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Neskuchaev's Method of Indexing Powder Patterns Applied to Systems of Intermediate Symmetry

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Neskuchaev's method for indexing powder patterns of crystals belonging to the tetragonal, hexagonal and rhombohedral systems is rationalized to include the effects of increasing Bragg angle, the linear dependence condition, the repetition of indices between systems and the 'equivalence' property. Sets of numbers corresponding to the possible indices of two initial lines of the pattern are systematically searched until a set is obtained that describes all the lines. The procedure is illustrated by means of the powder pattern for zinc.

Theoretical considerations

The usual equations connecting the lattice parameters and the Bragg angle or d spacing of the ith reflexion, for crystals of the tetragonal, hexagonal and rhombohedral systems, can be written in the form

$$f_i = Ax_i + By_i\,, \tag{1}$$

where $f_i = \sin^2\theta_i = \lambda^2/4d_i^2$, A and B are constants characteristic of the unit-cell geometry, and x_i, y_i are integers dependent on hkl and the crystal system. Values of x_i, y_i, subject to the condition $x_i, y_i \leq 4$, are given in Table 1 for the systems given above and all possible values of hkl. Higher values of x_i, y_i are given by Mirkin (1961).

Neskuchaev (1931) has shown that if two linearly independent values f_1, f_2 are selected from the first few values of f_i in equation (1), that is, values for which

$$D = \begin{vmatrix} x_1 y_1 \\ x_2 y_2 \end{vmatrix} \neq 0\,, \tag{2}$$

then the following relations hold:

$$f_i = m_i f_1 + n_i f_2\,, \tag{3}$$

and

$$\left.\begin{aligned} x_i &= m_i x_1 + n_i x_2 \\ y_i &= m_i y_1 + n_i y_2 \end{aligned}\right\}, \tag{4}$$

where

$$m_i = -\frac{\begin{vmatrix} x_2 y_2 \\ x_i y_i, \end{vmatrix}}{D} \quad n_i = \frac{\begin{vmatrix} x_1 y_1 \\ x_i y_i \end{vmatrix}}{D}\,, \tag{5}$$

and $i \geq 3$.

The procedure for indexing a powder pattern is then as follows. Two linearly independent values f_1 and f_2 are selected [*i.e.* values which satisfy equation (2)], and the remaining values of f_i are then expressed in terms of linear combinations of f_1 and f_2. This gives the set of numbers m_i, n_i, and using equations (4) and Table 2, definite values of x_1, y_1 and x_2, y_2 (each not greater than 4) are assigned to the two lines selected initially. From the tentative set of numbers $\begin{vmatrix} x_1 y_1 \\ x_2 y_2 \end{vmatrix}$, x_i, y_i are calculated from equation (4), and then compared with the values in Table 1. If the tentative set of numbers has been assigned correctly, and provided the experimental precision is adequate, all the values of x_i, y_i fit one or other of the crystal systems given in Table 1.

The number of tentative sets theoretically possible, with

$$x_i, y_i \leq 4\,, \tag{6}$$

is given by the permutations of 11, 11 and 6 quantities taken 2 at a time, and is thus

Table 1. *x,y as a function of hkl for tetragonal, hexagonal and rhombohedral systems* ($x, y \leq 4$)

Tetragonal system			Hexagonal system			Rhombohedral system		
hkl	$x=h^2+k^2$	$y=l^2$	hkl	$x=h^2+hk+k^2$	$y=l^2$	hkl	$x^2=h^2+k^2+l^2$	$y=hk+kl+lh$
001	0	1	001	0	1	100	1	0
002	0	4	002	0	4	$\bar{1}10$	2	$\bar{1}$
100	1	0	100	1	0	110	2	1
101	1	1	101	1	1	$\bar{1}11$	3	$\bar{1}$
102	1	4	102	1	4	111	3	3
110	2	0	110	3	0	200	4	0
111	2	1	111	3	1			
112	2	4	112	3	4			
200	4	0	200	4	0			
201	4	1	201	4	1			
202	4	4	202	4	4			

