E sites, and the lattice parameter changes follow the expected pattern. The *A*, *B* and *D* sites are the most invariant in the ordered state, *A* and *D* being occupied by Y atoms and *B* by X atoms, and must play an important role in the stability of the σ phase. They are prominent in the stacking arrangement of the structure, the *B* sites in one layer occupying positions between the *A* and *D* sites in the adjoining layers. The transformation to disorder must disturb the stable electronic configuration associated with these sites, and it is conceivable that the introduction of a large number of the larger X atoms into the 12 coordination sites is responsible for the distortion within the kagomé layers and the observed parameter changes.

The importance of the *D* site has been emphasized by the work on ternary σ phases containing silicon (Aronsson & Lundström, 1957; Stüwe, 1959; Gupta, Rajan & Beck, 1960) where an increasing silicon content in the *D* sites produces parameter changes of the same sign as those observed in irradiated σ phases. Wilson & Parselle (1965) discuss the irradiation effects in σ-MoRe in terms of order changes in the *E* site and the importance of the *E–E* bond, but Table 3 shows that the *E* site changes are relatively small and approximately the same for each alloy. In the opinion of the present author, therefore, the comparatively large changes in occupancy of the *A*, *B* and *D* sites are the most important in determining parameter changes in irradiated sigmas.

Since the theoretical knowledge of stability and ordering arrangement is so uncertain, it is impossible to conclude absolutely the reasons for the observed structural changes in irradiated binary σ phases, but it seems most likely that the destruction of order in the *A*, *B* and *D* sites, coupled with defect clusters between the (002) planes, is responsible for the distortion of these planes and the observed effects.

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On the Indexing of Powder Patterns for Polycrystalline Materials of the Orthorhombic System

BY I. A. BARABASH AND G. V. DAVYDOV
Chair of Solid State Physics, Pedagogical State Institute, Moscow, USSR

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An analytical method for indexing powder patterns of polycrystalline substances having orthorhombic symmetry is discussed. The technique is an extension of Neskuchaev's method for systems of intermediate symmetry. The procedure is applied to the indexing of the powder pattern for $NiAl_3$.

Introduction

An analytical method for indexing powder patterns of the orthorhombic system was suggested by Bradley & Taylor (1937) and later developed by Hesse (1948) and Lipson (1949). Neskuchaev (1931) suggested a method for indexing powder patterns of the tetragonal, hexagonal and rhombohedral systems and mentioned the possibility of extending it to include systems of lower symmetry. The method has not been widely applied to systems of intermediate or low symmetry, and in a previous paper (Barabash & Davydov, 1967) a development of

Neskuchaev's method for the former case has been considered. The present work considers a generalization of the method for indexing powder patterns of the orthorhombic system, and the powder pattern for $NiAl_3$ is indexed as an illustration of the procedure.

Theory

The usual equation connecting the lattice parameters and the Bragg angle or d spacing of the ith reflexion for crystals of the orthorhombic system is

$$\sin^2\theta_i = \frac{\lambda^2}{4d_i^2} = \frac{1}{a^2}h_i^2 + \frac{1}{b^2}k_i^2 + \frac{1}{c^2}l_i^2 , \qquad (1)$$

or

$$f_i = Ax_i + By_i + Cz_i . \qquad (2)$$

For given values of hkl, all possible values of x,y,z can be obtained, and these are given in Table 1, subject to the condition

$$x,y,z \leq 4 . \qquad (3)$$

Since measurements are always referred to a definite crystal system, (2) always has a solution. One can show by applying the Kronecker–Capelli theorem to (2) that if three linearly independent values f_1,f_2,f_3 are selected from the first few values of f_i in (2), that is, values for which

$$D = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \neq 0 , \qquad (4)$$

then the following relations hold:

$$f_i = m_i f_1 + n_i f_2 + p_i f_3 , \qquad (5)$$

and

$$\left.\begin{aligned} x_i &= m_i x_1 + n_i x_2 + p_i x_3 \\ y_i &= m_i y_1 + n_i y_2 + p_i y_3 \\ z_i &= m_i z_1 + n_i z_2 + p_i z_3 \end{aligned}\right\} . \qquad (6)$$

