GRAPHICAL REPRESENTATION
OF CORRELATIONS BETWEEN PEAK POSITIONS

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The properties of linear combinations of peak positions are analysed. It is concluded that the distribution of combinations contains the information on lattice constants. These combinations are represented by sharp maxima. Examples of the distribution for a powder pattern of orthorhombic symmetry are presented.

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Numerical methods of solving powder patterns include some elements of a trial-and-error procedure; application of any method becomes more and more difficult with decreasing symmetry, increasing unit-cell volume, increasing measurement error and increasing presence of spurious peaks. The trial-and-error strategies based on variation of Miller indices usually include search for certain correlations between the peak positions. Using the term "correlation between peak positions" we shall understand below the situation when a simple mathematical expression (like a ratio, a difference or a linear combination) of these positions adopts some special values, which may serve as a source of information about the unit cell. The simplest correlations between peak positions (the ratios) enable the hexagonal system to distinguish from the tetragonal one (see e.g. [1]).

The method worked out by Hesse and Lipson (see [1–4]) has been applied to solve orthorhombic unit cells. The equation of the plane spacings for an orthorhombic crystal is

$$q = Ah^2 + Bk^2 + Cl^2, \tag{1}$$

where $q = d^{-2}$, $A = a^{-2}$, $B = b^{-2}$ and $C = c^{-2}$. The method is based on the recognition of the fact that if two peaks have the same k and l indices, but their h indices are 0 and 1, respectively, the difference between their q values is equal to A. The statistics of such differences may indicate the values of A, as well as B and C.

The statistics of differences of positions of two peaks is rather poor especially if the available experimental peaks are not numerous. However, the method may be extended by taking linear combinations of N_t peaks from among N experimental peaks instead of the differences. Then any set composed of N_t (N_t may become 2,

3, ...) peaks produces a number of values (combinations), which may be treated as the subject of further analysis. The allowed coefficients in the combinations are small integers. It is convenient to consider the absolute value of the combination.

Let us consider an orthorhombic powder pattern composed of N peaks at positions q_i

$$q_i = Ah_i^2 + Bk_i^2 + Cl_i^2, \quad i = 1, \ldots, N. \tag{2}$$

The absolute value of the linear combination of a chosen set of q_i values will be denoted by x. For example all combinations of the peaks q_1, q_2, q_5 with coefficients $m, n, p \le M$ are given by $x = |mq_1 + nq_2 + pq_5|$, with $m = 0, \ldots, M$; $n = -M, \ldots, M$; $p = -M, \ldots, M$. Due to the properties of Eq. (2) some values of x may occur more frequently than the others. Therefore it is convenient to study the distribution of linear combinations (DLC). The distribution of differences described by Hesse and Lipson [1, 2] is a particular case of DLC. It may be expected that higher accuracy of the data obtained with modern diffractometers and the possibility of using fast computers could make such an approach a tool of analysis of powder patterns.

The possible x values include:

$A, 2A, 3A, \ldots B, 2B, 3B, \ldots C, 2C, 3C, \ldots$

$|C - A|, C + A, |C - 2A|, C + 2A, \ldots |C - B|, C + B, |C - 2B|, C + 2B, \ldots$

$|B - A|, B + A, |B - 2A|, B + 2A, \ldots$

$|C - B - A|, |C - B + A|, |C - B - 2A|, |C - B + 2A|, \ldots$

etc. Let us consider three examples of peak triplets:
a) set (110), (011), (101);
b) set (110), (011), (111);
c) set (110), (111), (211).

The values of x for these sets obtained with the simplest choice of parameters $(M = 1, N_t = 3)$ are shown in Table. The content of the table illustrates the reasons of the presence of mA, nB and pC values in the DLC pattern.

The observed maxima of DLC represent the correlations. The DLC pattern for $M = 2$ (Fig. 1) differs from that for $M = 3$ (Fig. 2). Some of observed maxima coincide with the positions of peaks of the powder pattern.

Usually, the distribution shows complex periodic behaviour (for example: the maxima for A, $2A$, $3A$ etc. are equidistant). The periodicity perfectness depends on the pattern and on the number of peaks chosen for the analysis as well as on the parameters of the algorithm. A short period is observed if there are some arithmetic relations between two or three lattice constants. In the example shown in the Figs. 1 and 2 the period equals 0.001578 [Å^{-2}]; this value is exactly equal to $A/16$, $B/3$ and $C/44$.

The difference pattern (Fig. 1) shows strong maxima for both A and C and a less pronounced maximum for B. The DLC pattern (Fig. 2) contains more

TABLE

Possible x values for three sets of peaks, $M = 1$, $N_t = 3$.

