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Generalized Atomic Displacements in Crystallographic Structure Analysis*

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Abstract

An attempt is made to summarize both theoretical and experimental aspects of generalized atomic displacement parameters (ADP's) in crystalline matter. Generalized displacement parameters are used to describe the weakening of Bragg intensities *via* the anharmonic (static or thermal) Debye-Waller factor (DWF) and its real-space counterpart, the generalized atomic probability density function (p.d.f.). The lattice dynamical base of the harmonic and anharmonic thermal DWF is discussed. It is pointed out that the static DWF frequently contains higher-order terms. The mathematical base for an experimental determination of generalized ADP's is given. The most popular current formulations (one-particle potential and statistical approaches) are reviewed and their individual limitations are discussed. Likewise the demands put on the quality and extent of experimental data are assessed. Some aids to the interpretation of generalized ADP's established by crystallographic least-squares procedures are given and a Monte-Carlo method for the calculation of errors in p.d.f. maps is presented. Finally, some prospects for future work are outlined and a more frequent comparison of theoretical calculations and experimental determinations of generalized ADP's is advocated.

1. Introduction

Crystallographic structure analysis is a well established tool of solid-state research ranging from biochemistry to solid-state physics. The crystal structure is of fundamental interest in many studies of crystalline matter as it controls a good part of the properties and functions of the material. Often a detailed understanding of a material needs a detailed knowledge of the structure. Likewise a deep theoretical understanding of matter allows the prediction of fine details in the structure. In both cases an adequate knowledge of the crystal structure is indicated. Not surprisingly, over the years what is considered as adequate knowledge of the structure has changed. Important progress has been made in experimental procedures and analytical techniques as well as theoretical understanding. As there is no direct experimental access to the accurate crystal structure usually a model of the crystal structure is refined by least-squares methods using Bragg intensity data as observations. For a long time a structure was considered as determined when the atom positions of the structure model were believed to be established. Atomic thermal motion was considered as perturbation of the structure and introduced later into the model with additional parameters to account for the weakening of Bragg intensities with increasing scattering angle. However, subjected to systematic errors in the data much more than the positional parameters, sometimes they did not receive a lot of attention and often were not fully acknowledged. On the other hand, there is overwhelming evidence that thermal motion or - more generally - atomic displacement parameters (ADP's)† may carry very useful information and deserve more attention. Usually thermal-motion analysis is restricted to a harmonic model, *i.e.* to a Gaussian probability distribution of the atoms. However, in an increasing number of cases the harmonic approximation is incommensurate with the quality of Bragg diffraction data. Moreover, valuable information concerning the structure and properties of materials is contained in model parameters describing the deviations from a Gaussian probability density distribution. It is the main concern of this paper to show where one has to expect such deviations, how they can be modelled and what may be learned from the results. In §§ 2 to 4 a summary of the theory of generalized atomic displacements is given starting from the harmonic case. This part may be useful as a guideline for beginners in the field; however it cannot replace some considerably more comprehensive treatments of the fairly involved subject given in the quoted literature. For the experts it may serve as a recapitulation of the essential features

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* *Editorial note*: This invited paper is one of a series of comprehensive Lead Articles which the Editors invite from time to time on subjects considered to be timely for such treatment.

† Since static and thermal atomic displacements cannot be distinguished easily, the wording ADP's has been advocated by Professor J. D. Dunitz to replace 'thermal' (or 'vibration') parameters and this wording is accepted in the crystallographic community.

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and they also will find a more detailed discussion of the main problems of analysing generalized atomic displacements in §§ 5 and 6. Furthermore, these sections are intended to provide for the beginners in the field conditions for the warranted use of higher-order displacement terms.

Waller (1927) had already investigated the influence of anharmonicity on Bragg and thermal diffuse scattering. His results suggested relatively small contributions and further theoretical work had to await the sixties. Hahn & Ludwig (1961), Krivoglaz & Tekhonova (1961), Maradudin & Flinn (1963), Wolfe & Goodman (1969) and Shukla & Hübschle (1989) worked out theories for the anharmonic contribution to the thermal scattering of X-rays (or neutrons). The authors of the latter three papers also calculated numerically the anharmonic contribution to the Debye–Waller factor (DWF) for the case of f.c.c. metals (Maradudin & Flinn, 1963; Wolfe & Goodman, 1969; Shukla & Plint, 1989). However, these lattice-dynamical treatments are extremely involved and seemed of little practical interest except for very simple crystal structures. It was only in the late sixties that anharmonic thermal motions were treated in a form readily accessible to crystal structure analysis of more complicated materials. The milestones on this route were Dawson's generalized structure-factor formalism, Willis's isolated-atom potential approach and Johnson's statistical treatment for thermal motion. A summary of these contributions is found in Dawson (1975), Willis & Pryor (1975) and Johnson (1970). Since then a few hundred papers of both theoretical and experimental natures have been published and it is probably timely to assess critically the merits and shortcomings of the different approaches as well as to indicate the needs of future research.

2. The harmonic approximation

Atoms in crystals are never at rest. As the interaction time of an X-ray photon with the electrons is several orders of magnitude shorter than the period of a lattice vibration, X-ray diffraction samples in space over many quasi-static atomic configurations. Moreover, as the investigated crystals contain very many symmetrically equivalent atoms, the quantity which affects Bragg intensities is the time-space average of the atomic displacements. Despite the larger interaction time of a thermal neutron with the nucleus the situation is essentially the same for neutron diffraction.

In the following we will discuss the description of atomic displacements in the harmonic approximation in so far as it is necessary to treat its generalization; comprehensive treatments of the harmonic case can be found in the literature (*e.g.* Krivoglaz 1969; Maradudin, Montroll, Weiss & Ipatova 1971; Willis & Pryor, 1975). A phenomenological approach to second-order ADP's is given in Dunitz, Schomaker & Trueblood (1988); this paper also gives a very good introduction into mechanistic models of thermal motion and the interconnection of ADP's with spectroscopic frequencies and force constants. The lattice-dynamical treatment chosen in the following may in many cases be too complicated for a rigorous theoretical calculation of the ADP's, but it solely can give deeper insight into the origin of deviations from harmonic behaviour.

