Similar considerations apply to some degree to all the tetragonal space groups. Even those which can be reduced to orthorhombic symmetry require the symmetry relations across the diagonal plane.

Table 3. *Modification of the two parts A and B of F_{hkl}*

Case	n	$A_{h'k'l'}$	$B_{h'k'l'}$
1	0	A	B
	1	$-A$	$-B$
2	0	A	B
	1	$-B$	A
	2	$-A$	$-B$
	3	B	$-A$
3	—	A	$-B$

The phase-symmetry relations are of the form

$$\alpha_{h'k'l'} = \alpha_{hkl} + n\pi \quad (1)$$

or

$$\alpha_{h'k'l'} = \alpha_{hkl} + n\tfrac{1}{2}\pi \quad (2)$$

or

$$\alpha_{h'k'l'} = -\alpha_{hkl} . \quad (3)$$

For either case (1) or (2) n is computed and the result taken modulo 2 for case (1) and modulo 4 for case (2). In some autocode systems a logical product instruction exists to do this directly. This value of n is then used to instruct the machine to modify the values of the two parts, A and B, of F_{hkl} (which will have been fed in as data) to produce the correct values for $F_{h'k'l'}$. The modifications are given in Table 3.

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The Likelihood Ratio Method for the Precise and Accurate Determination of Lattice Parameters for Tetragonal and Hexagonal Crystals*

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The Likelihood Ratio Method (LRM) for the precise and accurate determination of lattice parameters has been described (Beu, Musil, and Whitney, 1962) as it applies to crystals of cubic symmetry. This report gives the basic equations for the applications of the LRM to crystals of tetragonal and hexagonal symmetry.

Introduction

The Likelihood Ratio Method (LRM) for the precise and accurate determination of lattice parameters has been described (Beu, Musil & Whitney, 1962) as it applies to crystals of cubic symmetry. This report gives the basic equations for the application of the LRM to crystals of tetragonal and hexagonal symmetry. To save space, the reader is referred to the previous paper (Beu, Musil & Whitney, 1962) for the definition of terms not defined in this report and for a statistical analysis of the problem.

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Discussion

The development of the LRM is given below for the tetragonal case only. The development for the hexagonal case is identical if the expression $4/3(h_i^2+h_ik_i+k_i^2)$ is substituted for $(h_i^2+k_i^2)$ wherever the latter expression appears. The development of the LRM for tetragonal and hexagonal crystals is very similar to that for cubic crystals and most of the derivation details can be inferred from the cubic case;

however, a comprehensive report on the tetragonal and hexagonal applications is available from the authors.

Maximum likelihood estimates under the assumptions

The maximum likelihood estimates, $\hat{a}_0, \hat{c}_0, \hat{\sigma}_i, \hat{e}_i$, and $\hat{\theta}_i$ under the assumptions must satisfy the equations:

$$\sin^2 \hat{\theta}_i/K^2 = [(h_i^2+k_i^2)/\hat{a}_0^2] + (l_i^2/\hat{c}_0^2) \quad (1)$$

where $K = n\lambda/2$

$$\hat{\sigma}_i^2 = s_i^2 \quad (2)$$

$$\hat{e}_i = \psi_i - \hat{\theta}_i \quad (3)$$

$$\sum_i \hat{e}_i = 0\,. \quad (4)$$

The maximum of the logarithm of the sample density function under the assumptions is:

$$L(\hat{a}_0, \hat{c}_0, \hat{\sigma}_i, \hat{e}_i) = -N \ln (2\pi)^{\frac{1}{2}} - \sum_i n_i \ln s_i - N/2\,. \quad (5)$$

Maximum likelihood estimates under the hypothesis of 'no remaining systematic errors'