Table 2. *Possible values of* $D\left(=\begin{vmatrix} x_1 y_1 \\ x_2 y_2 \end{vmatrix}\right)$ *for tetragonal, hexagonal and rhombohedral systems* ($x, y \leq 4$)

Tetragonal system				Hexagonal system			
N	*D*	*N*	*D*	*N*	*D*	*N*	*D*
1	01	16	10	1	01	16	10
	10		01		10		01
	01		20		01		30
	20		01		30		01
	01		40		01		40
	40		01		40		01
	04		10		04		10
	10		04		10		04
	04		20		04		30
	20		04		30		04
	04		40		04		40
	40		04		40		04
2	01			2	01		
	11				11		
	01				01		
	21				31		
	01				01		
	41				41		
	04				04		
	14				14		
	04				04		
	24				34		
	04				04		
	44				44		
3	01			3	01		
	14				14		
	01				01		
	24				34		
	01				01		
	44				44		
4	04	17	11	4	04	17	11
	11		04		11		04
	04		21		04		31
	21		04		31		04
	04		41		04		41
	41		04		41		04
5	10			5	10		
	11				11		
	20				30		
	21				31		
	40				40		
	41				41		
	10				10		
	14				14		
	20				30		
	24				34		
	40				40		
	44				44		
6	10			22	10		
	21				31		
	10				10		
	24				34		
	20			23	30		
	41				41		
	20				30		
	44				44		

Tetragonal system				Hexagonal system			
N	*D*	*N*	*D*	*N*	*D*	*N*	*D*
7	10			7	10		
	41				41		
	10				10		
	44				44		
8	11			8	11		
	14				14		
	21				31		
	24				34		
	41				41		
	44				44		
9	11	18	20	24	11	32	30
	20		11		30		11
	14		20		14		30
	20		14		30		14
	21		40	25	31	33	40
	40		21		40		31
	24		40		34		40
	40		24		40		34
10	11			26	11		
	21				31		
	14				14		
	24				34		
	21			27	31		
	41				41		
	24				34		
	44				44		
11	11			28	11		
	24				34		
	21			29	31		
	44				44		
12	11	19	40	12	11	19	40
	40		11		40		11
	14		40		14		40
	40		14		40		14
13	11			13	11		
	41				41		
	14				14		
	44				44		
14	14	20	21	30	14	34	31
	21		14		31		14
	24		41	31	34	35	41
	41		24		41		34
15	14	21	41	15	14	21	41
	41		14		41		14

N is the number of each 'equivalence group'.

Rhombohedral system			
N	*D*	*N*	*D*
36	10	44	$2\bar{1}$
	$2\bar{1}$		10
	21		$2\bar{1}$
	$2\bar{1}$		21
37	10	45	21
	21		10
	$3\bar{1}$		40
	40		$3\bar{1}$
38	10	46	$3\bar{1}$
	$3\bar{1}$		10
	21		40
	40		21
39	10	47	33
	33		10
	$3\bar{1}$		33
	33		$3\bar{1}$
40	$2\bar{1}$	48	
	$3\bar{1}$		
	$2\bar{1}$		40
	40		$2\bar{1}$
41	$2\bar{1}$	49	33
	33		$2\bar{1}$
42	21	50	$3\bar{1}$
	$3\bar{1}$		21
43	21	51	33
	33		21
	40		33
	33		40

$11\times10+11\times10+6\times5=250$ (see Table 1).

Of these 250 sets, 22 are excluded by the linear dependence condition [equation (2)], and the obvious increase in Bragg angle with order of reflexion makes a further 65 sets inadmissible. There are thus 163 possible sets that could be tested to find the correct value of D. Certain sets are common to the tetragonal and the hexagonal or rhombohedral systems; thus the number is reduced to 125. However, if account is taken of the 'equivalence' property of certain reflexions, only 51 tests are necessary.