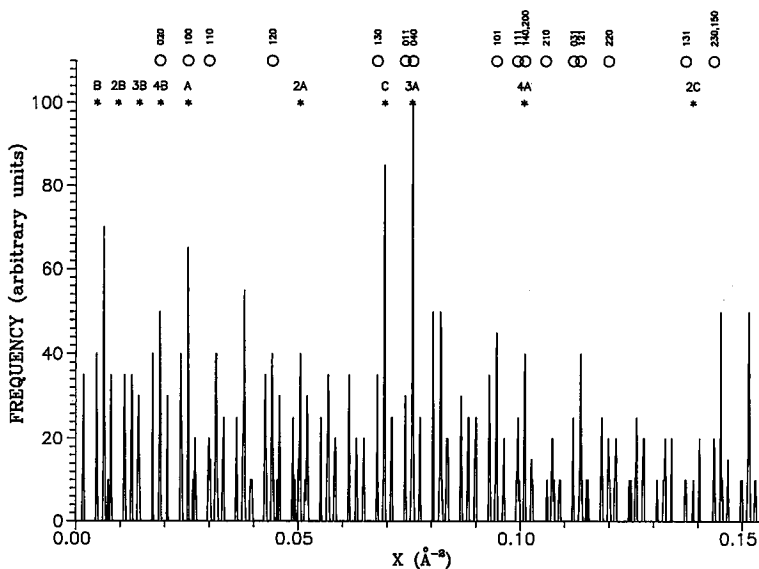| Coefficients			x		
m	n	p	set a)	set b)	set c)
0	0	1	$A + C$	$A + B + C$	$2A + B + C$
0	1	−1	$|-A + B|$	A	A
0	1	0	$B + C$	$B + C$	$A + B + C$
0	1	1	$A + B + 2C$	$A + 2B + 2C$	$3A + 2B + 2C$
1	−1	−1	$2C$	$B + 2C$	$2A + B + 2C$
1	−1	0	$|A - C|$	$|A - C|$	C
1	−1	1	$2A$	$2A + B$	$2A$
1	0	−1	$|B - C|$	C	$A + C$
1	0	0	$A + B$	$A + B$	$A + B$
1	0	1	$2A + B + C$	$2A + 2B + C$	$3A + 2B + C$
1	1	−1	$2B$	B	B
1	1	0	$A + 2B + C$	$A + 2B + C$	$2A + 2B + C$
1	1	1	$2A + 2B + 2C$	$2A + 3B + C$	$4A + 3B + 2C$

Fig. 1. Distribution of differences, $x = |q_i - q_j|$, for 30 initial peaks of $BaTi_4O_9$ [5]. Meaning of symbols: "o" — positions of peaks in the experimental pattern; "*" — values of A, B, C multiplied by 1 to 4.
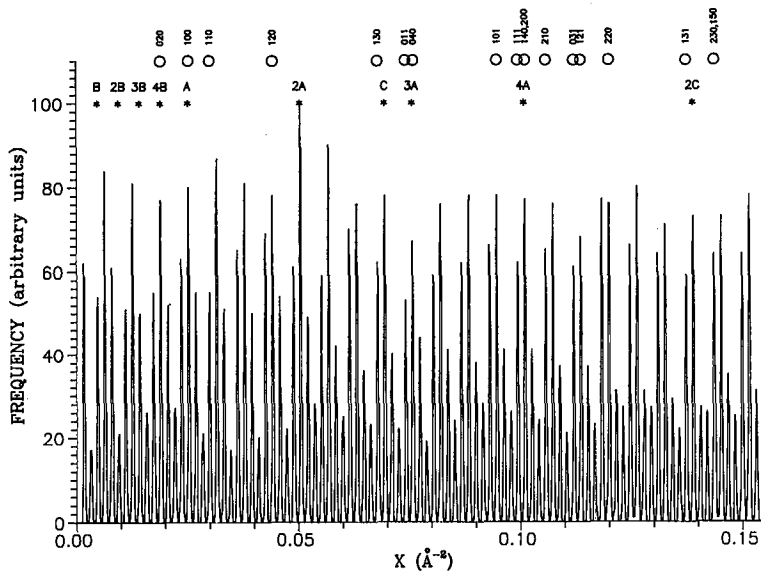
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Fig. 2.   Distribution of combinations defined by Eq. (3) for 30 initial peaks of $BaTi_4O_9$ [5]. Coefficients being equal to -1 and 1 were permitted. The combinations with all the three coefficients of the same sign were omitted because they cannot lead to A, B, nor C. Meaning of symbols: as for Fig. 1.

competing strong maxima than the difference pattern, but this kind of pattern has the advantage to be less dependent on systematic absences and on the number of available peaks. It is noteworthy that the peaks absent in the powder pattern have their homologues in DLC pattern, e.g. the maxima marked by B and C correspond to absent (010) and (001) peak, respectively.

The analysis of DLC patterns may facilitate the early stage of solving powder patterns. However, some features of DLC patterns need further investigation, among them:

— the optimum values of the algorithm parameters (M, N, N_t),

— the choice of the method of finding the values of A, B and C, (graphical, trial-and-error or Fourier methods may be applied),

— the possibility of application for lower symmetries.

Acknowledgements

References

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