The basic quantity that is measured in a scattering experiment with thermal neutrons is the partial differential cross section $d^2\sigma/d\Omega\, dE$ of the target sample, which gives the scattered intensity per element of solid angle $d\Omega$ and per energy interval dE. The scattering law can be expressed in terms of Fourier transforms of correlation functions with operators describing the scattering relevant properties of the target sample (*e.g.* Lovesey, 1984). The relevant quantity is the (time-dependent) pair correlation function $G(\mathbf{r}, t)$, which describes the averaged pair distribution of the N scattering particles located at $\mathbf{r}$, $\mathbf{r}'$ by means of particle density operators $\hat{\rho}_p$

$$G(\mathbf{r}, t) = 1/N^{-1} \int \langle \hat{\rho}_p(\mathbf{r}' - \mathbf{r}, 0)\hat{\rho}_p(\mathbf{r}', t)\rangle \, d\mathbf{r}' \quad (1)$$

with $\int G(\mathbf{r}, t)\, d\mathbf{r} = N$. Here and in the following the brackets $\langle \ldots \rangle$ indicate thermal time or ensemble averages. In a Bragg scattering experiment one measures the elastic coherent part of the total scattering cross section. The correlation function for elastic scattering is of course time independent; the two particle density operators in (1) thus become uncorrelated. Likewise $G(\mathbf{r}, t \to \infty)$ is given by

$$G(\mathbf{r}, \infty) = N^{-1} \int \langle \rho_p(\mathbf{r}' - \mathbf{r})\rangle \langle \rho_p(\mathbf{r}')\rangle \, d\mathbf{r}'. \quad (2)$$

If the target sample is a crystal, (2) is closely related to the well known Patterson function. With (2) the elastic coherent cross section is expressed as

$$(d\sigma/d\Omega) = N(\sigma_c/4\pi) \int G(\mathbf{r}) \exp(i\mathbf{rs})\, d\mathbf{r}$$
$$= \left|\int \langle \rho(\mathbf{r})\rangle \exp(i\mathbf{rs})\, d\mathbf{r}\right|^2 \quad (3)$$

giving the scattered intensity in a solid-angle element $d\Omega$ centred around the scattering vector $\mathbf{s}$. σ_c is the bound nucleus coherent cross section which is related to the averaged neutron scattering length b by $\sigma_c = 4\pi|b|^2$ and $\rho(\mathbf{r})$ is the scattering-length-weighted particle density.

The situation for elastic coherent X-ray scattering is slightly more complicated. However, it has been shown by Scheringer (1980) that the approach to elastic coherent thermal neutron scattering can be fully applied to the X-ray case in the limit of the Born–Oppenheimer approximation (instantaneous electronic–nuclear coupling on displacements). If the target sample is a crystal, scattering takes places only in directions $\mathbf{s}$ corresponding to the nodes $\mathbf{Q}$ of the reciprocal lattice of the crystal. Then the scattered intensity is obtained with (3) as

$$d\sigma/d\Omega = I(\mathbf{Q}) = F(\mathbf{Q})F(\mathbf{Q})^* = \Big|\int_{\text{cell}} \langle\rho(\mathbf{r})\rangle \exp(i\mathbf{r}\mathbf{Q})\, d\mathbf{r}\Big|^2 \quad (4)$$

and the structure factor $F(\mathbf{Q})$ is given as

$$F(\mathbf{Q}) = \int_{\text{cell}} \langle\rho(\mathbf{r})\rangle \exp(i\mathbf{r}\mathbf{Q})\, d\mathbf{r} \quad (5)$$

for both thermal neutron and X-ray scattering; $F(\mathbf{Q})^*$ denotes the complex conjugate of $F(\mathbf{Q})$.

Thus the structure factor is the Fourier transform of the averaged scattering density distribution in the unit cell of a crystal. $\langle\rho(\mathbf{r})\rangle$ contains not only the information on the atom positions but also on the total averaged atomic displacements. We now formally split $\langle\rho(\mathbf{r})\rangle$ into a static and a dynamic part for every atom α in the unit cell

$$\langle\rho(\mathbf{d},\mathbf{r},\mathbf{u})\rangle = \sum_\alpha \langle\rho(\mathbf{d}_\alpha)\rangle * \langle\rho(\mathbf{r}_\alpha)\rangle * \langle\rho(\mathbf{u}_\alpha)\rangle \quad (6)$$

the total scattering density being a convolution of three contributions of atomic, static and dynamic origin. Then the Fourier transform of $\langle\rho(\mathbf{d},\mathbf{r},\mathbf{u})\rangle$ is given as

$$F(\mathbf{Q}) = \sum_\alpha f_\alpha \langle\exp(i\mathbf{Q}\mathbf{r}_\alpha)\rangle_l \langle\exp(i\mathbf{Q}\mathbf{u}_\alpha)\rangle_{t,l} \quad (7)$$

where f_α denotes the atomic scattering factor, $\langle\ \rangle_l$ defines the static space average [the so-called static DWF $S_\alpha(\mathbf{Q})$] and $\langle\ \rangle_{t,l}$ the dynamic time-space average [the so-called thermal DWF $T_\alpha(\mathbf{Q})$].

Furthermore, by combining (5), (6) and (7) we may express these averages by their Fourier transforms

$$\langle\exp(i\mathbf{Q}\mathbf{u}_\alpha)\rangle_{t,l} \equiv T_\alpha(\mathbf{Q}) = \int \langle\rho(\mathbf{u}_\alpha)\rangle \exp(i\mathbf{Q}\mathbf{u}_\alpha)\, d\mathbf{u}_\alpha \quad (8a)$$

$$\langle\exp(i\mathbf{Q}\Delta\mathbf{r}_\alpha)\rangle_l \equiv S_\alpha(\mathbf{Q}) = \int \langle\rho(\Delta\mathbf{r}_\alpha)\rangle \exp(i\mathbf{Q}\Delta\mathbf{r}_\alpha)\, d\mathbf{r}_\alpha \quad (8b)$$

with

$$\langle\exp(i\mathbf{Q}\mathbf{r}_\alpha)\rangle_l = \exp(i\mathbf{Q}\mathbf{r}_\alpha)\langle\exp(i\mathbf{Q}\Delta\mathbf{r}_\alpha)\rangle_l \quad (8c)$$

where $\Delta\mathbf{r}_\alpha$ is the deviation from the averaged atomic position $\mathbf{r}_\alpha$.