Equivalent sets of numbers for the tetragonal and hexagonal systems are given by

$$\begin{vmatrix} x_1y_1 \\ x_2y_2, \end{vmatrix}, \begin{vmatrix} px_1y_1 \\ px_2y_2, \end{vmatrix}, \begin{vmatrix} x_1qy_1 \\ x_2qy_2 \end{vmatrix} \text{ and } \begin{vmatrix} px_1qy_1 \\ px_2qy_2 \end{vmatrix} \quad (7)$$

where p and q, in accordance with equations (2) and (6), are integers having the following values:

p_{tet} 1:2:4, p_{hex} 1:3:4 and $q_{\text{tet}}=q_{\text{hex}}$ 1:4.

It can be proved that the last set of numbers in (7) is characteristic of the other sets in the series. If the collection of numbers x_i,y_i corresponding to the last set in (7) does not compare with the values in Table 1, then neither will the other sets of the series. If x_i,y_i correspond to the values in Table 1, then other series given by (7) may be acceptable, and the true set is that which yields the collection of integers x_i,y_i having no common factor.

It can also be shown that there are series of 'equivalent' sets of numbers for the rhombohedral system, which can be denoted by

$$\begin{vmatrix} x_1y_1 \\ x_2y_2 \end{vmatrix} \text{ and } \begin{vmatrix} x_1'y_1' \\ x_2'y_2' \end{vmatrix}. \quad (8)$$

It follows from the above considerations that it is only necessary to test the last sets in series (7) and (8), and the number of tests thus reduces to 51. In practice, however, the number of tests will normally be considerably less than this.

All possible types of set, subject to condition (6), are listed in Table 2 for the systems under consideration. The 163 sets are divided into 51 'equivalence' groups, some of which are common to both the tetragonal and hexagonal systems. It is evident that m_i,n_i can have integral or fractional values, and that the fractions occurring most frequently are multiples of $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$.

Application to the indexing of the powder pattern of zinc

Data for zinc taken from *N.B.S. Circular No.* 539 (1953) have been indexed in order to illustrate the above procedure. Experimental quantities are denoted by f_i', *etc.*, and calculated values by f_i. The first two values of the data are linearly independent (that is, they satisfy the condition $f_2'/f_1' \neq$ an integer), and these may be taken as f_1' and f_2'. In this particular case, since suitable values of f_i' are available at higher angles, refined values of f_1' and f_2' can be obtained, namely, $f_1'=0{\cdot}1634$ and $f_2'=0{\cdot}1878$. Using the refined values, the remaining f_i' are expressed in terms of f_1' and f_2'. The most frequently occurring values of m_i,n_i with the corresponding values of m_if_1' and n_if_2', are given in Table 3, and f_i' for each line is given in column 2 of Table 4. m_if_1' and n_if_2' are combined according to equation (3) to give f_i, and values are selected to correspond with f_i', to within the experimental error. (In the case considered, the maximum error in f_i' $(=f_i'-f_i)$ is $\pm0{\cdot}0010$). f_i is listed in column 3 of Table 4.

The values of m_i,n_i in each of the linear combinations (columns 4 and 5) are then analysed in accordance with equations (4) to (6), and a search is made through the final entries in each 'equivalence group' in Table 2, giving possible tentative sets of numbers. There are in fact only 18 possible sets out of the total of 51. The corresponding values of x_i,y_i are then calculated from equation (4) for each set, and compared with the entries in Table 1. This yields the tentative set $\left|{}^{04}_{40}\right|$ in 'equivalence group' no. 1, hexagonal subdivision, in Table 2. It is evident from this procedure

Table 3. *mf_1' and nf_2' for the most frequently occurring values of m and n*

m or n	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{3}{4}$	1	2	3	4	5
mf_1'	0·0408	0·0545	0·0817	0·1089	0·1226	0·1634	0·3268	0·4902	0·6536	0·8170
nf_2'	0·0470	0·0626	0·0939	0·1252	0·1408	0·1878	0·3756	0·5634	0·7512	—

