of perovskites. In fact the only perovskites known to the author in which difficulty would occur are $NaNbO_3$ (phases *P* and *R*), $PbZrO_3$, possibly $AgNbO_3$ and $AgTaO_3$, and $KCuF_3$. In the last case the difficulty, as mentioned earlier, is the large Jahn–Teller distortion of the octahedra which dominates the symmetry. In the other cases, the difficulty lies in the fact that the tilt systems are not simple ones, but consist of combinations of the simple systems. However, even here it is possible to go some way towards deriving the correct structure, but great care is needed when attempting this. Fortunately such structures seem to be quite rare.

At present this general method is being used to analyse the complex sequence of phases in the system $Na/KNbO_3$ with considerable success. A preliminary note of this work has already been published (Ahtee & Glazer, 1974) in which tentative suggestions for the various structures have been made. Since then, many of these have been verified (manuscript in preparation), and this has shown that reliable trial models can be obtained very quickly even when there are many possible phases within a single solid-solution series.

I thank Dr H. D. Megaw for introducing me to the fascinating complexities of the perovskite structure, and the Wolfson Foundation for funds enabling this work to be carried out.

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Calculation of *E* values by Means of the Origin Peak in the Patterson Function

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(*Received* 17 *March* 1975; *accepted* 19 *March* 1975)

The origin peak in the Patterson function may be used to construct *E* values when the number and type of the atoms in the structure are known. This is illustrated by an example leading to an agreement value between the observed and calculated *E* values of 0·170. For comparison, a least-squares calculation of the best overall anisotropic temperature factor results in an *R* of 0·167. The result obtained from a Wilson plot is 0·188.

Introduction

The origin peak in the Patterson function obeys the point-group symmetry of the Patterson function, and can therefore be expanded in harmonic functions of the appropriate symmetry. If the origin peak, deconvoluted with respect to thermal motion, is known, an analysis of the terms in the expansion will provide some information about the overall anisotropic thermal movements. The applied method of analysis, revealing this information, follows closely the technique used in the analysis of the deformations of atoms (Kurki-Suonio & Meisalo, 1967; Kurki-Suonio, 1967, 1968).

Description of the method

The square of the overall temperature factor is written as

$$T(\mathbf{H}) = \sum_{n,\alpha} T_{n\alpha}(H) K_{n\alpha}(\theta_{\mathbf{H}}, \varphi_{\mathbf{H}}) .$$

The $K_{n\alpha}$ form a complete set of orthonormal harmonic functions adapted to the symmetry of the Patterson function, and H, $\theta_{\mathbf{H}}$ and $\varphi_{\mathbf{H}}$ are the spherical coordinates of the reciprocal-lattice vector **H**. The functions $T_{n\alpha}(H)$ are then calculated from the expression

$$T_{n\alpha}(H) = (4\pi)^2 V^{-1} \sum_{\mathbf{G}} A(\mathbf{G}) K^*_{n\alpha}(\theta_{\mathbf{G}}, \varphi_{\mathbf{G}}) \times \int_0^r j_n(2\pi H u) j_n(2\pi G u) u^2 \mathrm{d}u . \quad (1)$$

j_n is the nth-order spherical Bessel function, V the volume of the unit cell, $A(\mathbf{G})$ the intensity, observed at the reciprocal-lattice point defined by the vector $\mathbf{G}$, divided by the sum of the squares of the scattering factors

$$A(\mathbf{G}) = I(\mathbf{G}) / \sum_j f_j^2(G)$$

and r the radius of the sphere enclosing the origin peak. Equation (1) also forms the basis of a Fourier synthesis if $A(\mathbf{G})$ is replaced by $\Delta A(\mathbf{G}) = A(\mathbf{G}) - T(\mathbf{G})$, by which the effect of the cut-off in $(\sin\theta)/\lambda$ can be reduced. The resulting function $T(\mathbf{H})$ can be translated, by the method of least squares, to the conventional expression for an anisotropic temperature factor

$$T(\mathbf{H}) = c^2 \exp\left[-2(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\right] \quad (2)$$

in terms of which the result is easily interpreted.