In the following we will consider the static and thermal averages separately starting with the thermal case.

The thermal Debye-Waller factor

The well established theory of lattice dynamics (see *e.g.* Maradudin, Montroll, Weiss & Ipatova, 1971; Willis & Pryor, 1975) gives access to the individual atomic displacements $\mathbf{u}$ and allows one to calculate their thermodynamic averages. The crystal potential usually governs the atomic displacements (except for very light atoms in some cases) and a general form of the crystal potential V is given by a Taylor expansion in the atomic displacements $\mathbf{u}$

$$V = V_0 + V_1 + V_2 + V_3 + V_4 + \dots \quad (9)$$

where

$$V_0 = \text{constant}$$

$$V_1 = \sum_{\alpha,l} u_\alpha(l)\Phi_\alpha(l)$$

$$V_2 = (1/2!)\sum_{\alpha,l}\sum_{\beta,l'} u_\alpha(l)u_\beta(l')\Phi_{\alpha\beta}(l,l')$$

$$V_3 = (1/3!)\sum_{\alpha,l}\sum_{\beta,l'}\sum_{\gamma,l''} u_\alpha(l)u_\beta(l')u_\gamma(l'')\Phi_{\alpha\beta\gamma}(l,l',l'')$$

etc. $\Phi_{\alpha\dots}(l,\dots)$ are derivatives of the potential energy at $u=0$; α, β, $\gamma,\dots$ label the atoms and l, l', l'' label the cells. In a crystal $V_1 = 0$ except at the crystal surface under applied stress. In the harmonic approximation only the terms V_0 and V_2 are retained and the force constants (coupling parameters) $\Phi_{\alpha\beta}(l,l')$ describe the atomic interactions completely. Knowing the atomic masses m_α and the force constants, one can give the $3nN$ equations of classical motion of the n atoms in N unit cells of the crystal. These equations can be reformulated by introducing dimensionless normal coordinates $j\mathbf{q}$ ($j = 1, 2, \dots, 3n$) and the (mass-adjusted) dynamical matrix $\mathbf{D}$, whose elements $D_{\alpha\beta}(\mathbf{q})$ contain the force constants $\Phi_{\alpha\beta}(l,l')$ as Fourier coefficients in a sum over all unit cells. If one further assumes the displacements to have a time dependence $\exp(-i\omega t)$, the simultaneous solutions of the equations of motion are obtained from the eigenvalue equation

$$\omega_j^2(\mathbf{q})\mathbf{e}(j\mathbf{q}) = \mathbf{D}(\mathbf{q})\mathbf{e}(j\mathbf{q}) \quad (10)$$

where $\mathbf{q}$ runs over the N points of the Brillouin zone (= number of unit cells in the crystal). For each value of $\mathbf{q}$ there are three solutions for ω corresponding to three values of j; to each $\omega_j(\mathbf{q})$ belongs a polarization vector $\mathbf{e}(j\mathbf{q})$. The energy of each such normal mode is given as

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})[\tfrac{1}{2} + \{\exp[\hbar\omega_j(\mathbf{q})/(k_BT)] - 1\}^{-1}] \quad (11)$$

in the quantum-mechanical regime (k_B is Boltzmann's constant) and as

$$E_j(\mathbf{q}) = k_BT \quad (12)$$

in the classical regime of temperature. Then the instantaneous atomic displacement $u_\alpha(l,t)$ is given by a superposition of the displacements of all normal modes

$$\mathbf{u}_\alpha(l,t) = (Nm_\alpha)^{-1/2}\sum_{j\mathbf{q}}[E_j(\mathbf{q})/\omega_j^2(\mathbf{q})]^{1/2}\mathbf{e}_\alpha(j\mathbf{q}) \times \exp[i\mathbf{q}\mathbf{r}_\alpha(1) - i\omega_j(\mathbf{q})t] \quad (13)$$

where $\mathbf{e}_\alpha(j\mathbf{q})$ gives the polarization vector for atom α in the normal mode $j\mathbf{q}$. Each normal mode corresponds to a one-phonon state, *i.e.* a state with no interaction with any other phonon. In this case the total thermal energy of the crystal is calculated as the sum of the individual phonon contributions. It also follows that the number of phonons in a non-interacting harmonic crystal is fixed for a given temperature and correspondingly each phonon has an infinite lifetime. A change of temperature creates or annihilates phonons but it leaves the frequencies of the remaining phonons unchanged.

The thermodynamic average of all displacements given in (13) may be calculated from the eigenvalues and eigenvectors of the dynamical matrix

$$\langle \mathbf{u}_\alpha \mathbf{u}_\alpha^T \rangle = (Nm_\alpha)^{-1} \sum_{j\mathbf{q}} [E_j(\mathbf{q})/\omega_j^2(\mathbf{q})] \mathbf{e}_\alpha(j\mathbf{q}) \mathbf{e}_\alpha^*(j\mathbf{q})^T \tag{14}$$

where $\mathbf{e}_\alpha^{*T}$ is the complex transpose of $\mathbf{e}_\alpha$. The tedious procedure of diagonalizing the dynamical matrix $\mathbf{D}$ is in fact not necessary to calculate the atomic mean-square displacements (m.s.d.'s). Born (1942) has shown that the inverted dynamical matrix allows for a calculation of m.s.d.'s without loss of generality. In the classical regime one obtains

$$\langle \mathbf{u}_\alpha \mathbf{u}_\alpha^T \rangle = (k_B T / N m_\alpha) \sum_{\mathbf{q}} \mathbf{D}_{\alpha\alpha}^{-1}(\mathbf{q}) \tag{15}$$

where $\mathbf{D}_{\alpha\alpha}^{-1}(\mathbf{q})$ is a diagonal 3×3 block of the inverted dynamical matrix. By virtue of the matrix inversion the interatomic coupling (explicitly given in the off-diagonal elements of the dynamic matrix) enters into the individual atomic m.s.d.'s. Thus there is no need to introduce explicit coupling terms in the m.s.d.'s as they are contained in $\langle \mathbf{u}\mathbf{u}^T \rangle$ and there is no way to separate them in a Bragg diffraction experiment.

