. Thus, when studying phases displaying solid solubility, addition of a pure component as a standard may make possible very accurate measurements of the changes of the lattice parameters accompanying the solution phenomenon, provided that the changes are large enough to give good resolution of corresponding lines. For very accurate determinations of absolute cell dimensions, it may sometimes be advisable to use a standard giving more reflexions than those obtained from potassium chloride in order to be able to fix the correction line $\Delta s = \text{const} \times s_{obs}$ more accurately.

When evaluating the films an automatic correction for film shrinkage was obtained according to Hägg [10] by printing a scale (graduated to 0.1 mm) on the film prior to development. The films were measured in a projection comparator obtained by slightly modifying an ordinary 35 mm "Prado" projector. The high quality of the Guinier photographs allowed a linear magnification as high as 7 or 8 times to be used.

Following a procedure introduced by Österlöf [11], the measurement of the reflexions was made not, as has usually been the case, on the maximum den-

Table 1. Guinier powder pattern of Hg_3TeO_6. Cu$K\alpha_1$ radiation. a_{obs} = 13.3921±0.0013 Å.

Intensity	Σh^2	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$(\sin^2\Theta_{obs}-\sin^2\Theta_{calc}) \times 10^6$	$s^\circ - s_{calc}$ mm
m	14	0.046307	0.046312	− 5	−0.002
w	16	0.052964	0.052978	−14	−0.005
s	18	0.059541	0.059544	−3	−0.001
s	20	0.066188	0.066160	+28	+0.009
m	24	0.079411	0.079392	+19	+0.006
vw	30	0.099238	0.099240	− 2	−0.001
vw	34	0.112446	0.112472	−26	−0.006
vw	38	0.125692	0.125704	−12	−0.003
w	40	0.132321	0.132319	+ 2	±0.000
m	46	0.152170	0.152167	+ 3	+0.001
w	54	0.178701	0.178631	+70	+0.014
w	56	0.185184	0.185247	−63	−0.013
w	62	0.205118	0.205095	+23	+0.005
vw	64	0.211628	0.211711	−83	−0.016
w	66	0.218313	0.218327	−14	−0.003
w	68	0.225017	0.224943	+74	+0.014
vw	70	0.231582	0.231559	+23	+0.004
vw	78	0.258013	0.258023	−10	−0.002
w	80	0.264659	0.264639	+20	+0.004
vw	82	0.271316	0.271255	+61	+0.011
w	86	0.284484	0.284487	− 3	−0.001
vw	88	0.291125	0.291103	+22	+0.004
w	94	0.310940	0.310951	−11	−0.002
vw	96	0.317498	0.317567	−69	−0.012
w	104	0.344053	0.344031	+22	+0.004
vw	106	0.350618	0.350647	−29	−0.005
vw	110	0.363935	0.363879	+56	+0.009
vw	116	0.383669	0.383726	−57	−0.009
vw	118	0.390325	0.390342	−17	−0.003

sity but on the very sharp high-angle edge of the lines. Provided that the lines are of good quality and that their intensities are not very high or too low, this method has been found to give very good results. It is essential that the reflexions of the test substance and of the standard are similar in their sharpness.

The usefulness of the camera for accurate work was tested by studying the photographs of several substances. All the exposures were made at about 20°C. For several of the test substances, accurate lattice parameters at this temperature have been reported in the literature or could be calculated from data obtained at other temperatures and the values for the thermal coefficient.

Table 2. Lattice parameters for some cubic substances obtained from Guinier powder photographs.

