Table 1. *Relative peak height and rank of phase-invariant translation-function solutions for fragments of varying sizes*

Phase-invariant translation-function analysis of isoleucinomycin using triples, positive quartets, negative quartets and a combination of both positive and negative quartets. Column one notes the number of atoms out of 84 that describe the relative size of the molecular fragment. The columns labeled rank give the position of the solution vector in the magnitude-sorted peak list and ratio gives the relative size of the solution vector as compared to the largest spurious peak.

	Triples		Positive quartets		Negative quartets		Positive and negative quartets	
$N/84$	Rank	Ratio	Rank	Ratio	Rank	Ratio	Rank	Ratio
42	1	1.55	1	1.49	1	1.18	1	1.84
21	1	1.45	1	1.06	11	0.84	1	1.41
15	6	0.93	25	0.68	16	0.63	2	0.91
10	25	0.69	46	0.54	29	0.63	12	0.71

and relative size of the solution vector tends to decrease as the fragment becomes smaller, but the patterns of spurious peaks produced by the triples and negative quartets, or the positive and negative quartets, do not appear to be similar. As a consequence, the maps produced by these syntheses may be added, and the magnitude of the solution vector will be enhanced as the spurious peaks do not reinforce one another. This may be seen in Table 1 by inspecting the improvement in the peak rank and intensity ratio shown by the joint positive- and negative-quartet analysis as compared to the results produced by the positive and negative quartets separately.

The computational efficiency of the FFT algorithm as compared to the traditional methods of phase-invariant evaluation over the grid of the cell is impressive. The three-dimensional analysis for the structure which is presented in Table 1 required less than 10 min on a VAX 8600 computer system. The traditional method would require 2 or 3 d, a time saving on the order of 500-fold.

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The Generalized Debye–Waller Factor for Atoms in a Twisted Environment. I. Sites at the Core of a Double Helix

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Dedicated to Professor H. Jagodzinski on his 75th birthday

Abstract

Lattice sites which have a proper or improper subgroup of 222 as the site group may exhibit an anharmonic twisted local potential. The generalized Debye–Waller factor for atoms occupying such sites is derived. If the twist axis is fixed by symmetry considerations the approximation used needs, in addition to three harmonic parameters, one anharmonicity parameter, essentially the local pitch. In the most general case with no symmetry restrictions three Eulerian angles are needed in addition to the pitch.

I. Introduction

In 1907 Einstein published a seminal paper on Planck's theory of radiation and on the theory of specific heat. This paper contains what we now are accustomed to call the independent-particle or harmonic-oscillator model of solids: a crystal is imagined as being composed of uncoupled, three-dimensional, anisotropic oscillators which have a positive-definite Gaussian density-distribution function $\rho(\mathbf{r})$. Planck's radiation formula is used for the extrapolation of specific heats to low temperatures, i.e. into the regime where the Boltzmann approximation must be replaced by quantum statistics.

The Fourier transform of Einstein's density $\rho(\mathbf{r})$ is the well known Debye–Waller factor (DWF). The improvement in the accuracy of Bragg diffraction data and the investigation of crystals containing atoms with large thermal amplitudes, e.g. ionic conductors and molecular crystals with weak bonds, have called for a generalization of the old concept of a harmonic DWF. This generalization was made along three major lines: by the introduction of anharmonic potentials (Willis & Pryor, 1975), by the Gram–Charlier (Johnson & Levy, 1974) and the Edgeworth (Johnson, 1969) series approximations, respectively.

Anharmonic potentials $V_{\text{ANH}}(\mathbf{r})$ used in a Boltzmann factor $\exp\left[-\beta V_{\text{ANH}}(\mathbf{r})\right]$ have the intrinsic property of making the density distribution automatically positive-definite. The parameters in $V_{\text{ANH}}(\mathbf{r})$ can be directly compared with atom–atom potentials. The potential $V_{\text{ANH}}(\mathbf{r})$ is usually written in terms of symmetry-adapted homogeneous polynomials. The Fourier transform of $\rho_{\text{ANH}}(\mathbf{r})$ cannot be given in a closed algebraic form. For weak anharmonic contributions, series expansions are possible and they give results which make physical sense if done properly. One of the conditions to be met is, for instance, that the potential must be convex in the limit of large $|\mathbf{r}|$, i.e. the highest term in $V_{\text{ANH}}(\mathbf{r})$ must be even since otherwise the particle cannot be kept in a finite region of space by the potential. Strongly anharmonic potentials, for instance the double-well potential $V(x) = -ax^2 + bx^4$, with $a > 0$, $b > 0$, can only be Fourier transformed by numerical procedures.

