A GRAPHICAL METHOD FOR THE RECOGNITION OF X-RAY DIFFRACTION POWDER PATTERNS OF HEXAGONAL CRYSTALS AND THE ESTIMATION OF THEIR PARAMETERS

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In the case of cubic crystals, the interplanar spacings are similar for all compounds, differing only by the factor, **a**, the unit cell length, as indicated by the formula for the interplanar spacings.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

With some experience, the powder pattern of a face-centered cubic crystal can be recognized at a glance. Simple charts can be made (1) for estimation of the parameter **a** and determination of the indices of the powder lines of cubic crystals. More complicated charts, involving the use of $1/d^2$, log d, or c/a, have been suggested for use with crystals of the tetragonal system (2, 3, 4). Similar charts can be prepared for use with hexagonal crystals.

Since the actual lines on the powder photographs are spaced on the cylindrical film in proportion to the Bragg diffraction angle, theta, we decided to try the possibility of arranging a series of lines correlating the position of the hk0 lines on the powder diffractogram of hexagonal crystals with all possible values of **a**. The general formula for interplanar spacings in the hexagonal system is

$$d = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}}}$$

When l is O, this formula reduces to

$$d = \frac{0.866\ a}{\sqrt{h^2 + hk + k^2}} = \frac{\lambda}{2 \sin \theta}$$

Using copper radiation of average wave length 1.5405 Å, and the General Electric Co. powder camera of 14.32 cm. diameter, in which L, the distance of the line from the center spot, is equal to $\theta/4$, the values of L were calculated for the first ten hkO lines when **a** varies from 1 to 24. The results of these calculations are given in Table I.

TABLE I

Distance in cm. (L) of hkO lines from Center Spot in General Electric Co. Powder Camera using Copper K α Radiation at Various Values of a

a	$\frac{1}{a}$	Indices of hkO Lines									
		100	110	200	210	300	220	310	400	320	410
1	1.0000	15.70	----	----	----	----	----	----	----	----	----
2	0.5000	6.60	12.60	15.70	----	----	----	----	----	----	----
3	0.3333	4.31	7.73	9.09	12.93	15.70	----	----	----	----	----
4	0.2500	3.21	5.66	6.60	9.01	10.46	12.59	13.33	15.70	18.94	----
5	0.2000	2.57	4.49	5.21	7.02	8.07	9.54	9.98	11.34	12.71	13.73
6	0.1667	2.13	3.72	4.31	5.77	6.60	7.72	8.08	9.09	10.15	10.70
7	0.1429	1.83	3.18	3.68	4.91	5.60	6.53	6.82	7.64	8.41	8.91
8	0.1250	1.60	2.78	3.21	4.28	4.87	5.66	5.91	6.60	7.25	7.66
9	0.1111	1.42	2.47	2.85	3.79	4.31	5.01	5.22	5.82	6.38	6.73
10	0.1000	1.28	2.22	2.56	3.40	3.87	4.49	4.68	5.21	5.70	6.02
11	0.0909	1.16	2.01	2.33	3.09	3.51	4.07	4.24	4.72	5.16	5.44
12	0.0833	1.06	1.85	2.13	2.83	3.21	3.72	3.88	4.31	4.71	4.97
13	0.0769	0.98	1.70	1.97	2.61	2.96	3.43	3.57	3.97	4.34	4.57
14	0.0714	0.91	1.58	1.83	2.42	2.75	3.18	3.31	3.68	4.02	4.23
15	0.0667	0.85	1.48	1.70	2.26	2.56	2.96	3.09	3.43	3.75	3.94
16	0.0625	0.78	1.38	1.60	2.12	2.40	2.78	2.89	3.21	3.51	3.69
17	0.0588	0.75	1.30	1.50	1.99	2.26	2.61	2.72	3.02	3.25	3.47
18	0.0555	0.71	1.23	1.42	1.88	2.13	2.47	2.57	2.85	3.11	3.27
20	0.0500	0.64	1.11	1.28	1.69	1.92	2.22	2.31	2.56	2.80	2.94
22	0.0455	0.58	1.01	1.16	1.54	1.74	2.01	2.10	2.33	2.54	2.61
24	0.0417	0.53	0.92	1.06	1.41	1.60	1.85	1.92	2.13	2.33	2.45

When the figures in Table I are plotted with **a** as ordinate and L as abscissa, excessive curvature of the lines renders them difficult to use. Plotting **log a** against L results in some improvement, but the best results are obtained by plotting 1/a as ordinate against L as abscissa. This plot is shown in Figure 1.