An example

The above method was tested on the structure of 2,7-di-t-butylpyrene (Hazell & Lomborg, 1972). In the space group $P\bar{1}$ the only symmetry element in the Patterson function, besides translational symmetry elements, is a centre of inversion, which limits the possible harmonics to spherical harmonics of even order. Based on the refined parameters two sets of intensities, one with a cut-off in $(\sin\theta)/\lambda$ at 0·6 Å^{-1}, and the other at 0·4 Å^{-1}, were calculated and used in the analysis as observed intensities. The results shown in Tables 1 and 2 are obtained by carrying out the analysis to second order with $r = 0{\cdot}8$ Å,

$$\Delta A(\mathbf{G}) = A(\mathbf{G}) - c^2 \exp\left[-2B(\sin\theta)^2/\lambda^2\right]$$

and

$$\Delta A(\mathbf{O}) = c^2\{(\sum_j Z_j)^2 / \sum_j Z_j^2 - 1\},$$

where Z_j is the atomic number of atom j and c and B are the scale factor and the isotropic temperature factor found from the Wilson plot (Wilson, 1942). The agreement values are calculated by

$$R(E) = \{\sum (|E_{\mathrm{calc}}| - |E_{\mathrm{obs}}|)^2 / \sum |E_{\mathrm{calc}}|^2\}^{1/2},$$

where E_{calc} are the calculated E values, and, for the space group $P\bar{1}$, $E_{\mathrm{obs}} = (A/T)^{1/2}$. The last row in Table 1 shows the agreement between $\eta(\mathbf{H})$, the vector-independent part of $|E_{\mathrm{obs}}(\mathbf{H})|^2$, and unity.

Table 1. *Agreement values between observed and calculated E values*

	Wilson plot		Present method	
Cut-off radius (Å^{-1})	0·6	0·4	0·6	0·4
Number of reflexions	1591	464	1591	464
c	0·958	0·804	1·026	0·965
B	3·083	2·320		
$R(E)$	0·188	0·176	0·170	0·106
$R(E \geq 1)$	0·141	0·169	0·114	0·086
$R(\eta)$	0·217	0·347	0·070	0·150

Table 2. *Anisotropic temperature factors* ($\times 10^4$)

R value	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0·167	131	330	120	150	121	163
0·170	128	299	116	145	112	135
0·106	128	238	110	111	75	63

The agreement obtained illustrates that the origin peak in the Patterson function, based on $|E|^2$ values, to a large extent can be approximated by the Fourier transform of the function $T(\mathbf{H})$, and the R of 0·07 may then be interpreted as a measure of the efficiency with which the origin peak can be removed.

The temperature factors found are shown in Table 2. The first row shows the result obtained by minimizing $\sum_{\mathbf{H}}[T(\mathbf{H}) - A(\mathbf{H})/|E_{\mathrm{calc}}(\mathbf{H})|^2]^2$ for $|E_{\mathrm{calc}}| > 0{\cdot}01$, and $(\sin\theta_{\max})/\lambda = 0{\cdot}6$ Å^{-1}. In this case a scale factor of 0·986 was found, and the R between calculated and observed E values was 0·167. The second and third rows show the parameters found from equation (2) with $(\sin\theta_{\max})/\lambda$ equal to 0·6 Å^{-1} and 0·4 Å^{-1}, respectively. It should be remarked that no correction for the cut-off in the Patterson function has been made.

Conclusion

As demonstrated by the example, the result of an analysis of the origin peak can lead to an overall anisotropic temperature factor very close to the best possible. Furthermore it is seen that even with a severe cut-off in $(\sin\theta)/\lambda$, a case in which the Wilson plot produces unreliable results, reasonable temperature factor parameters and scale factor are obtained.

The deviation from sphericity of the origin peak is considered to be due to thermal motion. However, any modification of the data of the form $I(\mathbf{H}) = T(\mathbf{H})|F(\mathbf{H})|^2$ can be dealt with by the method. For example a preliminary correction for absorption can be achieved by using the full data set and by including harmonic functions which are forbidden by the space-group symmetry.

All calculations were performed on the IBM 370/165 at NEUCC, Technical University of Denmark.

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