In the Gram–Charlier approximation a harmonic DWF is multiplied by a series of symmetry-adapted homogeneous polynomials in the components h, k, l of the scattering vector $\mathbf{H}$, whereas in the Edgeworth series-expansion approximation one replaces the Gaussian exponent of the DWF by a general series of homogeneous polynomials. The Gram–Charlier and Edgeworth methods are in other words approximations in reciprocal space. They can both be easily incorporated into the usual structure-factor formalism, at least in principle. In both cases however the physically relevant thermal distribution density is not necessarily positive-definite and the interpretation of the parameters resulting from refinements, for example derivatives of atom–atom potentials, is at least nontrivial (Johnson & Levy, 1974). It has to be pointed out that free series expansions, i.e. expansions which are not based on a thermodynamic model, conceal the nonlinear constraints which exist among the tensor expansion coefficients: the single non-harmonic term in the potential $V(x) = x^2 + \gamma x^4$ gives rise to an infinite number of terms in a Gram–Charlier or Edgeworth expansion which of course all depend on γ. Analogous difficulties occurring in the analysis of orientational disorder (Prandl, 1981) and the Boltzmannian way of avoiding them have been discussed earlier (Vogt & Prandl, 1983).

We have recently investigated (Prandl & Dunstetter, 1992) the strong rotation–translation coupling found in solid oxygen (Dunstetter, 1988; Dunstetter & Delapalme, 1989) by a thermodynamic model. In this investigation, potentials having a twist turned out to be essential. The simplest case of a twisted potential, the double-helix case, and its corresponding generalized Debye–Waller factor (GDWF) is supposed to occur quite often in crystals, and it is this case which is dealt with in the present communication. We use, in contrast to a 'free' Cartesian tensor series for $V(\mathbf{r})$, a twisted potential, an approximation which is conceptually very close to an anisotropic harmonic potential and which at the same time is directly adapted to the additional symmetry of a double helix. The twisted potential contains only one parameter for a helix direction constrained by symmetry and four parameters for an unrestricted helix direction in addition to the usual harmonic force constants.

The paper is organized in the following way. After the short §II on notation we introduce in §III the twisted potential $V_k(\mathbf{r})$ in terms of unit representations of the point group 222. §IV describes the Fourier transform of the relevant $\rho(\mathbf{r})$. The resulting GDWF is discussed in §V. The case of several symmetry-related helix axes, described by their local wave vectors, is treated in §VI. Possible applications are summarized in §VII.

II. Notations and definitions

$\rho(\mathbf{r}), \rho(\mathbf{Q})$	the density, the Fourier transformed density $\equiv$ the generalized Debye–Waller factor (GDWF)
$V(\mathbf{r}), V_0(\mathbf{r})$	the potential in general, a harmonic potential
$V_k(\mathbf{r})$	the potential in the core region of a double helix with wave vector $\mathbf{k}$
$\mathbf{k}, k$	the wave vector, the length of the wave vector of the helix

λ	the wavelength = the pitch of the helix
A, B, C	force constants in $V(\mathbf{r})$, $V_0(\mathbf{r})$, $V_k(\mathbf{r})$
$\mathbf{M}_0 \equiv \mathbf{M}(\Phi = 0)$	diagonal matrix with elements A, B, C
$\mathbf{M}(\Phi)$	$\mathbf{M}_0$ after a rotation by angle Φ about the axis z
$\mathbf{Q} = 2\pi\mathbf{H}$	scattering vector
$\mathbf{Q} = (q\cos\alpha,$ $q\sin\alpha, q_3)$	$\mathbf{Q}$ in a cylindrical coordinate system
k_B	Boltzmann's constant
T	temperature
$\beta = 1/(k_B T)$	
$Z(0), Z(\mathbf{Q})$	the partition function; cf. (2)
E	the exponent of the Boltzmann factor $\exp(-E)$
$\mathbf{R}(\Phi)$	a rotation matrix
U, V	defined in (24), (25)
$I_m(z)$	modified Bessel functions; defined and tabulated in, for example, Abramowitz & Stegun (1966)
$\hat{I}_m(z) = e^{-z} I_m(z)$	normalized Bessel functions
$\mathbf{g}, \boldsymbol{\Omega}$	metric tensors: (39), (40)
$\mathbf{R}_y(\alpha), \mathbf{R}_z(\alpha)$	rotation matrices with rotation axes y, z: (43)
$R_{(m)}$	equivalent atomic sites; $m = 1, 2, \ldots, M$
$\mathbf{S}_{(m)}, \mathbf{S}'_{(m)}$	matrices of crystallographic rotations in an orthonormal and a lattice-adapted basis system, respectively
$\boldsymbol{\tau}_{(m)}$	nonprimitive translation of a space-group element.