From (6)

$$m_i = \frac{\begin{vmatrix} x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \\ x_i & y_i & z_i \end{vmatrix}}{D} , \quad n_i = \frac{\begin{vmatrix} x_3 & y_3 & z_3 \\ x_1 & y_1 & z_1 \\ x_i & y_i & z_i \end{vmatrix}}{D} ,$$

and

$$p_i = \frac{\begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_i & y_i & z_i \end{vmatrix}}{D} \qquad (7)$$

for $i \geq 4$. It follows from (4) to (7) that the procedure for indexing powder patterns of the orthorhombic system is similar to the one given by Barabash & Davydov (1967) for two linearly independent variables. The number of tentative sets

$$\begin{bmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{bmatrix}$$

theoretically possible, subject to (3), is given by the permutation of 26 quantities taken 3 at a time (see Table 1), and is thus

$$26 \times 25 \times 4 \times P_3 = 2600P_3 ,$$

where P_3 is the number of permutations of each set.

Equivalent sets of numbers for the orthorhombic system are given by

$$\begin{bmatrix} x_1y_1z_1 \\ x_2y_2z_2 \\ x_3y_3z_3 \end{bmatrix}, \begin{bmatrix} y_1z_1x_1 \\ y_2z_2x_2 \\ y_3z_3x_3 \end{bmatrix}, \begin{bmatrix} z_1x_1y_1 \\ z_2x_2y_2 \\ z_3x_3y_3 \end{bmatrix},$$
$$\begin{bmatrix} x_1z_1y_1 \\ x_2z_2y_2 \\ x_3z_3y_3 \end{bmatrix}, \begin{bmatrix} z_1y_1x_1 \\ z_2y_2x_2 \\ z_3y_3x_3 \end{bmatrix}, \begin{bmatrix} y_1x_1z_1 \\ y_2x_2z_2 \\ y_3x_3z_3 \end{bmatrix}, \qquad (8)$$

and

$$\begin{bmatrix} x_1y_1z_1 \\ x_2y_2z_2 \\ x_3y_3z_3 \end{bmatrix}, \begin{bmatrix} ux_1y_1z_1 \\ ux_2y_2z_2 \\ ux_3y_3z_3 \end{bmatrix}, \begin{bmatrix} x_1vy_1z_1 \\ x_2vy_2z_2 \\ x_3vy_3z_3 \end{bmatrix}, \begin{bmatrix} x_1y_1wz_1 \\ x_2y_2wz_2 \\ x_3y_3wz_3 \end{bmatrix},$$
$$\begin{bmatrix} ux_1vy_1z_1 \\ ux_2vy_2z_2 \\ ux_3vy_3z_3 \end{bmatrix}, \begin{bmatrix} x_1vy_1wz_1 \\ x_2vy_2wz_2 \\ x_3vy_3wz_3 \end{bmatrix},$$
$$\begin{bmatrix} ux_1y_1wz_1 \\ ux_2y_2wz_2 \\ ux_3y_3wz_3 \end{bmatrix}, \begin{bmatrix} ux_1vy_1wz_1 \\ ux_2vy_2wz_2 \\ ux_3vy_3wz_3 \end{bmatrix}, \qquad (9)$$

Table 1. *x,y,z as a function of hkl for the orthorhombic system* ($x,y,z \leq 4$)

hkl	$x=h^2$	$y=k^2$	$z=l^2$	hkl	$x=h^2$	$y=k^2$	$z=l^2$	hkl	$x=h^2$	$y=k^2$	$z=l^2$
				100	1	0	0	200	4	0	0
001	0	0	1	101	1	0	1	201	4	0	1
002	0	0	4	102	1	0	4	202	4	0	4
010	0	1	0	110	1	1	0	210	4	1	0
011	0	1	1	111	1	1	1	211	4	1	1
012	0	1	4	112	1	1	4	212	4	1	4
020	0	4	0	120	1	4	0	220	4	4	0
021	0	4	1	121	1	4	1	221	4	4	1
022	0	4	4	122	1	4	4	222	4	4	4

where u,v,w, in accordance with (3) and (4), have the values 1 or 4. If account is taken of this 'equivalence' property, the number of possible sets reduces to $228P_3$.

