THE AMERICAN MINERALOGIST, VOL. 54, MAY–JUNE, 1969

INDEXING POWDER PATTERNS FOR CUBIC MATERIALS

F. DONALD BLOSS, *Department of Geological Sciences, Virginia Polytechnic Institute, Blacksburg, Virginia 24060*

ABSTRACT

Powder diffraction patterns for isometric crystals become self-indexing if one calculates the quotients d_1^2/d_1^2, d_1^2/d_2^2, $\cdots$, d_1^2/d_n^2 where d_1 is the largest interplanar spacing observed and d_2, $\cdots$, d_n are successively smaller ones. The resultant set of squared quotients will then identify with one of the columns in Table 1 whereupon all lines become indexed. An advantage of this method over the commonly used graphic method is that reflections for which 2θ and $(h^2+k^2+l^2)$ are large are indexed as easily as those for which 2θ and $(h^2+k^2+l^2)$ are small.

INTRODUCTION

Graphical indexing of powder diffraction data for cubic materials by means of the standard chart becomes less satisfactory for *hkl* reflections wherein $(h^2+k^2+l^2)$ is large in value. Consequently, one sometimes needs to index the simpler *hkl* reflections first, then calculate a cell edge on the basis of these reflections in order to index the back reflections. By contrast the method to be described indexes these back reflections as easily as it does those forward reflections for which 2θ and $(h^2+k^2+l^2)$ are small in value.

METHOD

To index the powder pattern of a cubic material, first determine the interplanar spacings d_1, d_2, d_3, $\cdots$, d_n, where d_1 is the largest spacing observed and d_2, d_3, $\cdots$, d_n are successively smaller spacings. Next compute d_1^2/d_1^2, d_1^2/d_2^2, d_1^2/d_3^2, $\cdots$, d_1^2/d_n^2. This set of squared quotients will identify with one of the columns in Table 1–that is, all values present in the set will be present in that column. The column so identified then permits an indexing of the lines of the diffraction record by inspection.

An example will illustrate the simplicity of the method. Table 2 contains d_1^2/d_1^2, d_1^2/d_2^2, $\cdots$, d_1^2/d_n^2 values as computed for synthetic spinel, $MgAl_2O_4$, from the interplanar spacings measured from a routine Debye-Scherrer powder photograph (114.6 mm diameter camera, Cu$K\alpha$ radiation). This set of squared quotients is seen to be drawn from the population of numbers represented by column (3) in Table 1. Hence diffraction indices *hkl* are assignable to each *d* spacing, these values being those entered in the *hkl* column in Table 2. Note that, for the spinel data, the numerous *hkl* extinctions provide no difficulty in indexing whatsoever. As a check, the cell edge *a* was calculated for each line indexed from the relationship

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (1)$$

The conformity of these cell-edge values thus confirms the assignment of the individual indices.

The derivation of Table 1 is readily apparent. Let $h_1k_1l_1$ represent the reflection index for the largest spacing d_1 and let hkl be the index corresponding to any other spacing d. For isometric crystals

$$a^2 = d^2(h^2 + k^2 + l^2) = d_1^2(h_1^2 + k_1^2 + l_1^2)$$

Thus

$$\frac{d_1^2}{d^2} = \frac{(h^2 + k^2 + l^2)}{(h_1^2 + k_1^2 + l_1^2)} \quad (2)$$

Depending upon whether the $h_1k_1l_1$ reflection is 100, 110, 111, 200, 210, 211, or 220, $(h_1^2+k_1^2+l_1^2)$ in Eq. 2 will respectively equal 1, 2, 3, 4, 5, 6, or 8. Hence the set of quotients represented by d_1^2/d_1^2, d_1^2/d_2^2, d_1^2/d_3^2, $\cdots$, d_1^2/d_n^2 will contain only integers (col. 1, Table 1) if $h_1k_1l_1$ is 100, (*b*) integers plus half intervals (col. 2, Table 1), if $h_1k_1l_1$ is 110, (c) integers plus one-third intervals (col. 3, Table 1), if $h_1k_1l_1$ is 111, (*d*) integers plus one-quarter intervals (col. 4), if $h_1k_1l_1$ is 200, (*e*) integers plus one-fifth intervals (col. 5), if $h_1k_1l_1$ is 210 and, in general, integers plus $1/N_1$th intervals between them where $N_1=(h_1^2+k_1^2+l_1^2)$.