III. The single-particle potential with curvature*

The aim of this paper is, firstly, to derive a potential $V(\mathbf{r})$ which obeys locally the noncrystallographic symmetry at the core of a double helix and, secondly, to obtain the generalized Debye–Waller factor (GDWF), i.e. the Fourier transform of the thermal probability density in an algebraic form.

Let the thermal (number) density of an atom moving in $V(\mathbf{r})$ be given in the Boltzmann approximation by

$$\rho(\mathbf{r}) = Z^{-1} \exp[-\beta V(\mathbf{r})] \qquad (1)$$

where Z is the partition function. Defining

$$Z(\mathbf{Q}) = \int \exp[-\beta V(\mathbf{r}) + i\mathbf{Q}\mathbf{r}] \, d\tau, \qquad (2)$$

one finds the GDWF

$$\rho(\mathbf{Q}) = Z(\mathbf{Q})/Z(0) \qquad (3)$$

because $Z(0) = Z$.

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* In §§III, IV and V an orthonormal system Σ of basis vectors $\mathbf{e}_i$ is used throughout. The wave vector $\mathbf{k}$ of the helix is always parallel to $\mathbf{e}_3$.

The single-particle potential $V_k(\mathbf{r})$ along the core of a double helix is chosen as a simple and natural extension of the triaxial harmonic potential $V_0(\mathbf{r})$

$$V_0(\mathbf{r}) = \tfrac{1}{2}(Ax^2 + By^2 + Cz^2) \qquad (4)$$

where the A, B, C are, as usual, force constants. $V_0(\mathbf{r}) = $ constant represents a triaxial ellipsoid with the three principal axes μ_1, μ_2, μ_3 given by

$$(\mu_1, \mu_2, \mu_3) = \text{constant}$$
$$\times [(2/A)^{1/2}, (2/B)^{1/2}, (2/C)^{1/2}]. \qquad (5)$$

To adapt this ellipsoid to the noncrystallographic symmetry of the helix we apply to (4) a twist which allows the main axes $\xi(z)$ and $\eta(z)$ in planes with $z = $ constant to follow the pitch of the helix whereas the third axis of this twisted potential $V_k(\mathbf{r})$ remains invariably parallel to z, the axis of the helix. Mathematically we arrive at $V_k(\mathbf{r})$ in the following way:

$$V_k(\mathbf{r}) = \tfrac{1}{2}\mathbf{r}\mathbf{M}(\Phi)\mathbf{r} \qquad (6)$$

where

$$\mathbf{M}(\Phi) = \mathbf{R}\mathbf{M}(0)\mathbf{R}^{-1} \qquad (7)$$

$$\mathbf{M}(0) = \begin{bmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{bmatrix} \qquad (8)$$

$$\mathbf{R} = \begin{bmatrix} c & -s & 0 \\ s & c & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (9)$$

$$c = \cos\Phi; \quad s = \sin\Phi \qquad (10); (11)$$

and

$$\Phi = kz + \Phi_0 \qquad (12)$$

is the angle by which, at different levels of z, the local axes $\xi(z)$, $\eta(z)$ have been rotated with respect to their orientation at $z = 0$. The latter, the original orientation, is allowed to have an arbitrary offset angle Φ_0 with respect to the x direction. So in summary we can imagine that for fixed values of z the restoring forces towards the z axis are linear, i.e. 'harmonic' in the local deviation ξ, η with, however, force constants which depend on the particular value of z. Taken as a three-dimensional object, $V_k(\mathbf{r})$ is anharmonic with the single anharmonicity parameter $k = 2\pi/\lambda$. The offset Φ_0 enters only into the orientation of $V_k(\mathbf{r})$ with respect to the x axis.