From the linear-independence condition (3) and the obvious increase in Bragg angle with order of reflexion,

$$\left.\begin{aligned} x_k \le x_j \le x_i \,, \\ y_k \le y_j \le y_i \,, \\ \text{and} \qquad z_k \le z_j \le z_i \,, \end{aligned}\right\} \qquad (10)$$

where $k>j>i$, and the number of tests reduces to 458. (In (10) the inequality cannot exist in all expressions simultaneously since one would then have $f_k=f_j=f_i$.) From these considerations a table can then be compiled of all possible sets, subject to condition (3). Inspection of such a table shows that m_i,n_i,p_i are rational numbers, and that the fractions occurring most frequently are multiples of $\frac{1}{4}$ and $\frac{1}{16}$. Arising from the full 'equality' of x,y,z values, the above 458 tests reduces to the 19 tests given in Table 2.

Example

The practical application of the above procedure to the indexing of the powder pattern for $NiAl_3$ will now be considered. A rapid test of the experimental values for f_i, from Mirkin (1964) and Henry, Lipson & Wooster (1951), shows that the substance under investigation does not belong to a system of intermediate symmetry. The first three values of f_i' are linearly independent, since they satisfy the conditions $f_3'/f_1', f_3'/f_2'$ and $f_2'/f_1' \neq$ an integer and $f_1'+f_2' \neq f_3'$, $f_1'+4f_2' \neq f_3'$, $4f_1'+f_2' \neq f_3'$, *etc.*, and these may be taken as f_1', f_2' and f_3'. (Experimental quantities are denoted by f_i', *etc.*, and calculated values by f_i.) Using suitable values of f_i' at higher angles, refined values of f_1', f_2' f_3', f can be obtained, namely, $f_1'=0{\cdot}0495$, $f_2'=0{\cdot}0530$ and $f_3'=0{\cdot}0592$. Using the refined values, the remaining f_i' are expressed in terms of f_1', f_2' and f_3' from (5). The most frequently occurring values of m,n,p with the corresponding values of mf_1', nf_2' and pf_3' are given in Table 3, and f_i' for each line is given in column 2 of Table 4. mf_1', nf_2' and pf_3' are combined according to (5) to give f_i, and values are selected to correspond with f_i', to within the experimental error. (The maximum error in $f_i'(=f_i'-f_i)$ is $\pm 0{\cdot}0010$.) These values of f_i are listed in column 3 of Table 4.

The values of m_i,n_i,p_i in each of the linear combinations (columns 4, 5 and 6) are then analysed in accordance with (3), (6) and (7), and suitable tentative sets of x,y,z are chosen from Table 2. The corresponding values of x_i,y_i,z_i are then calculated from (6) for each set, and compared with the entries in Table 1, giving sets 2, 5 and 12 of Table 2, or

$$\begin{bmatrix}041\\440\\004\end{bmatrix}.$$

In accordance with the 'equivalence' series (9), all sets of numbers from the series

$$\begin{bmatrix}011\\110\\004\end{bmatrix}, \begin{bmatrix}011\\410\\004\end{bmatrix}, \begin{bmatrix}041\\140\\004\end{bmatrix} \text{ and } \begin{bmatrix}041\\440\\004\end{bmatrix}$$

must be tested. The only set which fits the data in Table 1 and provides a collection of integers x_i,y_i,z_i that does not contain a common integral factor is

$$\begin{bmatrix}011\\110\\004\end{bmatrix}.$$

Table 3. *mf_1', nf_2' and pf_3' for the most frequently occurring values of m, n and p*