Measurement error is largest for d_1 but successively decreases from d_1 to $d_2, \cdots$, to d_n. Thus in obtaining the set of d_1^2/d^2 values, d^2 is known with increasing accuracy as the smaller values near to d_n are considered. Consequently the method indexes diffraction peaks for which 2θ exceeds 90° almost as readily as it indexes peaks for which 2θ is small in value.

Any method of indexing will result in ambiguities if (*1*) the observed d values contain large experimental errors, especially if (*2*) $h_1k_1l_1$ represents a reflection for which $(h_1^2+k_1^2+l_1^2)$ is relatively large in value. To illustrate this, consider d_1^2/d^2 values for an iron manganese garnet (Table 3) as calculated from d values reported by Vermaas (1952, p. 947). The smallest interplanar spacing, d_1, is cited as 2.92 Å whereas it actually is slightly in excess of 2.94Å. Moreover, $h_1k_1l_1$ subsequently was found to be 400, which meant that correct d_1^2/d^2 values could differ by as little as 1/16 or 0.0625 units. Even with this error in d_1, however, the first six d_1^2/d^2 values for this garnet permitted unequivocal rejection of columns (1) to (6) in Table 1. The observed d_1^2/d^2 values which prompted rejection of columns (7) to (13) are: (7), 1.86; (8), 1.49; (9), 1.24, 1.49; (10), 1.24, 1.49; (11), 1.24; (12), 1.49, 2.35; and (13), 1.24, 1.61. These six d_1^2/d^2 values always fall within 0.02 of a value in column (14) which was thus used to index the first seven lines. If the experimental error in d_1 had gone

TABLE 1. SETS OF d_1^2/d^2 QUOTIENTS FOR INDEXING POWDER DIFFRACTION PATTERNS OF ISOMETRIC CRYSTALS

		True reflection index corresponding to d_1:													
hkl for *d*	Lattice Type[a]	100 (1)	110 (2)	111 (3)	200 (4)	210 (5)	211 (6)	220 (7)	300, 221 (8)	310 (9)	311 (10)	222 (11)	320 (12)	321 (13)	400 (14)
100		1													
110	I	2	1												
111	F	3	1.5	1											
200	I, F	4	2	1.33	1										
210		5	2.5	1.67	1.25	1									
211	I	6	3	2	1.5	1.2	1								
220	I, F	8	4	2.67	2	1.6	1.33	1							
300, 221		9	4.5	3	2.25	1.8	1.5	1.12	1						
310	I	10	5	3.33	2.5	2	1.67	1.25	1.11	1					
311	F	11	5.5	3.67	2.75	2.2	1.83	1.37	1.22	1.10	1				
222	I, F	12	6	4	3	2.4	2	1.5	1.33	1.20	1.09	1			
320		13	6.5	4.33	3.25	2.6	2.17	1.62	1.44	1.30	1.18	1.08	1		
321	I	14	7	4.67	3.5	2.8	2.33	1.75	1.56	1.40	1.27	1.17	1.08	1	
400	I, F	16	8	5.33	4	3.2	2.67	2	1.78	1.60	1.45	1.33	1.23	1.14	1
410, 322		17	8.5	5.67	4.25	3.4	2.83	2.12	1.89	1.70	1.55	1.42	1.31	1.21	1.06
411, 330	I	18	9	6	4.5	3.6	3	2.25	2.00	1.80	1.64	1.50	1.38	1.29	1.13
331	F	19	9.5	6.33	4.75	3.8	3.17	2.37	2.11	1.90	1.73	1.58	1.46	1.36	1.18
420	I, F	20	10	6.67	5	4	3.33	2.5	2.22	2.00	1.82	1.67	1.54	1.43	1.25
421		21	10.5	7	5.25	4.2	3.5	2.62	2.33	2.10	1.91	1.75	1.62	1.50	1.31
332	I	22	11	7.33	5.5	4.4	3.67	2.75	2.44	2.20	2.00	1.83	1.69	1.57	1.38
422	I, F	24	12	8	6	4.8	4	3	2.67	2.40	2.18	2.00	1.85	1.71	1.50
500, 430		25	12.5	8.33	6.25	5	4.17	3.12	2.78	2.50	2.27	2.08	1.92	1.79	1.56
510, 431	I	26	13	8.67	6.5	5.2	4.33	3.25	2.89	2.60	2.36	2.17	2.00	1.86	1.63
511, 333	F	27	13.5	9	6.75	5.4	4.5	3.37	3.00	2.70	2.45	2.25	2.08	1.93	1.69
520, 432		29	14.5	9.67	7.25	5.8	4.83	3.62	3.22	2.90	2.64	2.42	2.23	2.07	1.81
521	I	30	15	10	7.5	6	5	3.75	3.33	3.00	2.73	2.50	2.31	2.14	1.88
440	I, F	32	16	10.67	8	6.4	5.33	4	3.56	3.20	2.91	2.67	2.46	2.29	2.00
522, 441		33	16.5	11	8.25	6.6	5.5	4.12	3.67	3.30	3.00	2.75	2.54	2.36	2.06
530, 433	I	34	17	11.33	8.5	6.8	5.67	4.25	3.78	3.40	3.09	2.83	2.62	2.43	2.13
531	F	35	17.5	11.67	8.75	7	5.83	4.37	3.89	3.50	3.18	2.92	2.69	2.50	2.19
600, 442	I, F	36	18	12	9	7.2	6	4.5	4.00	3.60	3.27	3.00	2.76	2.57	2.25
610		37	18.5	12.33	9.25	7.4	6.17	4.62	4.11	3.70	3.36	3.08	2.85	2.64	2.31
611, 532	I	38	19	12.67	9.5	7.6	6.33	4.75	4.22	3.80	3.45	3.17	2.92	2.71	2.38
620	I, F	40	20	13.33	10	8	6.67	5	4.44	4.00	3.64	3.33	3.08	2.86	2.50
443, 621, 540		41	20.5	13.67	10.25	8.2	6.83	5.12	4.56	4.10	3.73	3.42	3.15	2.93	2.56
541	I	42	21	14	10.5	8.4	7	5.25	4.67	4.20	3.82	3.50	3.23	3.00	2.63
533	F	43	21.5	14.33	10.75	8.6	7.17	5.37	4.78	4.30	3.91	3.58	3.31	3.07	2.69
622	I, F	44	22	14.67	11	8.8	7.33	5.5	4.89	4.40	4.00	3.67	3.38	3.14	2.75
630, 542		45	22.5	15	11.25	9	7.5	5.62	5.00	4.50	4.09	3.75	3.46	3.21	2.81
631	I	46	23	15.33	11.50	9.2	7.67	5.75	5.11	4.60	4.18	3.83	3.54	3.29	2.88