The dynamically averaged probability density function (p.d.f.), sometimes called thermal smearing function, of a system of independent harmonic oscillators has been calculated by Bloch (1932). The p.d.f. is given in the classical and quantum regime as a trivariate Gaussian centred at the atomic position $\mathbf{r}_\alpha$

$$\begin{aligned} \langle \rho(\mathbf{u}_\alpha) \rangle &\equiv \text{p.d.f.}_\alpha(\mathbf{u}) \\ &= [(\det \mathbf{P}_\alpha)^{1/2}/(2\pi)^{3/2}] \exp[-(1/2)\mathbf{u}^T \mathbf{P}_\alpha \mathbf{u}] \end{aligned} \tag{16}$$

where $\mathbf{P}_\alpha = \mathbf{U}_\alpha^{-1}$ and $\mathbf{U}_\alpha \equiv \langle \mathbf{u}_\alpha \mathbf{u}_\alpha^T \rangle$; the atomic position is defined as the mean value of this distribution. By virtue of (8*a*), the atomic thermal DWF (temperature factor) $T_\alpha(\mathbf{Q})$ is given by the Fourier transform of the trivariate Gaussian p.d.f. Thus it is also a trivariate Gaussian with inverse halfwidth

$$T_\alpha(\mathbf{Q}) = \exp[(-1/2)\langle(\mathbf{Q}\cdot\mathbf{u})^2\rangle] \tag{17}$$

which may be expressed with $\mathbf{Q} = 4\pi\mathbf{h}|\mathbf{a}|$ in a form more familiar to the crystallographer as*

$$T_\alpha(\mathbf{h}) = \exp(-2\pi^2 h_i |\mathbf{a}^i| h_j |\mathbf{a}^j| U_\alpha^{ij}) \tag{18}$$

where h_i are (covariant) Miller indices, a^i are reciprocal-cell axes, $U^{ij} = \langle u^i u^j \rangle$ with $i, j = 1, 2, 3$. For computational convenience one often writes

$$T_\alpha(\mathbf{h}) = \exp(-h_i h_j \beta_\alpha^{ij}) \tag{19}$$

with $\beta_\alpha^{ij} = 2\pi^2 |\mathbf{a}^i||\mathbf{a}^j| U_\alpha^{ij}$ (no summation).

The static Debye–Waller factor

While the theory of the thermal Debye–Waller factor in harmonic approximation is very well established, the same does not hold true for the static Debye–Waller factor. Yet it is of considerable importance for a wide variety of substances ranging from crystals with point defects to orientationally disordered materials, all exhibiting deviations from strict crystallographic periodicity. It is precisely this variable non-ideality which prevents working out a comprehensive theory. A description of the physical origin of static displacements in crystals cannot be cast in the form of the lattice-dynamical normal mode theory for thermal displacements, because the distortion fields in the neighbourhood of a defect are of widely different range and nature and may be correlated with each other to a variable degree. This situation calls for an explicit treatment of the individual atomic contributions in the distortion field of interest, *e.g.* by evaluation of real- and/or reciprocal-space lattice sums. Still one may treat the static Debye–Waller factor in an approximate manner equivalent to the thermal harmonic case in that one only considers a quadratic $\mathbf{Q}$ dependence. One first assumes that the deviations $\Delta\mathbf{r}_{\alpha,l}$ from the ideal lattice site l_α obey the constraint $\sum_l \Delta\mathbf{r}_{\alpha,l} = 0$ as the crystal is considered macroscopically not deformed. Then, under the assumption of a Gaussian distribution of the deviations $\Delta\mathbf{r}_\alpha$, one obtains in analogy to (17)

$$S_\alpha \equiv \langle \exp(i\mathbf{Q}\Delta\mathbf{r}_\alpha) \rangle_l \propto \exp[-1/2\langle(\mathbf{Q}\Delta\mathbf{r}_\alpha)^2\rangle]. \tag{20}$$

Clearly S_α is a function of the concentration of the defects as well as the number of neighbours α around the defect. Furthermore, S_α is usually taken as temperature independent in which case one may extract the static part of the Debye–Waller factor as a constant addition to the linearly temperature-dependent harmonic dynamic part. A study of this temperature dependence of the total Debye–Waller factor conducted in the classical regime allows the static contribution to be obtained by extrapolation to zero temperature. A few comments are in order at this point. Firstly, there is little physical justification for a

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* Here and in the following tensor notation is employed to allow for a coherent description of anharmonic terms. Implicit summation over repeated indices is assumed unless stated otherwise.

Gaussian distribution of the static displacements $\Delta \mathbf{r}_\alpha$. As Krivoglaz (1969) pointed out, the distribution indeed is hardly ever Gaussian; in contrast to statements in the literature the central-limit theorem of statistics (which is valid for large and statistically independent quantities) cannot be invoked here as - despite the large number of atoms affected by the lattice defects - their shifts are highly dependent on the distance from the defect. Secondly, the experimental separation of static and dynamic parts is not necessarily a straightforward procedure as there may be non-additive contributions describing the coupling of thermal and static displacements. For a proper treatment of such cases a dynamic model for the defect environment needs to be worked out either theoretically or experimentally (*e.g.* by spectroscopic techniques). Nevertheless, useful information on static displacements in the quadratic approximation of (20) may be obtained under certain assumptions and experimental precautions; if one studies systems with moderate defect concentrations (*i.e.* no defect clustering) and restricts the analysis to the low-Q Bragg diffraction data, the deviations from the quadratic approximation are usually fairly small and the results are amenable to a semiquantitative analysis (*e.g.* Metzger, Behr & Peisl, 1982). Finally, one should mention that a great deal of information on disordered crystallographic systems is contained in the elastic diffuse scattering, a discussion of which is beyond the scope of the paper, but may be found in the literature (*e.g.* Bauer, 1979; Dederichs, 1973).