m, n or p	mf_1'	nf_2'	pf_3'
1/16	0·0031	0·0033	0·0037
1/8	0·0062	0·0066	0·0074
3/16	0·0093	0·0099	0·0111
1/4	0·0124	0·0132	0·0148
5/16	0·0155	0·0166	0·0185
3/8	0·0186	0·0199	0·0222
7/16	0·0216	0·0232	0·0259
1/2	0·0248	0·0265	0·0296
9/16	0·0278	0·0298	0·0333
5/8	0·0309	0·0331	0·0370
11/16	0·0340	0·0364	0·0407
3/4	0·0371	0·0398	0·0444
13/16	0·0402	0·0431	0·0481
7/8	0·0433	0·0464	0·0518
15/16	0·0464	0·0497	0·0555
1	0·0495	0·0530	0·0592
2	0·0990	0·1060	0·1184
3	0·1485	0·1590	0·1776
4	0·1990	0·2120	0·2368
5	0·2475	0·2650	0·2960
6	0·2970	0·3180	0·3552
7	0·3465	0·3710	0·4144
8	0·3960	0·4240	0·4736
9	0·4455	0·4770	
10	0·4950		

Table 2. *Possible values of* $\begin{matrix}x_1, y_1 & z_1\\ x_2 \;\; y_2 & z_2\\ x_3 \;\; y_3 & z_3\end{matrix}$ *for the orthorhombic system*

$(x,y,z \le 4)$

Set No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
x	0	0	4	0	4	4	0	1	4	0	4	1	1	1	4	1	4	4	4
y	0	4	0	4	4	0	1	4	0	4	1	0	1	4	1	4	4	1	4
z	4	0	0	4	0	4	4	0	1	1	0	4	4	1	1	4	1	4	4

Table 4. *Indexing of the powder pattern for* $NiAl_3$

Line No.	f_i'	f_i	m_i	n_i	p_i	x_i	y_i	z_i	hkl
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	0·0496	0·0495	1	0	0	0	1	1	011
2	0·0530	0·0530	0	1	0	1	1	0	110
3	0·0591	0·0592	0	0	1	0	0	4	002
4	0·0678	0·0678	0	1	$\frac{1}{4}$	1	1	1	111
5	0·0882	0·0880	−4	4	$\frac{5}{4}$	4	0	1	201
6	0·1082	0·1079	−3	4	$\frac{3}{4}$	4	1	0	210
7	0·1230	0·1227	−3	4	1	4	1	1	211
8	0·1325	0·1324	−4	4	2	4	0	4	202
9	0·1386	0·1388	4	0	−1	0	4	0	020
10	0·1565	0·1571	3	1	$-\frac{3}{4}$	1	4	0	120
11	0·1672	0·1671	−3	4	$\frac{7}{4}$	4	1	4	212
12	0·1716	0·1719	3	1	$-\frac{1}{2}$	1	4	1	121
13	0·1858	0·1862	0	1	$\frac{1}{4}$	1	1	9	113
14	0·1980	0·1980	4	0	0	0	4	4	022
15	0·1999	0·1994	−8	9	2	9	1	0	310
16	0·2063	0·2064	−4	4	$\frac{13}{4}$	4	0	9	203
17	0·2156	0·2163	3	1	$\frac{1}{4}$	1	4	4	122
18	0·2266	0·2268	0	4	$\frac{1}{4}$	4	4	1	221
19	0·2366	0·2368	0	0	4	0	0	16	004
20	0·2587	0·2586	−8	9	3	9	1	4	312

Finally, x_i, y_i, z_i and hkl are given in columns 7 to 10 of Table 4.

Conclusion

The present paper gives the development and generalization of Neskuchaev's method for indexing powder patterns of the orthorhombic system. The method is applied to a specific example from this system, and is to be recommended compared with other methods (Bradley & Taylor, 1937; Hesse, 1948; Lipson, 1949; Henry, Lipson & Wooster, 1951), as it appears to be very easy to apply in the case of orthorhombic symmetry. Moreover, together with more general methods of indexing (Ito, 1949; Stosic, 1949; Zsoldos, 1958; Azároff & Buerger, 1958; Peiser, Rooksby & Wilson, 1960; de Wolff, 1962; Virodov, 1964), the method can be used as an auxiliary means of providing additional verification that the substance under investigation belongs to the orthorhombic system. The present paper, together with the previous one (Barabash & Davydov, 1967), gives a useful practical method of indexing powder patterns that is both simple and direct.

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