[a] Entries in this column indicate whether the reflection index cited at left is possible for a body centered lattice (*I*) or for a face centered lattice (*F*) in addition to a primitive lattice.

TABLE 1.—(*continued*)

hkl for *d*	Lattice Type a	True reflection index corresponding to d_1: 100 (1)	110 (2)	111 (3)	200 (4)	210 (5)	211 (6)	220 (7)	300, 221 (8)	310 (9)	311 (10)	222 (11)	320 (12)	321 (13)	400 (14)
444	I, F	48	24	16	12	9.6	8	6	5.33	4.80	4.36	4.00	3.69	3.43	3.00
700, 632		49	24.5	16.33	12.25	9.8	8.17	6.12	5.44	4.90	4.45	4.08	3.77	3.50	3.06
710, 550, 543	I	50	25	16.67	12.50	10	8.33	6.25	5.56	5.00	4.55	4.17	3.85	3.57	3.13
711, 551	F	51	25.5	17	12.75	10.2	8.5	6.37	5.67	5.10	4.64	4.25	3.92	3.64	3.19
640	I, F	52	26	17.33	13	10.4	8.67	6.5	5.78	5.20	4.73	4.33	4.00	3.71	3.25
720, 641		53	26.5	17.67	13.25	10.6	8.83	6.62	5.89	5.30	4.82	4.42	4.08	3.79	3.31
721, 633, 552	I	54	27	18	13.50	10.8	9	6.75	6.00	5.40	4.91	4.50	4.15	3.86	3.38
642	I, F	56	28	18.67	14	11.2	9.33	7	6.22	5.60	5.09	4.67	4.31	4.00	3.50
722, 544		57	28.5	19	14.25	11.4	9.5	7.12	6.33	5.70	5.18	4.75	4.38	4.07	3.56
730	I	58	29	19.33	14.5	11.6	9.67	7.25	6.44	5.80	5.27	4.83	4.46	4.14	3.63
731, 553	F	59	29.5	19.67	14.75	11.8	9.83	7.37	6.56	5.90	5.36	4.92	4.54	4.21	3.69
650, 643		61	30.5	20.33	15.25	12.2	10.17	7.62	6.78	6.10	5.55	5.08	4.69	4.36	3.81
732, 651	I	62	31	20.67	15.5	12.4	10.33	7.75	6.89	6.20	5.64	5.17	4.77	4.43	3.88
800	I, F	64	32	21.33	16	12.8	10.67	8	7.11	6.40	5.82	5.33	4.92	4.57	4.00
810, 740, 652		65	32.5	21.67	16.25	13	10.83	8.12	7.22	6.50	5.91	5.42	5.00	4.64	4.06
811, 741, 554	I	66	33	22	16.50	13.2	11	8.25	7.33	6.60	6.00	5.50	5.08	4.71	4.13
733		67	33.5	22.33	16.75	13.4	11.17	8.37	7.44	6.70	6.09	5.58	5.15	4.79	4.19
820, 644	I, F	68	34	22.67	17	13.6	11.33	8.5	7.56	6.80	6.18	5.67	5.23	4.86	4.25
821, 742		69	34.5	23	17.25	13.8	11.5	8.62	7.67	6.90	6.27	5.75	5.31	4.93	4.31
653	I	70	35	23.33	17.5	14	11.67	8.75	7.78	7.00	6.36	5.83	5.38	5.00	4.38
822, 660	I, F	72	36	24	18	14.4	12	9	8.00	7.20	6.55	6.00	5.54	5.14	4.50
830, 661		73	36.5	24.33	18.25	14.6	12.17	9.12	8.11	7.30	6.64	6.08	5.62	5.21	4.56
831, 750, 743	I	74	37	24.67	18.5	14.8	12.33	9.25	8.22	7.40	6.73	6.17	5.69	5.29	4.63
751, 555	F	75	37.5	25	18.75	15	12.5	9.37	8.33	7.50	6.82	6.25	5.77	5.36	4.69