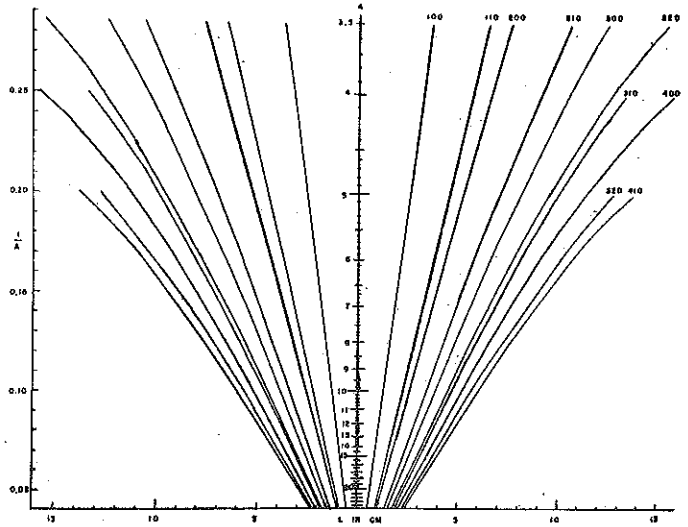

Figure 1. Curves for Matching the hkO Spacings in X-ray Powder Diffractograms of Hexagonal Crystals.

In making the comparisons between the powder diffractogram and the curves in Figure 1, it is desirable to transcribe the midpoints of the X-ray diffraction lines to the edge of a sheet of paper, which is then moved vertically with the diffraction center on the 1/a axis and the array of line positions parallel to the L axis. In the case of hexagonal crystals, it may be expected that approximately 1/3 of the lines will be hkO. Trials are made with each line in order down the diffractogram centered on the 100 curve, and the coincidence of other lines noted. Owing to the fact that some lines may be weak and not visible on the diffractogram, coincidence of eight lines out of a possible ten is a reasonable fit, and the numerical value of 1/a (or **a**) may be read from the ordinate. Coincidence of the 200, 300 and 400 lines is less significant than the other lines, since these are orders of the 100 line.

Once the crystal has been determined to be hexagonal, the hkO lines can be eliminated. It might be expected that one of the remaining lines would be the 001 line, in which case it might be expected to be prominent and to be succeeded by its orders, 002, 003, 004, etc. In applying this concept, it was found in most cases that it was not possible to pick an 001 line accurately, so that any guess for the parameter **c** is very difficult.

TABLE II

Results Obtained in Using the Curves in Figure 1 for the Recognition of Hexagonal Crystals

Compound	a from curves	Known a	Coincidence of lines	Estimate of c	Known c	001 line present or absent
α-hydroquinone	22.2	22.07	9 of 10 in first 10	3.22*	5.62	±
d,l-Menthol	12.6	11.82	8 of 10 in first 19	6.95	---	
Apatite	9.25	9.36	7 of 10 in first 21	2.80*	6.88	–
beryl	9.15	9.21	9 of 10 in first 17	2.85*	9.17	–
benzil	8.3	8.15	7 of 9 in first 25	6.4*	13.46	–
l-cystine	5.35	5.43	6 of 6 in first 21	---	---	
Quartz	4.90	4.90	8 of 9 in first 31	3.7*	5.39	±
Covellite	4.1*	3.80	6 of 8 in first 29	8.1*	16.43	–
Zincite	3.3	3.24	3 of 3 in first 8	6.5*	5.18	–
Molybdenite	3.2	3.15	5 of 5 in first 31	6.2*	12.30	–
Graphite	3.98*	2.45	5 of 6 in first 33	6.9	6.69	+
tourmaline (ditrigonal)	no fit	16.23				
corundum (rhombohedral)	9.2*	5.12	8 of 10 in first 19			
sphalerite (cubic)	3.5*	5.43	6 of 6 in first 16			

*erroneous estimates

The results of the application of this technic to a group of hexagonal crystals are listed in Table II above, the chart comparison and the estimates of the parameters **a** and **c** having been made in advance of looking up the known parameters in the handbook. In the case of l-cystine, **a** was not found in the literature, but was measured directly by the rotating crystal technic in order to get a figure for comparison with the estimation of **a.** It is interesting to note that in attempting to run greenockite (CdS), which was present as inclusions in a sample of sphalerite (ZnS, cubic), the run was actually made on sphalerite and a reasonable match obtained. This is understandable in view of the fact that a nearly accurate hexagon can be drawn by connecting the appropriate points on a square grid. In attempting to use this graphical method, it is desirable to first eliminate the possibilities of cubic and tetragonal symmetries.

Inspection of Table II indicates that reasonably good results are obtained in the recognition of hexagonal crystals and in the estimation of **a** when **a** is greater than 4. With lower values of **a,** it would be better to use molybdenum radiation as this would bring the lines closer to the center spot. In most cases, the OO1 line was so faint as to not be visible. With hydroquinone the 001 line was masked by a coincident line in the hkO series, with quartz the 001 line was very faint, with covellite and molybdenite the 002 lines were chosen, and only with graphite was a reasonable approximation for **c** obtained.

It had been expected that the curves would be useful in making decisions as to whether certain microcrystalline materials were in the hexagonal system, but in view of the falsely positive results obtained in systems that might be considered as pseudohexagonal, the technic is not suitable for positive identification of hexagonal symmetry in unknown samples. The technic is useful for estimation of **a** and indexing of hkO lines in known hexagonal crystals.

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