We may develop $V_k(\mathbf{r})$ into a series of Cartesian tensor contributions

$$V_k(\mathbf{r}) = V_k^{(2)}(\mathbf{r}) + V_k^{(3)}(\mathbf{r}) + V_k^{(4)}(\mathbf{r}) + \ldots$$
$$= M_{rs}^{(2)} x_r x_s + M_{rst}^{(3)} x_r x_s x_t$$
$$+ M_{rstu}^{(4)} x_r x_s x_t x_u + O(x^5), \qquad (13)$$

where the M are tensor components and the x_r are the components of $\mathbf{r}$.

In (13) the summation convention is assumed to be valid. Introducing

$$D = (A - B)/2 \qquad (14)$$

and setting $\Phi_0 = 0$, one finds the nonzero tensor components up to and including fourth-order terms:

$$M_{11}^{(2)} = A/2; \qquad M_{22}^{(2)} = B/2; \qquad (15); (16)$$

$$M_{33}^{(2)} = C/2 \qquad M_{123}^{(3)} = 2kD \qquad (17); (18)$$

$$M_{1133}^{(4)} = -M_{2233}^{(4)} = -k^2 D. \qquad (19)$$

From (13)–(19) we draw two conclusions. Firstly, a single nonzero anharmonicity parameter gives rise to Cartesian tensors up to arbitrary order. Secondly, the direction of the helix axis shows up only in the fourth- and higher-order tensors.

The potential $V_k(\mathbf{r})$ given in (6)–(12) has the orthorhombic point symmetry 222. In the special case $\Phi_0 = 0$ chosen in (13)–(19), the twofold axes coincide with the x, y and z axes, respectively. An inspection of the character tables for the point group 222 reveals that the $V_k^{(m)}(\mathbf{r})$ are unit irreducible representations. In other words, the twisted potential $V_k(\mathbf{r})$ is built up from symmetry-adapted functions of the Γ_1 representation of 222. For $C = 0$, the restoring forces towards $z = 0$ vanish: it is only in this case that $V_k(\mathbf{r})$ exhibits true helical symmetry. In a crystal twisted potentials may occur whenever the site group P permits a twist. This is, to be specific, true for all sites for which P is a proper or improper subgroup of 222. If $P = 222$, then $\mathbf{k}$ must be parallel to one of the twofold axes. For $P = 2$ the wave vector $\mathbf{k}$ may be either parallel or perpendicular to the axis.

IV. The Fourier transform

The exponent E occurring in the Boltzmann factor of (2) can be written explicitly as

$$E = -\tfrac{1}{2}\beta \mathbf{r} \mathbf{R}(z) \mathbf{M}(0) \mathbf{R}^{-1}(z) \mathbf{r} + i \mathbf{Q} \mathbf{r}. \qquad (20)$$

Introducing new transformed variables

$$\mathbf{s}(z) = \mathbf{R}^{-1}(z)\mathbf{r} = (\xi, \eta, \zeta)^T \qquad (21)$$

where $(\xi, \eta, \zeta)^T$ is a column vector, (20) is simplified to

$$E = -\tfrac{1}{2}\beta \mathbf{s}(z)\mathbf{M}(0)\mathbf{s}(z) + i\mathbf{Q}\mathbf{R}(z)\mathbf{s}(z)$$

$$= [-\beta A \xi^2/2 + i\xi q \cos(kz + \Phi_0 - \alpha)]$$

$$+ [-\beta B \eta^2/2 - i\eta q \sin(kz + \Phi_0 - \alpha)]$$

$$+ [-\beta C \zeta^2/2 + i\zeta q_3]. \qquad (22)$$

The Jacobi determinant of the transformation (21) is $+1$. The integration to give $Z(\mathbf{Q})$ with the exponent E [(22)] can then be performed in two steps: one first determines the integrals of the terms containing

the variables ξ and η, respectively, using (A1) given in the Appendix. The remaining terms depending on z are then transformed into a series of modified Bessel functions $I_m(\ldots)$ by the application of the generating function (A2). This series can be integrated term by term and one obtains

$$Z(\mathbf{Q}) = (2\pi/\beta)^{3/2}(ABC)^{-1/2} \exp(-u)$$

$$\times \sum_{m=-\infty}^{\infty} (-1)^m \exp[2im(\Phi_0 - \alpha)]$$

$$\times \exp[-(q_3 + 2mk)^2/(2\beta C)]I_m(V) \qquad (23)$$

where

$$U = [q^2/(4\beta)](1/A + 1/B) \qquad (24)$$

$$V = [q^2/(4\beta)](1/A - 1/B). \qquad (25)$$

[The parameter V should not be confused with the potential: potentials will always be written in the form $V(\mathbf{r})$, i.e. with their arguments explicitly given.]