3. The generalized Debye–Waller factor

It has been shown in the preceeding section that the atomic Debye–Waller factor may be described as the Fourier transform of a trivariate Gaussian p.d.f. characterized by a set of mean-square displacement parameters. Nevertheless such a procedure is always an approximation to the true physical situation of a crystal (which may however be adequate in many instances). It is worth remembering that many properties of crystalline matter depend partly or entirely on anharmonic atomic interactions. Likewise, the disordered nature of real crystals is often expressed in non-Gaussian atomic p.d.f.'s. It is precisely the concern of this section to discuss why and where such deviations occur and how they influence Bragg diffraction data.

The thermal anharmonic Debye-Waller factor

Thermal expansion, the limited thermal conductivity in insulators or third-order elastic constants are direct manifestations of lattice anharmonicity, and many other physical properties like the specific heat or the scattering by phonons are affected by the presence of anharmonic terms in the crystal Hamiltonian. A great deal of work has been devoted in the past to give theoretical access to and clarify the role of these anharmonic contributions in crystalline materials (*e.g.* Leibfried & Ludwig, 1961; Choquard, 1967; Cowley, 1968; Glyde & Klein, 1971; Samathiyakanit & Glyde, 1973). The main results have meanwhile entered into physics textbooks (*e.g.* Ashcroft & Mermin, 1976). The effect of lattice anharmonicity on the thermal DWF is certainly less prominent than the examples quoted above; yet it is fairly easy to access experimentally as will be shown in the following chapters, and definitely merits some discussion.

The harmonic approximation discussed in § 2 fails in two instances. Firstly, the crystal potential itself is not harmonic. The true crystal potential may be approximated to any desired degree of accuracy by the addition of higher-order terms in the atomic interactions as given in (9). Retention of third- and fourth-order terms in this expansion is generally assumed to suffice in all cases where a perturbation treatment of anharmonicity (as discussed below) is adequate. Even then the theoretical procedure is rather involved and an extension to fifth- and sixth-order terms, which is formally easily done, often is forbiddingly cumbersome to accomplish. It should be mentioned that third- and fourth-order contributions to the crystal potential are often found to be of similar magnitude and thus both terms should be retained in theoretical as well as in experimental work. Clearly, higher-order terms in the crystal potential will become increasingly important with increasing atomic displacements. Owing to the different distance dependencies, anharmonic effects will be dominated by short-range repulsive forces rather than by Coulombic interactions (which gave the legitimation for the predominant use of central force models to describe anharmonicity). However, more recently it has been shown that contributions from long-range interactions are essential for a quantitative description of anharmonicity (Shukla, 1981; Shukla & Mountain, 1982). Large atomic displacements are expected for weak interatomic forces and for small atomic masses (in the quantum regime) and of course are always encountered at temperatures approaching the melting point of a crystal. Likewise, important anharmonic contributions due to large displacements are likely to be encountered when the structure is about to undergo a phase transition. A second instance where the harmonic approximation dramatically fails is evoked by the uncertainty principle in a quantum crystal like solid helium (*e.g.* Koehler, 1975). Here - despite a supposedly harmonic crystal potential - a kinetic-energy term modifies, by virtue of its proportionality to the square of atomic momentum, the effective Hamiltonian of the crystal resulting in a highly anharmonic (bimodal) p.d.f. for every atom. This is in sharp contrast to a classical system of (harmonic) oscillators, where kinetic and potential energy are constantly interchanged with equal averaged contributions. This parity is always violated in an anharmonic crystal, however not in such a fundamental way as encountered in a quantum crystal.

We now discuss the effects of lattice anharmonicity on the thermal DWF. The most obvious, though not necessarily the most pronounced, influence comes from the increased flexibility (additional isotropic and anisotropic terms) of the anharmonic crystal potential. Those terms originate in two-body central interactions with more than two displacement coordinates $i, j, k, \ldots$ (terms like $u^i_\alpha u^j_\alpha u^k_\gamma \Phi_{\alpha\alpha\gamma}$) or in many-body interactions (terms like $u^i_\alpha u^j_\beta u^k_\gamma \Phi_{\alpha\beta\gamma}$) entering in (9); naturally there are also self-terms (like $u^i_\alpha u^j_\alpha u^k_\alpha \Phi_{\alpha\alpha\alpha}$), however, only terms of even order in the displacements are different from zero (see Leibfried & Ludwig, 1961). Theoretical treatments are usually restricted to the two-body contributions for the lack of good many-body potential parameters; good-quality pair coupling parameters (between even fairly distant atoms) are available in many cases from elastic constant and inelastic neutron scattering data. Formally the anharmonic DWF is given by the thermodynamic average over all contributions $\mathbf{u}_\alpha$ in the expression $\langle \exp(i\mathbf{Q}\mathbf{u}_\alpha)\rangle_{t,l}$ of (7). Here it is not necessary to evaluate the full partition function

$$Z = \int \exp[-V(\mathbf{u})/(k_BT)]\,\mathrm{d}\mathbf{u}. \tag{21}$$

It suffices to determine the diagonal terms of the inverted dynamical matrix [*cf.* (14) and (15)] and its higher-order equivalents. Thus

$$\langle \exp(i\mathbf{Q}\mathbf{u}_\alpha)\rangle_{t,l} = \frac{\operatorname{trace}\{\exp(i\mathbf{Q}\mathbf{u}_\alpha)\exp[-V(\mathbf{u}_\alpha)/(k_BT)]\}}{\operatorname{trace}\{\exp[-V(\mathbf{u}_\alpha)/(k_BT)]\}} \tag{22}$$