Table 4. *Indexing of the powder pattern for zinc*

Line no.	f_1'	$f_i=m_if_1'+n_if_2'$	m_i	n_i	x_i	y_i	hkl
1	2	3	4	5	6	7	8
1	0·1635	$0{\cdot}1634=f_1'$ (refined)	1	0	0	4	002
2	0·1877	$0{\cdot}1878=f_2'$ (refined)	0	1	1	0	100
3	0·2287	$0{\cdot}2286=\frac{1}{4}f_1'+f_2'$	$\frac{1}{4}$	1	1	1	101
4	0·3514	$0{\cdot}3512=f_1'+f_2'$	1	1	1	4	102
5	0·5553	$0{\cdot}5554=\frac{2}{4}f_1'+f_2'$	$\frac{2}{4}$	1	1	9	103
6	0·5636	$0{\cdot}5634=3f_2'$	0	3	3	0	110
7	0·6535	$0{\cdot}6536=4f_1'$	4	0	0	16	004
8	0·7269	$0{\cdot}7268=f_1'+3f_2'$	1	3	3	4	112
9	0·7512	$0{\cdot}7512=4f_2'$	0	4	4	0	200
10	0·7921	$0{\cdot}7920=\frac{1}{4}f_1'+4f_2'$	$\frac{1}{4}$	4	4	1	201

that for the linear combinations given by equation (3) only those which yield the least difference between f_i' and f_i are in general acceptable.

The next step is to establish the true set of numbers which corresponds to the two lines selected initially. This is achieved by testing all sets in the above group in accordance with the 'equivalence' property defined by (7) and (8). Using the values of m_i, n_i obtained previously, equation (4) gives fractional values of y_i for the first three sets, which is inadmissible. Of the remaining sets only $|^{04}_{10}|$ fits the data for the hexagonal system in Table 1 and also yields a collection of integers x_i y_i that do not contain a common integral factor. The substance under investigation thus belongs to the hexagonal system and for the first two lines, $x_1=0$, $y_1=4$ and $x_2=1$, $y_2=0$. The values of *hkl* for each line are then obtained from Table 1. x_i, y_i and *hkl* are given in columns 6, 7 and 8 of Table 4.

Conclusion

Neskuchaev's method for indexing powder patterns, incorporating the rationalization suggested above, not only becomes more general, but also simpler than other methods employed for systems of intermediate symmetry. The method is therefore recommended as the principal one for patterns in this symmetry range, and as a subsidiary one for patterns of low symmetry. In the latter case, it is possible to establish that the substance under investigation belongs to a low-symmetry system, thus simplifying the application of more general methods of indexing (Ito, 1949, 1950; Peiser, Rooksby & Wilson, 1955; Azároff & Buerger, 1961).

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Parameter Errors in Polar Space Groups Caused by Neglect of Anomalous Scattering

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A simple formula is given for the atomic coordinate error when $\Delta f''$ is neglected. With Cu $K\alpha$ radiation the effect is important for most elements and can reach 0·08 Å.

1

Ueki, Zalkin & Templeton (1966) have recently pointed out the serious coordinate errors which can result from the neglect of the imaginary component $\Delta f''$ of the anomalous scattering in the ten polar point groups. In these groups the position of the origin in one or more dimensions is not fixed by reference to symmetry elements. In Ueki's example of thorium nitrate pentahydrate, space group *Fdd*2, Mo $K\alpha$ radiation, the neglect of $\Delta f''=9$ for thorium caused an error of about 0·05 Å in the *z* coordinate of Th relative to those of the lighter atoms.

In the present note we consider the problem further and in particular point out that the serious consequences of the neglect of $\Delta f''$ are not confined to heavy elements. As we have remarked elsewhere (McDonald & Cruickshank, 1967) the effect of the inclusion, with Cu $K\alpha$ radiation, of $\Delta f''=0{\cdot}6$ for the S atoms in S_3O_9, space group $P2_1nb$, was to produce changes of 0·02 Å in some bond lengths.

2

For a centrosymmetric crystal the relation $|F(hkl)|=|F(h\bar{k}\bar{l})|$ holds by virtue of the symmetry. For a non-centrosymmetric crystal the same relation is true, provided $\Delta f''$ is negligible (Friedel's law). In consequence

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