662	I, F	76	38	25.33	19	15.2	12.67	9.5	8.44	7.60	6.91	6.33	5.85	5.43	4.75
832, 654		77	38.5	25.67	19.25	15.4	12.83	9.62	8.56	7.70	7.00	6.42	5.92	5.50	4.81
752	I	78	39	26	19.5	15.6	13	9.75	8.67	7.80	7.09	6.50	6.00	5.57	4.88
840	I, F	80	40	26.67	20	16	13.33	10	8.89	8.00	7.27	6.67	6.15	5.71	5.00
900, 841, 744, 663		81	40.5	27	20.25	16.2	13.5	10.12	9.00	8.10	7.36	6.75	6.23	5.79	5.06
910, 833	I	82	41	27.33	20.5	16.4	13.67	10.25	9.11	8.20	7.45	6.83	6.31	5.86	5.13
911, 753	F	83	41.5	27.67	20.75	16.6	13.83	10.37	9.22	8.30	7.55	6.92	6.38	5.93	5.19
842	I, F	84	42	28	21	16.8	14	10.5	9.33	8.40	7.64	7.00	6.46	6.00	5.25
920, 760		85	42.5	28.33	21.25	17	14.17	10.62	9.44	8.50	7.73	7.08	6.54	6.07	5.31
921, 761, 655	I	86	43	28.67	21.50	17.2	14.33	10.75	9.56	8.60	7.82	7.17	6.62	6.14	5.38
664	I, F	88	44	29.33	22	17.6	14.67	11	9.78	8.80	8.00	7.33	6.77	6.29	5.50

unnoticed, column (14) would have misindexed those indices marked *a* in Table 3. However, one would have been alerted to the error because $\Delta d_1^2/d_2$, the difference between d_1^2/d^2 (observed) compared to what it

TABLE 2. OBSERVED 2θ AND CALCULATED d_1^2/d^2 VALUES FOR A POWDER FILM OF SYNTHETIC SPINEL, $MgAl_2O_4$

2θ (obs)	d	d_1^2/d^2	hkl	N[a]	a (calc)[b]
19.02α	4.6658	1	111	3	8.0814
31.30α	2.8577	2.666	220	8	8.0828
36.894α	2.4365	3.667	311	11	8.0810
44.84α	2.0212	5.329	400	16	8.0848
55.702α	1.6501	7.994	422	24	8.0838
59.427α	1.5553	8.999	511/333	27	8.0816
65.287α	1.4291	10.659	440	32	8.0842
68.736α	1.3656	11.673	531	35	8.0790
74.19α	1.2781	13.327	620	40	8.0834
77.388α	1.2331	14.317	533	43	8.0860
82.691α	1.1670	15.984	444	48	8.0852
85.78α	1.1327	16.968	711/551	51	8.0891
94.171α_1	1.0517	19.678	731/553	59	8.7826
94.451α_2	1.0520				8.0806
99.37α_1	1.0102	21.337	800	64	8.0816
99.72α_2	1.0101				8.0808
107.92α_1	.95257	23.994	822/660	72	8.0828
108.327α_2	.95248				8.0821
111.26α_1	.93318	24.995	751/555	75	8.0816
111.656α_2	.93330				8.0826
116.944α_1	.90365	26.665	840	80	8.0825
117.45α_2	.90345				8.0807
120.50α_1	.88719	27.667	911/753	83	8.0827
121.074α_2	.88686				8.0797
130.744α_1	.84733	30.321	931	91	8.0836
131.366α_2	.84734				8.0831
138.028α_1	.82497	31.987	844	96	8.0830
138.785α_2	.82495				8.0828