The maximum likelihood estimates, $\hat{\hat{a}}_0, \hat{\hat{c}}_0, \hat{\hat{\sigma}}_i^2$, and $\hat{\hat{\theta}}_i$ under the hypothesis must satisfy the equations:

$$\sin^2 \hat{\hat{\theta}}_i/K^2 = [(h_i^2+k_i^2)/\hat{\hat{a}}_0] + l_i^2/\hat{\hat{c}}_0 \quad (6)$$

$$\hat{\hat{\sigma}}_i^2 = s_i^2 + (\psi_i - \hat{\hat{\theta}}_i)^2. \quad (7)$$

The maximum of the logarithm of the sample density function under the hypothesis and assumptions is:

$$L(a_0, c_0, \hat{\hat{\sigma}}_i) = -N \ln (2\pi)^{\frac{1}{2}} - \tfrac{1}{2} \sum_i n_i \ln [s_i^2 + (\psi_i - \hat{\hat{\theta}}_i)^2] - N/2\,. \quad (8)$$

Determination of $\hat{\hat{a}}_0$, $\hat{\hat{c}}_0$, s_{a_0}, and s_{c_0}

The values of $\hat{\hat{a}}_0$ and $\hat{\hat{c}}_0$, the maximum likelihood estimates of these parameters under the hypothesis of 'no remaining systematic errors', can now be obtained by finding those values of a_0 and c_0 which maximize $L(a_0, c_0, \hat{\hat{\sigma}}_i)$ or, equivalently, which minimize the function:

$$W(a_0, c_0) = -2[L(a_0, c_0, \hat{\hat{\sigma}}_i) - L(\hat{a}_0, \hat{c}_0, \hat{\sigma}_i, \hat{e}_i)] = \sum_i n_i \ln [1 + \{(\psi_i - \theta_i)^2/s_i^2\}] \quad (9)$$

subject to:

$$\sin^2 \theta_i/K^2 = [(h_i^2+k_i^2)/a_0^2] + (l_i^2/c_0^2)\,.$$

The minimum of $W(a_0, c_0)$, designated W_m, is distributed approximately like chi-square and is equal to $-2 \ln \lambda_{LR}$ (Mood, 1950):

$$W_m = -2 \ln \lambda_{LR} = -2[L(\hat{\hat{a}}_0, \hat{\hat{c}}_0, \hat{\hat{\sigma}}_i) - L(\hat{a}_0, \hat{c}_0, \hat{\sigma}_i, \hat{e}_i)]\,. \quad (10)$$

In practice, $\hat{\hat{a}}_0$ and $\hat{\hat{c}}_0$ are determined as follows, based on equations (9) and (10): It is assumed that approximately accurate values of a_0 and c_0 are already known. A grid of a_0 and c_0 values is chosen in this region and corresponding $W(a_0, c_0)$ values calculated. The minimum region of $W(a_0, c_0)$ can then be determined and a finer grid of a_0 and c_0 values chosen, if necessary, until W_m is determined as accurately as is needed for comparison with the critical value of the chi-square distribution, w_ε. If W_m is less than w_ε, $\hat{\hat{a}}_0$ and $\hat{\hat{c}}_0$ have been determined. (If W_m is equal to or greater than w_ε, $\hat{\hat{a}}_0$ and $\hat{\hat{c}}_0$ cannot be determined at the ε significance level until the remaining systematic errors have been removed from the Bragg angle measurements, ψ_i). After $\hat{\hat{a}}_0$ and $\hat{\hat{c}}_0$ have been determined, estimates of the standard deviations, s_{a_0} and s_{c_0}, may be calculated based on the equations:

$$s_{a_0}^2 = \frac{\hat{\hat{a}}_0^6/4}{K^4 \sum_i \dfrac{n_i(h_i^2+k_i^2)^2}{\hat{\hat{\sigma}}_i^2 \sin^2 2\hat{\hat{\theta}}_i}} \quad (11)$$

$$s_{c_0}^2 = \frac{\hat{\hat{c}}_0^6/4}{K^4 \sum_i \dfrac{n_i l_i^4}{\hat{\hat{\sigma}}_i^2 \sin^2 2\hat{\hat{\theta}}_i}} \quad (12)$$

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