as given by Krivoglaz & Tekhonova (1961) and Wolfe & Goodman (1969).*

At low temperatures the crystal potential $V(\mathbf{u})$ has to be replaced by the appropriate Hamiltonian of the crystal. A theoretical calculation of the anharmonic DWF tries to evaluate the right-hand side of (22). Still in the language of lattice dynamics, anharmonic effects may be discussed by introducing interactions between normal modes (*i.e.* phonons) as perturbations. Then anharmonic contributions to the DWF are due to the creation or annihilation of phonons (at constant temperature) and are given in terms of phonon coordinates or phonon creation and annihilation operators. Phonons will have a finite lifetime due to these interactions (which is seen as a broadening of phonon peaks in inelastic neutron scattering experiments). Of course Bragg diffraction as a zero-phonon scattering process is affected only through the modified displacement patterns and not directly by the phonon decay visible in phonon scattering processes. Indeed, (22) may be expressed with the aid of phonon coordinates (which contain the frequencies and polarization vectors of the phonons) which are allowed to interact as described by thermodynamic Green functions (*e.g.* Shukla & Hübschle, 1989). The different interactions allowed for a given order of anharmonic contributions to the DWF were frequently obtained by diagrammatic techniques (*e.g.* Wolfe & Goodman, 1969; Mair 1980). It turns out that in a perturbation treatment the contribution of the third-order anharmonic term shows a quadratic, that of the fourth-order term (as well as that of the squared third-order term*) a cubic dependency on the absolute temperature (Maradudin & Flinn, 1963; Wolfe & Goodman, 1969; Mair, 1980). The explicit calculation of the anharmonic DWF involves real- and/or reciprocal-space integrations and has been carried out for simple crystallographic structures only. The calculations differ in the method of real- and/or reciprocal-space summation and also by the acquisition of the higher-order terms of the crystal Hamiltonian.

While the explicit evaluation of anharmonic contributions to the DWF on the basis of the crystal potential is always very cumbersome, there exists a very convenient way to express the left-hand side of (22) by a power series in $\mathbf{u}$ (which by dimensional arguments is equivalent to powers in $\mathbf{Q}$). Such an expression obviously is not usable for a theoretical evaluation, but is well suited for the analysis of experimental results. As we have seen in the previous chapter the distribution function of $\mathbf{Q}\cdot\mathbf{u}_\alpha$ is approximately Gaussian. Thus a generalized distribution of $\mathbf{Q}\cdot\mathbf{u}_\alpha$ may be represented by moments and cumulants

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* Note that in several papers the DWF is given as

$$\langle \exp(i\mathbf{Q}\mathbf{u}_\alpha - i\mathbf{Q}\mathbf{u}_\beta)\rangle = \frac{\int \exp[i\mathbf{Q}\mathbf{u}_\alpha - i\mathbf{Q}\mathbf{u}_\beta]\exp[-V(\mathbf{u}_\alpha)/(K_BT)]\,\mathrm{d}\Omega}{\int \exp[-V(\mathbf{u}_\alpha)/(K_BT)]\,\mathrm{d}\Omega} \tag{22a}$$

with $\mathrm{d}\Omega$ as phase-space element. This is an unnecessary complication as Bragg diffraction by virtue of (2) cannot give direct information on correlated atomic displacements as expressed in (22*a*); such information is carried solely by the diffuse scattering of a crystal. However, the interdependencies of the atomic displacements (as given in the mixed terms of the atomic coupling parameters) contribute to the thermal average affecting the Debye-Waller factor in an analogous way as described in the harmonic case by (15) and formally stated in (22).

* Quadratic third-order terms originate from pairwise occurrences of phonon creation or annihilation processes involving three phonons each. In total there are two phonons in the initial and two phonons in the final stage of the interaction. Thus, such quadratic third-order terms have a $Q^2Q^2 = Q^4$ dependency. It is remembered that the simple third-order term comes from the creation (or annihilation) of a phonon, *i.e.* 1(2) phonons in the initial state and 2(1) phonons in the final state, thus exhibiting a $QQ^2(Q^2Q) = Q^3$ dependency. In the harmonic case the phonon remains unchanged and one has a $QQ = Q^2$ dependency. Similar to quadratic third-order terms there also exist quadratic and higher-order contributions of all other terms.

(Kendall & Stewart, 1977). The moments are defined by a moment generating function $M(\mathbf{Q})$

$$M(\mathbf{Q}) \equiv \langle \exp i\mathbf{Q}\mathbf{u}_\alpha \rangle = \sum_{N=0}^{\infty} (1/N!)\langle (\mathbf{Q}\cdot\mathbf{u}_\alpha)^N \rangle. \quad (23)$$

The moments $\langle (\mathbf{Q}\cdot\mathbf{u}_\alpha)^N \rangle$ of order N may be expressed in terms of cumulants $\langle (\mathbf{Q}\cdot\mathbf{u}_\alpha)^N \rangle_{\text{cum}}$ by the identity

$$\begin{aligned} &\sum_{N=0}^{\infty} (1/N!)\langle (\mathbf{Q}\cdot\mathbf{u}_\alpha)^N \rangle \\ &\quad \equiv \exp \sum_{N=1}^{\infty} (1/N!)\langle (\mathbf{Q}\cdot\mathbf{u}_\alpha)^N \rangle_{\text{cum}} \\ &\quad = \exp \langle \exp i\mathbf{Q}\mathbf{u}_\alpha - 1 \rangle_{\text{cum}}. \end{aligned} \quad (24)$$

In a purely harmonic system all cumulants (but not all moments) of order >2 are identically equal to zero. Thus the evidence for lattice anharmonicity (and indeed for any other deviation from a Gaussian distribution of $\mathbf{Q}\cdot\mathbf{u}_\alpha$) will be found in terms of higher-order cumulants in the general expression of the DWF. By means of Fourier transformation those higher-order cumulants will translate into higher-order modulations of the atomic p.d.f.'s as discussed in the next section.