The GDWF (3) is finally, in a condensed form,

$$\rho(\mathbf{Q}) = \exp(-U) \sum_{m=-\infty}^{\infty} (-1)^m \exp[2im(\Phi_0 - \alpha)]$$

$$\times \exp[-(q_3 + 2mk)^2/(2\beta C)]I_m(V). \qquad (26)$$

For actual calculations it is more convenient to separate the real and imaginary parts:

$$\rho(\mathbf{Q}) = \exp[-(U - \sigma|V|)] \exp[-q_3^2/(2\beta C)]$$

$$\times \left\{ \hat{I}_0(|V|) + \sum_{m=1}^{\infty} (-1)^m \sigma^m \hat{I}_m(|V|) \right.$$

$$\times \exp[-2k^2m^2/(\beta C)]$$

$$\times [\cos 2m(\Phi_0 - \alpha) \cosh(2mkq_3)/(\beta C)$$

$$\left. + i \sin 2m(\Phi_0 - \alpha) \sinh(2mkq_3)/(\beta C)] \right\}$$

$$(27)$$

with

$$\sigma = \begin{cases} +1 & \text{for } V > 0 \\ -1 & \text{for } V < 0 \end{cases} \qquad (28)$$

and

$$U - \sigma|V| = \begin{cases} q^2/(2B) & \text{for } V > 0 \\ q^2/(2A) & \text{for } V < 0. \end{cases} \qquad (29)$$

The specific form of (27) has been chosen for the purpose of numerical applications: the functions

$$\hat{I}_m(z) = e^{-z}I_m(z), \quad z \geq 0, \qquad (30)$$

are bounded for positive arguments (Abramowitz & Stegun, 1966):

$$\hat{I}_m(z) \leq 1, \quad m \geq 0. \qquad (31)$$

They can be calculated easily by efficient algorithms (Press, Flannery, Teukolsky & Vetterling, 1986).

V. Discussion and special cases

For a discussion of special values for the parameters A, B, C, k and Φ_0 we will use (26) rather than (27)–(29). In order to let the twofold axes of the point group 222 coincide with the x, y and z directions, we will set $\Phi_0 = 0$ unless stated otherwise.

(1) $\lambda \to \infty$

This is the limiting case of no torsion at all. Since $k = 0$ all the terms in (26) can be summed algebraically by ($A2$). With the additional choice $\Phi_0 = 0$ which corresponds to a rotation of $V_k(\mathbf{r})$ about the z axis we arrive at

$$\rho(\mathbf{Q}) = \exp\left[-(q_1^2/A + q_2^2/B + q_3^2/C)\right] \qquad (32)$$

$$= \exp\left[-(U - \sigma|V|)\right]$$

$$\times \left\{ \hat{I}_0(|V|) + 2\sum_{m=1}^{\infty} (-1)^m \sigma^m \hat{I}_m(|V|) \cos 2m\alpha \right\} \qquad (32a)$$

which is, as expected, the harmonic DWF corresponding to the harmonic potential $V_0(\mathbf{r})$ given in (4).

(2) $A = B$

Isotropy in the xy plane. Since $V = 0$ [(25)] in this case, the only nonzero term in the sum of (26) is $\sim I_0(0) = 1$ and

$$\rho(\mathbf{Q}) = \exp\left\{ -[(q_1^2 + q_2^2)/A + q_3^2/C] \right\}. \qquad (33)$$

It is again clear that any anharmonic effects must vanish since $V_k(\mathbf{r})$ is a rotationally symmetric harmonic potential [compare (6)–(11)].