[a] $N=h^2+k^2+l^2$
[b] $a=d\sqrt{N}$

should be to conform precisely to column (14), systematically increases from 0.01 for 420 to 0.04 for reflection 444. One could correct these observed d_1^2/d^2 values either by (1) taking d as 2.94 and recomputing or (2) adding the value of $\Delta d_1^2/d^2$ for each previously indexed line to the d_1^2/d^2 value for the next higher angle line to be indexed. To illustrate this second method, 0.04 the $\Delta d_1^2/d^2$ value for 444 would be added to the 3.20 value to make it 3.24, which brings it close enough to its error-free

TABLE 3. INDEXING AN IRON MANGANESE GARNET

Observed		From Table 1, col. 14				
d	d_1^2/d^2	hkl	d_1^2/d^2	$\Delta\, d_1^2/d^2$	N	a
2.92	1	400	1		16	11.68
2.62	1.24	420	1.25	0.01	20	11.72
2.39	1.49	422	1.50	0.01	24	11.71
2.30	1.61	510,431	1.63	0.02	26	11.73
2.14	1.86	521	1.88	0.02	30	11.72
1.906	2.35	611,532	2.38	0.03	38	11.75
1.698	2.96	444	3.00	0.04	48	11.76
1.632	3.20	640[a]	3.25	0.05	52	11.77
1.574	3.44	642[a]	3.50	0.06	56	11.78
1.474	3.92	800[a]	4.00	0.08	64	11.79
1.316	4.92	840[a]	5.00	0.08	80	11.77
1.288	5.14	842[a]	5.25	0.11	84	11.80
1.257	5.40	664[a]	5.50	0.11	88	11.79
1.095	7.11				116[b]	11.79
1.077	7.35				120[b]	11.80
1.043	7.69				128[b]	11.80
0.983	8.82		Beyond		144[b]	11.80
0.971	9.04		Table 1		148[b]	11.81
0.968	9.10				149[b]	11.82

[a] Denotes a reflection index which would have been misindexed if the error in d_1 (2.92 Å) had not been detected through failure to recognize the systematic increase in error, $\Delta\, d_1^2/d^2$, where this equals $(d_1^2/d^2)_{\text{Table}}$ minus $(d_1^2/d^2)_{\text{obs.}}$, for hkl 400 to 444.

[b] These values of N lead to values for the cell edge a which continue the trend in computed a established by reflections for which N was 88 or less. Knowledge of these N values thus permits indexing the reflections whose d_1^2/d^2 values exceeded those given in Table 1.

value of 3.25 to permit its ready indexing as 640. Without such correction, column (14) would have misindexed the line as 711, 551. Using such corrections the lines were correctly indexed down to 1.257 Å.

For each of these indexed lines, the cell edge a was then computed by using Eq. 1. Taking the value of a as 11.80 or 11.79Å, one can determine N for the as yet nonindexed lines because

$$N^2 = \frac{a^2}{d^2}$$

Results again agree with Vermaas' indexing except for $d=0.968$ whose index should be 12.2.1, 10.7.0, 9.8.2 and/or 8.7.6 rather than 12.2.2 and/or 10.6.4.

Acknowledgments

I wish to thank my colleagues, Profs. G. V. Gibbs, and P. H. Ribbe, as well as Dr. Joan Clark of the U. S. Geological Survey for reading and criticizing the manuscript. The 2θ values for synthetic spinel were kindly supplied by Mr. Judson T. Mitchell.

Reference Cited

Vermaas, F. H. S. (1952) Manganese iron garnet from Otjosondu, Southwest Africa, *Mineral. Mag.* **29**, 946–951.

Manuscript received, January 27, 1969, accepted for publication, February 27, 1969.