The effect of lattice anharmonicities on the dynamic behaviour of a crystal is fully accounted for by considering the anharmonic Hamiltonian of the system. In very many cases a less-involved approach seems desirable with regard to the tremendous efforts needed to evaluate (22). One effect of anharmonicity is that the coupling parameters Φ (9) become temperature dependent. Such an effect may be accounted for by temperature-dependent normal-mode frequencies ω in (13) (and is then sometimes call the implicit anharmonic effect). Experimentally one expects deviations from the linear behaviour of $\langle \mathbf{u}_\alpha^2 \rangle$ with temperature in this case. In the so-called quasiharmonic approximation the inverse square of ω in (13) is replaced by

$$\omega_{\text{quasiharmonic}}^{-2} = \omega^{-2}(1 + 2\gamma_G \chi T) \quad (25)$$

where γ_G is known as the Grüneisen constant and χ is the volume coefficient of expansion; thus the entirely anharmonic effect of thermal expansion is used as a scaling parameter in the quasiharmonic theory.

An anomalous (anharmonic) behaviour of the DWF near structural phase transitions has frequently been advocated (see *e.g.* Bruce & Cowley, 1981), yet relatively little work has been done in detail, mainly within the framework of quasiharmonic theory. The anharmonic interactions of phonons are generally believed to drive a structural phase transition by a softening of certain phonon frequencies; the corresponding normal mode in the low-temperature phase freezes in as a static displacement of atoms. The soft phonons provoke the so-called central peak in the quasielastic response, but their contributions to the DWF remain unimportant. It has been shown (in a treatment restricted to terms quadratic in $\mathbf{Q}$) that the critical part of the DWF near the phase transition of (anti)ferroelectric and similar materials is rigorously determined by the renormalized static phonon frequencies (originating in a shift of sublattices due to static distortions) and exhibits a cusp shape near T_c (Meissner & Binder, 1975; Binder, Meissner & Mais, 1976). A marginal cusp shape of the quadratic DWF was also obtained in a mean-field treatment of a two-dimensional (anti)ferrodistortive transition, while a molecular-dynamics treatment of the same system gave a smooth behaviour of the DWF across the phase transition (Mair, 1986). Clearly, in these cases a purely dynamic treatment is no longer sufficient because in the low-temperature phase static contributions to the DWF are dominant.

In general it may be said that - though useful in some instances - the quasiharmonic theory of the DWF is often not of sufficient quality to explain the experimental evidence, especially at high temperatures (see *e.g.* Lima & Tsallis, 1980). Unfortunately, the explicit theoretical treatment of anharmonicity in the dynamic DWF nowadays lags behind the experimental capabilities and this is true also for the static DWF as will be discussed in the following section.

The static non-harmonic Debye–Waller factor

In contrast to the thermal DWF the origin of static displacements in crystals is manyfold and any general theory will be less concise for this reason. As mentioned in § 2 the static DWF is likely to behave distinctly non-quadratically in $\mathbf{Q}$. This has been stressed by Krivoglaz (1969), who gives a theoretical treatment for some specific cases of static disorder. In an ideal solid solution with small defect concentrations (*e.g.* in some alloys, H in metals) the static displacements and thus the static DWF may be calculated by means of lattice theory. Usually the displacements are split into two parts, one influenced by atoms fairly distant from the defect atom under consideration, where continuum theory is appropriate, and

$$\mathbf{u}_\alpha^{\text{distant}} = C\mathbf{d}/d^3 \quad (26)$$

with the constant C describing the defect strength and $\mathbf{d}$ the distance from the defect labelled α. To describe the vicinity of a defect (in terms of so-called core deformations) one approximates the true force fields by introduction of an ideal host lattice described by Green's function $\mathbf{G}$ as obtained from phonon dispersion curves (see *e.g.* Tewary, 1973) and Kanzaki forces $\mathbf{F}$ (Kanzaki, 1957)

$$\mathbf{u}_\alpha^{\text{core}} = \mathbf{G}_{\alpha,\beta}\cdot\mathbf{F}_\beta. \quad (27)$$

The contributions to the displacement of the defect atom α coming from nearest and more distant neighbours β may be calculated in this approach (see *e.g.* Metzger, Behr & Peisl, 1982) and the total (in general distinctly non-Gaussian) distribution of displacements evaluated and compared to the experiment. Formally the static DWF for a given defect concentration c in a solid solution (under the tacit assumption of equal probabilities for positive and negative displacements) is expressed according to Krivoglaz (1969) by means of a binomial defect displacement distribution $\Delta \mathbf{r}_\alpha$ as

$$\langle \exp(i\mathbf{Q}\cdot\Delta\mathbf{r}_\alpha)\rangle_l = \exp\{(1/2)\sum_{\alpha'} \ln[1+2c(1-c)(\cos\mathbf{Q}\cdot\mathbf{u}_{\alpha,\alpha'}-1)]\} \tag{28}$$

If $\Delta\mathbf{r}_\alpha$ can be described by a linear superposition of individual defect displacements $\mathbf{u}_{\alpha,\alpha'}$,

$$\Delta\mathbf{r}_\alpha = \sum_{\alpha'} c\mathbf{u}_{\alpha,\alpha'} \tag{29}$$

where $\mathbf{u}_{\alpha,\alpha'}$ gives the displacement of the affected atom α on replacing a perfect lattice atom in its neighbourhood by a defect atom α'. For small $\mathbf{Q}\cdot\mathbf{u}_{\alpha,\alpha'}$ (28) may be expanded in powers of $\mathbf{Q}\cdot\mathbf{u}_{\alpha,\alpha'}$ and

$$\begin{aligned}\langle \exp(i\mathbf{Q}\cdot\Delta\mathbf{r}_\alpha)\rangle_l &= \tfrac{1}{2}c(1-c)\sum_{\alpha'}(\mathbf{Q}\cdot\mathbf{u}_{\alpha,\alpha'})^2 \\ &\quad -\tfrac{1}{24}c(1-c)[1-6c(1-c)] \\ &\quad \times\sum_{\alpha'}(\mathbf{Q}\cdot\mathbf{u}_{\alpha,\alpha'})^4+\ldots.\end{aligned} \tag{30}$$

Thus higher-order terms of the static DWF of defect atoms as well as of their p.d.f.'s have to be expected. These are considerably greater in interstitial solutions than in solid solutions of the substitution type. By combining (30) with (26) and (27) one may obtain a theoretical estimate of the static DWF.