(3) The general case: $A \neq B \neq C \neq 0$; $k \neq 0$

(3.1) Symmetry. The point group 222 transforms $\rho(\mathbf{r})$ as well as $\rho(\mathbf{Q})$ into itself. The inversion center and the mirror planes perpendicular to x, y and z in the corresponding Laue group mmm take $\rho(\mathbf{Q})$ into $\rho^*(\mathbf{Q})$:

$$\rho(-\mathbf{Q}) = \rho^*(\mathbf{Q}) \qquad (34)$$

$$\rho(q_1, q_2, -q_3) = \rho(q_1, -q_2, q_3) = \rho(-q_1, q_2, q_3)$$

$$= \rho(-q_1, -q_2, -q_3). \qquad (35)$$

Equations (34) and (35) are of course in agreement with Friedel's rule. Reversal of k, which is equivalent to a change from a right-handed ($k = +kz$) to a left-handed helix, has the same effect:

$$\rho_{-k}(\mathbf{Q}) = \rho_k^*(\mathbf{Q}). \qquad (36)$$

(3.2) $\mathbf{Q} = (0, 0, q_3)$. In this case the sums in (26) or (27) are reduced to one term $I_0(0) = 1$, and the GDWF becomes Gaussian:

$$\rho(\mathbf{Q}) = \exp(-q_3^2/C). \qquad (37)$$

(3.3) $\mathbf{Q} = q(\cos\alpha, \sin\alpha, 0)$. We find from (27)

$$\rho(\mathbf{Q}) = \exp\left[-(U - \sigma|V|)\right]$$

$$\times \left\{ \hat{I}_0(|V|) + 2\sum_{m=1}^{\infty} (-1)^m \sigma^m \hat{I}_m(|V|) \right.$$

$$\left. \times \exp\left[-2k^2 m^2/(\beta C)\right] \cos 2m(\Phi_0 - \alpha) \right\}. \qquad (38)$$

It was shown earlier that, for $k = 0$ and $\Phi_0 = 0$, (38) is the harmonic DWF (32). When one compares (32a) and (38), the effect of a nonvanishing torsion becomes evident immediately: the additional damping factor $\exp(-2k^2 m^2/\beta C)$ in (38) appreciably reduces higher-order anisotropic contributions, which are present in (32a). The principal axes of anisotropy of $\rho(\mathbf{Q})$ in (32) and (38), and of $|\rho(\mathbf{Q})|^2$, however, coincide in the plane $(q_1, q_2, 0)$ chosen. For $q_3 \neq 0$ the additional imaginary contributions present in the general expression (27) of $\rho(\mathbf{Q})$ provide for a higher anisotropy in the planes $(q_1, q_2$ or $q_3 = $ constant) without, however, a change of the direction of the anisotropy.

VI. Several equivalent helical sites*

All the calculations of §§III to V refer to an orthonormal basis system Σ specified by the basis vectors $\mathbf{e}_i$, $i = 1, 2, 3$. It has been pointed out by Johnson & Levy (1974) that the parameters relevant for thermal disorder have an obvious and immediate physical interpretation only in an orthonormal system. In the present case these are the quantities A, B, C with dimension [erg cm^{-2} = dyn cm^{-1} = mN m^{-1}] and the wave vector k with the dimension [Å^{-1}].

In a crystal having M equivalent helical sites $\mathbf{R}_{(m)}$, $m = 1, 2, \ldots, M$, one should accordingly introduce M transformed orthonormal systems $\Sigma_{(m)}$, calculate the cylindrical coordinates of $\mathbf{Q}$ in these coordinate systems and use (27). We prefer, as is usual in the treatment of the thermal motion (Johnson & Levy, 1974), to apply the inverse transformations to the scattering vector $\mathbf{Q}$. In this way M transformed vectors $\mathbf{Q}_{(m)}$ are generated which all have to be used in the standard system Σ.

