A SIMPLE METHOD FOR INDEXING POWDER DIFFRACTION PATTERNS OF CUBIC MATERIALS:(I) USING THE θ -VALUES OF REFERENCE

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ABSTRACT

From the values of $\sin^2\theta$ taken from powder photographs of the cubic crystal system, a variable constant, K, which is a multiple of $(h^2+k^2+l^2)$ can be determined. The smallest value of $\sin^2\theta_1$ gives rise to a multiple of one, two, or three which corresponds to the smallest value of $\sum h l^2$ for the primitive, bcc and fcc crystals, respectively. The old assumption that when indexing, the occurrence of numbers of the form $(h^2+k^2+l^2) = 8n+7$, where n = 0,1,2,3.... should cause each of $(h^2+k^2+l^2)$ to be multiplied first by two before indexing, is disapproved.

INTRODUCTION

There is some uncertainty in indexing procedures of the cubic crystal system by means of the powder method. It is common practice that given the glancing angle θ-values, the quotient obtained from the $\sin^2\theta_n$ and either $\sin^2\theta_1$ or the average difference between successive $\sin^2\theta$-values should give the sum of $(h^2+k^2+l^2)$, from which the (hkl)-indices can be deduced. If it is found that this sum gives numbers of the form $(h^2+k^2+l^2) = 8n+7$, where n=0,1,2,3,... then indexing is impossible, and it has been suggested that each of the $(h^2+k^2+l^2)$ numbers be multiplied first by two before indexing (Guinier 1952, Klug & Alexander 1954, Peiser *et al.* 1955, Bragg 1955, Henry *et al.* 1960, Azaroff & Buerger 1958, Azaroff 1968, Miller & Sinkankas 1984, Newman 1987, Wilson 1987, Moore & Reynolds 1994). It must be warned that this procedure is wrong.

ANALYSIS

Consider the following two examples, where θ-values of sodium chloride (fcc) and tungsten (bcc) were measured, using $\lambda(CuK\alpha) = 1.5418$ Å and $\lambda(MoK\alpha) = 0.71354$ Å, respectively, and we know that the lattice constants of these substances are a = 5.63Å and 3.16Å, respectively, with slight deviations depending on the temperature at which data were collected and the

precision with which the θ-values were taken. Thus in the case of fcc crystals like sodium chloride, both ways as contemplated above do not work. In the case of the bcc crystals like tungsten both methods at first glance seem to work. In both the fcc and bcc crystals given here, the sum of $h^2+k^2+l^2 = 8n+7$ occurs. If we multiply each of these values by two according to the citations given above, we obtain the wrong lattice constant (and type) for the fcc crystal, while we get correct answers for the bcc crystal.

The snag with the multiplication by two is that the authors seem to work with a miraculous multiple- from without. It would certainly be wise if this multiple were to be taken from within the crystal data, that is, from $\sin^2\theta$. In fact the occurrence of $h^2+k^2+l^2 = 8n+7$ only signalizes the presence of, and search for, a hidden constant, which is a multiple of these reflections. It is suggested in this article that there is a constant, K, such that

$$\sin^2\theta = K(h^2+k^2+l^2) \quad \ldots\ldots(1)$$

Surely, a multiple of one, two and three for the smallest value of $\sin^2\theta_1$ should firstly be sought for, for the three categories, respectively; yet the existence of a constant, K, should always be borne in mind. The (hkl)-indices when $h^2+k^2+l^2 = 8n+7$ imply only that these numbers are unindexable, although the reflections may be real. Certainly they may be of higher orders than those of a multiple of two.

RESULTS AND DISCUSSION

Therefore, the correct indexing, using the K constant, is

Table 1(a): Sodium chloride *(fcc)*

$\theta(^0)$	$\sin^2\theta$	$\Delta\sin^2\theta$	$\sin^2\theta = K(h^2+k^2+l^2)$	hkl
14.0	0.06		0.020 X 3	(111)
		0.02		
16.25	0.08		4	(200)
		0.05		
21.0	0.13		7	(-)
		0.02		
23.0	0.15		8	(220)
		0.06		
27.5	0.21		11	(311)
		0.02		
28.5	0.23		12	(222)
		0.08		
33.5	0.31		16	(400)
		0.05		

Table 1(a) (Continued)

$\theta(^0)$	$\sin^2\theta$	$\Delta\sin^2\theta$	$\sin^2\theta = K(h^2+k^2+l^2)$	hkl
37.0	0.36		19	(331)
		0.03		
38.5	0.39		20	(420)
		0.07		
42.5	0.46		23	(-)

K = 0.020

Table 1(b): Tungsten (bcc)

$\theta(^0)$	$\sin^2\theta$	$\Delta\sin^2\theta$	$\sin^2\theta = K(h^2+k^2+l^2)$	hkl
9.20	0.026		0.013 x 2	(110)
		0.02		
13.07	0.052		4	(200)
		0.03		
16.02	0.08		6	(211)
		0.02		
18.60	0.10		8	(220)
		0.03		
20.85	0.13		10	(310)
		0.02		
23.02	0.15		12	(222)
		0.03		
25.02	0,18		14	(321)
		0.02		
26.88	0.20		16	(400)
		0.03		
28.62	0.23		18	(330)
		0.03		
30.33	0.26		20	(420)
		0.02		
31.93	0.28		22	(332)
		0.03		
33.90	0.31		24	(422)
		0.02		
35.10	0.33		26	(510)
		0.02		

K = 0.013

Table 2. Alpha tin (cubic diamond lattice)

No.	$\sin^2\theta$	$\Delta\sin^2\theta$	$\sin^2\theta = K(h^2+k^2+l^2)$	hkl
1	0.04		0.014 x 3	(111)
		0.07		
2	0.11		8	(220)
		0.05		
3	0.16		11	(311)
		0.07		
4	0.23		16	(400)
		0.01		
5	0.24		19	(331)
		0.10		
6	0.34		24	(422)
		0.05		
7	0.39		27	(333)
		0.06		
8	0.45		32	(440)
		0.04		
9	0.49		35	(531)
		0.07		
10	0.56		40	(620)
		0.05		
11	0.61		45	(542)
		0.07		
12	0.68		48	(444)
		0.05		
13	0.72		51	(551)
		0.07		
14	0.79		56	(642)
		0.04		
15	0.83		59	(553)

K = 0.0.14, a = 6.489Å, λ = 1.54051Å.

If it is observed that there is a multiple of two between successive $\sin^2\theta$-values, then P or bcc lattice types are inferred. The difference between these two lattice types is that the 6th value in $\Delta\sin^2\theta$ simply jumps or doubles. Therefore, the correct multiple for the first $\sum h_i^2$ for P is unity.

The difference between fcc and cubic diamond lattices is that certain reflections like (200), (222), 420), (600),... miss in the latter (i.e. reflections

of type $h^2+k^2+l^2 = 4n$, where n-odd are missing), and in general the $\Delta\sin^2\theta$-values of the cubic diamond lattice alternate.

θ_1 may be termed the θ_1-powder diffraction value of reference, whose corresponding $\sum h_i^2$-value must be 1, 2, or 3 depending on the lattice type.

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