Substance	a_{obs} (20°C)	a_{lit} (21°C)	Reference
Al	4.0492±0.0004 Å	4.04922	8, 14
$Pb(NO_3)_2$	7.8560±0.0012 Å	7.8562	8
TlBr	3.9846±0.0006 Å	3.98506	14
NaCl	5.6396±0.0008 Å	5.64006	8

Table 3. Guinier powder pattern of MoO_3. Cu$K\alpha_1$ radiation. Lattice parameters found

$$a = 3.9628 \pm 0.0009 \text{ Å}$$
$$b = 13.855 \pm 0.004 \text{ Å}$$
$$c = 3.6964 \pm 0.0008 \text{ Å}$$

Intensity	*hkl*	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$(\sin^2\Theta_{obs} - \sin^2\Theta_{calc}) \times 10^5$
w	020	0.01246	0.01236	+10
vs	110	0.04094	0.04087	+ 7
m	040	0.04948	0.04945	+ 3
m	120	0.05025	0.05014	+11
vs	021	0.05586	0.05578	+ 8
vw	130	0.06566	0.06560	+ 6
m	101	0.08122	0.08120	+ 2
s	111	0.08432	0.08429	+ 3
vw	041	0.09282	0.09287	− 5
vw	060	0.11122	0.11126	− 4
vw	150	0.11507	0.11505	+ 2
vw	141	0.13055	0.13065	−10
m	200	0.15113	0.15112	+ 1
m	210	0.15428	0.15421	+ 7
s	002	0.17361	0.17368	− 7
vw	022	0.18605	0.18605	± 0
w	221	0.20684	0.20691	− 7
m	112	0.21444	0.21456	−12
w	171	0.23264	0.23264	± 0
w	081	0.24122	0.24122	± 0
vw	062	0.28494	0.28495	− 1
vw	152	0.28880	0.28873	+ 7
vw	212	0.32787	0.32790	− 3
w	232	0.35259	0.35262	− 3
vw	023	0.40324	0.40315	+ 9

Table 4. Guinier powder pattern of Ti_5O_9. Cu$K\alpha_1$ radiation. Lattice parameters found

$$a = 5.569 \text{ Å},\ b = 7.120 \text{ Å},\ c = 8.865 \text{ Å}$$
$$\alpha = 97.55°,\ \beta = 112.34°,\ \gamma = 108.50°$$

Intensity	*hkl*	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$(\sin^2\Theta_{obs} - \sin^2\Theta_{calc}) \times 10^5$
vw	001	0.00973	0.00962	+11
w	$10\bar{1}$	0.02194	0.02189	+ 5
vw	100	0.02665	0.02664	+ 1
st	$10\bar{2}$	0.03643	0.03638	+ 5
vw	101	0.05063	0.05061	+ 2
v st	$1\bar{2}0$	0.05226	0.05224	+ 2
vw	$02\bar{1}$	0.05294	0.05294	± 0
w	020	0.05676	0.05674	+ 2
w	$12\bar{1}$	0.06091	0.06091	± 0
v st	$1\bar{2}1$	0.06278	0.06279	− 1
w	$02\bar{2}$	0.06841	0.06837	+ 4
v st	$10\bar{3}$	0.07010	0.07011	− 1
m	021	0.07986	0.07978	+ 8
st	$20\bar{1}$	0.08737	0.08744	− 7
vw	$12\bar{2}$	0.08886	0.08882	+ 4
st	102	0.09384	0.09382	+ 2
st	$12\bar{1}$	0.09633	0.09635	− 2
vw	$2\bar{2}0$	0.10081	0.10100	−19
m	$02\bar{3}$	0.10297	0.10303	− 6
w	200	0.10654	0.10654	± 0
w	$22\bar{2}$	0.10867	0.10887	−20

The cylindrical form and the adjustment of the camera were checked by means of the diagram obtained from mercuric tellurate, Hg_3TeO_6. According to Hägg and Holmberg [12], this substance is cubic with the cube edge equal to 13.4 Å. A sample prepared according to Hutchins [13] was kindly lent by Professor Hägg. The powder photograph (Table 1) indicated that the form and adjustment of the camera were perfect. The 29 observed reflexions give the relative value of the lattice parameter to ±0.004 % (confidence limits for 95 % probability). The absolute value for the parameter, given in Table 1, lacks significance due to the inadequate knowledge of the purity of the sample. The differences between the s values corresponding to $\sin^2\Theta_{\text{obs}}$ and $\sin^2\Theta_{\text{calc}}$, given in the column $s^{\circ}-s_{\text{calc}}$ of Table 1, show that the error in the readings is of the magnitude of 0.01 mm. The use of a vernier for the film measurements thus seems warranted. However, it ought to be emphasized that the maximum error of the scale printed on the film is also of this magnitude [10].