Let $\mathbf{a}_i$, $\mathbf{a}_i^*$ ($i = 1, 2, 3$) be the basis and the reciprocal basis, respectively, of the crystal. The orientation of the $\mathbf{e}_i$ and the $\mathbf{a}_i$ bases with respect to each other is completely free. There are, however, a few obvious choices (Johnson & Levy, 1974) and one natural $i.e.$ unique choice (Patterson, 1952) which will not be dealt with here. Of importance in our case is the relative orientation which will be described by two

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* In this section bold-face symbols, $e.g.$ H, refer to the orthonormal basis system Σ described in the text. Primed bold-face symbols, $e.g.$ H', refer to the lattice-adapted bases $\mathbf{a}_i$ and $\mathbf{a}_i^*$.

metric tensors $\mathbf{g}$ and $\boldsymbol{\Omega}$

$$g_{ik} = (\mathbf{a}_i \cdot \mathbf{a}_k) \tag{39}$$

and

$$\Omega_{ik} = (\mathbf{e}_i \cdot \mathbf{a}_k). \tag{40}$$

The transposed tensors will be written $\mathbf{g}^T$ and $\boldsymbol{\Omega}^T$. The $\mathbf{g}$, $\boldsymbol{\Omega}$ and their inverses are connected by

$$\mathbf{g} = \boldsymbol{\Omega}^T \boldsymbol{\Omega} \tag{41}$$

$$\mathbf{g}^{-1} = \boldsymbol{\Omega}^{-1}(\boldsymbol{\Omega}^T)^{-1}. \tag{42}$$

The set of sites $\mathbf{R}_{(m)}$ is generated from $\mathbf{R}_{(1)}$ by the space-group elements $\mathbf{g}_{(m)} = \{\mathbf{S}_{(m)}|\boldsymbol{\tau}_{(m)}\}$. Let $\mathbf{T}$ be the rotation which transforms Σ into $\Sigma_{(1)}$:

$$\mathbf{T} = \mathbf{R}_z(\varphi_1)\mathbf{R}_y(\psi)\mathbf{R}_z(\varphi_2), \tag{43}$$

where $\mathbf{R}_y(\ldots)$ and $\mathbf{R}_z(\ldots)$ are rotations with axes along the y and z directions of Σ, respectively. Then the rotation taking Σ to $\Sigma_{(m)}$ is

$$\mathbf{T}_{(m)} = \mathbf{S}_{(m)}\mathbf{T}. \tag{44}$$

Following the recipe given above we apply the inverse transformation to $\mathbf{Q}$ to arrive at

$$\mathbf{Q}_{(m)} = \mathbf{T}^{-1}\mathbf{S}_{(m)}^{-1}\mathbf{Q}. \tag{45}$$

All quantities in (45) are written in the orthonormal system Σ. In actual calculations it is, however, more convenient to use lattice-adapted quantities $\mathbf{S}'_{(m)}$ and $\mathbf{Q}'$ which are connected with the $\mathbf{S}_{(m)}$ and $\mathbf{Q}$ by

$$\mathbf{S}_{(m)} = \boldsymbol{\Omega}\mathbf{S}'_{(m)}\boldsymbol{\Omega}^{-1} \tag{46}$$

$$\mathbf{Q} = (\boldsymbol{\Omega}^T)^{-1}\mathbf{Q}'. \tag{47}$$

From (45)–(47) we find finally in the system Σ

$$\mathbf{Q}_{(m)} = \mathbf{T}^{-1}\boldsymbol{\Omega}\mathbf{S}'^{-1}_{(m)}\mathbf{g}^{-1}\mathbf{Q}'. \tag{48}$$

The partial structure factor for the M atoms having a helical GDWF is given by

$$F(hkl) = \sum f(\mathbf{Q})\rho[\mathbf{Q}_{(m)}]\exp[2\pi i\mathbf{H}'\mathbf{R}'(m)] \tag{49}$$

where $f(\mathbf{Q})$ is the X-ray form factor or the neutron scattering length, respectively, $\mathbf{R}'_{(m)}$ refers to the basis $\mathbf{a}_i$ and $\rho(\mathbf{Q}_{(m)})$ is given by (27) with

$$q_{(m)3} = Q_{(m)3} \tag{50}$$

$$q_{(m)} = [Q^2_{(m)1} + Q^2_{(m)2}]^{1/2} \tag{51}$$

and

$$\cos\alpha_{(m)} = Q_{(m)1}/q_{(m)}. \tag{52}$$

The new physical parameters which enter into the description of the system as soon as $M > 1$ are the three Eulerian angles φ_1, ψ and φ_2.

VII. Concluding remarks

So far we have used the term 'double-helix environment' as a short-hand notation for local environments supporting a twisted potential $V_k(\mathbf{r})$. The local nature of the present formalism is enforced by requiring nonzero force constants A, B and C. Global helices are therefore not necessary for the GDWF to be applicable. Keeping this in mind, $\rho(\mathbf{Q})$ of (26) can be interpreted anew: it describes, in the lowest approximation, the thermodynamic effects of a local torsion with, now, a wave vector $\mathbf{k}$, the length of which is determined by the local twist. The direction of $\mathbf{k}$ is restricted if the site symmetry is 2 or 222. No restrictions occur for the general position in any space group which always has the site group 1. We emphasize in particular the importance of the sites on a screw axis.

Twisted internal surfaces in crystallographic spaces, i.e. in spaces exhibiting space-group symmetry, have been discussed recently from the geometrical (Fischer & Koch, 1989; Koch & Fischer, 1989) and from the chemical (Anderson, Hyde & von Schnering, 1984; von Schering & Nesper, 1987) points of view: they may be helpful for the identification of sites with an intrinsically strong twist. In passing, a few sites having a twisted environment are given explicitly:

sites at the core of a double helix;

centers of orthorhombic bisphenoids, sites which are quite frequent in minerals and inorganic compounds;

sites linking the twisted paddles in polyphenyls.

There remains the question as to which diffraction method is best adapted for an analysis of this kind. In recent years single-crystal diffraction data of high accuracy have been determined from X-ray measurements taken at synchrotron-radiation sources. It will certainly be an interesting task to unravel the electronic and thermal effects which both contribute to the twisted electron density. The unique assignment of twisted densities to a thermal origin is, however, expected to be more feasible from a careful analysis of high-accuracy neutron diffraction data. In the latter case, both the availability of data with high momentum transfer and the independence of the scattering length from $\mathbf{Q}$ will contribute to improve the analysis.

APPENDIX

For convenience we quote here two formulae which have been used several times in this paper: the Fourier transform of a Gaussian [(A1); Gradshteyn & Rhyzik (1965)] and the generating function for the modified

Bessel functions $I_m(z)$ [(A2); Abramowitz & Stegun (1966)]:

$$\int \exp(-q^2x^2) \exp[ip(x+\lambda)]\,dx$$
$$= (\pi^{1/2}/q) \exp[-p^2/(4q^2)] \cos p\lambda \qquad (A1)$$
$$\exp(z\cos\theta) = \sum \exp(im\theta)I_m(z). \qquad (A2)$$

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Accuracy in Laue X-ray Diffraction Analysis of Protein Structures

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Abstract

The accuracy in protein structure analysis based on Laue X-ray diffraction has been investigated for the example of two orthorhombic structures of bovine pancreatic trypsin (BPT). The precision in the Laue structure factors and the contrast in electron-density maps were used as criteria. A comparison with the results of previous analyses based on conventional crystal rotation methods showed that high resolution around 1.4 Å may be reached with both monochromatic and polychromatic techniques. Electron-density maps exhibited significantly lower contrast when calculated on the basis of Laue structure amplitudes, due to inefficient exploration of reciprocal space at low resolution by the Laue method even in the case of a broad bandwidth and inclusion of exposures from several different crystal orientations. Laue data were recorded on photographic film and processed using the program *LAUEMAD* [Bartunik & Borchert (1989). *Acta Cryst.* A45, 718–726]. The empirically derived wavelength scaling factors based on a comparison of equivalent reflection intensities were in good agreement with theoretical estimates over a broad wavelength range. One BPT structure was refined on the basis of Laue structure amplitudes (current R factor 24% at 1.8 Å resolution).

Introduction

Laue diffraction techniques using synchrotron radiation permit the recording of a large number of simultaneously excited reflections during short exposure times. This provides a means for investigating enzyme kinetics and protein dynamics based on crystal structure analysis of transient states (Moffat, Szebenyi & Bilderback, 1984; Helliwell, 1985; Hajdu, Acharya, Stuart, Barford & Johnson, 1988; Hajdu & Johnson, 1990). A first application of this method to structural analysis of an enzyme reaction intermediate with a lifetime of several minutes has recently been reported (Schlichting, Rapp, John, Wittinghofer, Pai & Goody, 1989). Even much shorter time scales are within reach. In the case of well diffracting crystals of medium-size protein structures such as trypsin, lysozyme or myoglobin, exposure times in the range of 1–10 ms suffice to obtain Laue diffraction patterns extending to atomic resolution at presently operational storage rings (*e.g.* Moffat, 1989; Bartunik, 1991). In addition

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