Table 2 gives lattice parameters obtained for samples of aluminium (99.99% pure), thallous bromide (British Drug Houses), sodium chloride (Merck, Analytical reagent) and lead nitrate (Riedel — E. de Haën p.a.). The influence of refraction has been considered when warranted. The confidence limits are given for 95 % probability. The agreement with precision data reported in the literature is satisfactory. It is evident that the accuracy obtained is high enough to require that the temperature is maintained constant to within about ± 1°C during the exposure.

Lattice parameters may also be obtained with a considerable degree of accuracy for substances of symmetry lower than cubic. This is illustrated in Tables 3 and 4 which give the powder patterns of orthorhombic molybdenum trioxide (C. P., Baker's Analyzed) and triclinic pentatitanium enneaoxide (prepared from titanium metal and titanium dioxide, both of high purity) [4]. The very satisfactory agreement between observed and calculated values of $\sin^2\Theta$ clearly suggests the suitability of Guinier camera data for the analytical methods of indexing powder patterns.

The camera with $\mathrm{Cu}K(\alpha_1+\alpha_2)$ radiation has also been found to give data of rather high accuracy although it does not completely match the $\mathrm{Cu}K\alpha_1$ camera in this respect. The superposition or close vicinity of the α_1 and α_2 reflexions and the shift of their relative position ($\Theta_{\alpha_2}-\Theta_{\alpha_1}$ negative for $\Theta < 14.3°$ and positive for higher values of Θ) makes it somewhat difficult to apply the Österlöf measuring technique within extensive parts of the diffraction range. However, measurements of the sharp α_1 reflexion edge for Θ values below 14.3°, of the α_2 reflexion edge for unresolved doublets at higher values of Θ and of the edges of both components for well resolved doublets have been found to give results which compare favourably with those obtained from measurements on the maximum density of the lines.

Acknowledgements. The authors wish to express their sincere gratitude to Professor G. Hägg, Uppsala, and to Dr. J. Österlöf of this Institute for valuable information and discussions. Several members of the research staff have contributed to the results reported in this article by their observations and discussions of previous experiences. Thanks are especially due to Mr. Sten Andersson, Mr. Ulf Kuylenstierna, Mrs. Stina Nord and Docent Herbert Pestmalis.

REFERENCES

1. Klug, H. P. and Alexander, L. E. *X-Ray diffraction procedures for polycrystalline and amorphous materials.* John Wiley & Sons Inc., New York 1954.
2. Peiser, H. S., Rooksby, H. P. and Wilson, A. J. C. *X-Ray diffraction by polycrystalline materials.* The Institute of Physics, London 1955.
3. Magnéli, A., Blomberg-Hansson, B., Kihlborg, L. and Sundkvist, G. *Acta Chem. Scand.* **9** (1955) 1382.
4. Andersson, S. and Magnéli, A. *Naturwiss.* **43** (1956) 495.
5. Guinier, A. *X-Ray Crystallographic Technology.* Hilger & Watts Ltd., London 1952.
6. Bacon, G. E. *Acta Cryst.* **1** (1948) 337.
7. Andrews, K. W. *Acta Cryst.* **4** (1951) 562.
8. Parrish, W. *Technical Report* No. 68, Philips Laboratories (1953).
9. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
10. Hägg, G. *Rev. Sci. Instruments* **18** (1947) 371.
11. Österlöf, J. *To be published.*
12. Hägg, G. and Holmberg, K. E. *Unpublished experiments.*
13. Hutchins, E. B. *J. Am. Chem. Soc.* **27** (1905) 1157.
14. Smakula, A. and Kalnajs, J. *Phys. Rev.* **99** (1955) 1737.

Received July 8, 1957.