Very little theoretical work has been done for cases with deviations from a solid-solution behaviour. A discussion of correlations in the static DWF in the quadratic approximation has been given by Krivoglaz (1969). Such correlations are of considerable importance in H-bonded orientationally disordered crystals and it has been shown experimentally (Kuhs & Lehmann, 1986) that third- and fourth-order terms in the DWF are needed to explain the crystallographic data. Likewise a very limited amount of work has been done on the influence of static displacements on the thermal DWF, Krivoglaz (1969) gives a formal discussion of the problem stating that the terms containing both static and thermal components of the generalized DWF exhibit a fourth-power dependency on $\mathbf{Q}$. As mentioned above, many structural phase transitions are characterized by static displacements in the low-temperature phase and dynamic displacements in the high-temperature phase with fluctuations involving static and dynamic components in the vicinity of the phase transition. All contributions are reflected in the experimentally established DWF. Up to now the importance of higher-order terms in the DWF of a crystal near a structural phase transition has not been assessed quantitatively. However, it is quite clear that higher- (especially fourth-) order terms are important, certainly for transitions of the order–disorder type but also for displacive transitions (Fujii & Matsubara, 1987). It seems that experimental evidence for strong fourth-order terms in the DWF is indicative for an order–disorder phase transition in (anti)ferroelectric materials (*e.g.* McMahon, Nelmes, Piltz & Kuhs, 1990).

The Debye–Waller factor for curvilinear motion

To conclude this section we will briefly discuss contributions to the DWF originating in curvilinear atomic or molecular motions, which also lead to anharmonic terms in the DWF. Even if this case formally is covered by the lattice-dynamical treatment of the thermal DWF outlined above it merits some special attention. It is remembered that the coupling parameters of second order are constrained by the translational invariance (absence of external forces) of the crystal. Likewise there are restrictions on the coupling parameters due to a rotational invariance (conservation of angular momentum); yet to fulfil this invariance one has to constrain coupling parameters of second and third order (Leibfried, 1964). This leads to an induced anharmonicity, which in most materials is fairly small compared with third-order terms of purely translational origin. Yet in some cases (*e.g.* in molecular crystals) these induced terms are important and need to be considered explicitly. It is then convenient to split up the crystal Hamiltonian into translational and rotational terms. Higher-order terms in this approach originate from the rotational–translational coupling of normal modes (see *e.g.* Michel, 1986). A detailed theoretical treatment of its influence on the thermal DWF has not been given, but the general appearance of the DWF will be identical to the DWF originating in purely translational anharmonicity with, for example, temperature or $\mathbf{Q}$ dependency. Thus for ordered molecular crystals it will generally be sufficient to consider terms up to fourth order. Terms of even higher order may become important merely in the case of orientationally disordered molecular crystals. In this case the generalized distribution of $\mathbf{Q}\cdot\mathbf{u}_\alpha$ given in (23) and (24) (still perfectly valid) is sometimes more conveniently expressed by means of symmetry-adapted spherical harmonics (Hüller & Press, 1979) or some other appropriate function (Johnson & Levy, 1974). A detailed discussion of these approaches is beyond the scope of this article; see however Prandl, Hoser & Brückel (1988) for a recent summary.

4. Mathematical formulation

A generalized treatment of atomic displacements in crystal structure analyses demands a suitable parametrization of higher-order contributions in the (static or thermal) DWF entering in the structure-factor equation (7). To be of general use the mathematical formulation should be applicable to all crystal structures with due allowance for a reduction of the number of parameters in the case of high symmetry. It would also be highly desirable that the higher-order terms obtained in a crystallographic least-squares refinement could be directly translated into a least-squares-filtered real-space representation of scattering densities, rather than displaying the usual Fourier summation

$$\langle\rho(\mathbf{x})\rangle = V^{-1}\sum_{\mathbf{Q}} F(\mathbf{Q})\exp(i\mathbf{x}\mathbf{Q}) \qquad (31)$$

with its inherent fallacies of series-termination effects and error pile-up at high-symmetry positions.

It has been realized by Dawson (1967) that both the atomic form factor f_α and the thermal DWF may contain imaginary contributions and this fact is exploited in all formulations of a generalized treatment of the DWF. It means that in the generalized structure factor

$$F(\mathbf{Q}) = A(\mathbf{Q}) + iB(\mathbf{Q}) \qquad (32a)$$

one has to separate centrosymmetric ($T_{\alpha,c}$) and antisymmetric ($T_{\alpha,a}$) parts of the DWF for real f_α:

$$A(\mathbf{Q}) = \sum_\alpha f_\alpha[T_{\alpha,c}(\mathbf{Q})\cos(\mathbf{Q}\cdot\mathbf{r}_\alpha) - T_{\alpha,a}(\mathbf{Q})\sin(\mathbf{Q}\cdot\mathbf{r}_\alpha)] \qquad (32b)$$

$$B(\mathbf{Q}) = \sum_\alpha f_\alpha[T_{\alpha,c}(\mathbf{Q})\sin(\mathbf{Q}\cdot\mathbf{r}_\alpha) + T_{\alpha,a}(\mathbf{Q})\cos(\mathbf{Q}\cdot\mathbf{r}_\alpha)]. \qquad (32c)$$

The coordinate $\mathbf{r}_\alpha$ gives the atomic position in the usual (harmonic) sense, which however is no longer a well defined quantity in the presence of anharmonic terms as discussed below.

Two different routes of access are conceivable: the first is by expressing the r.h.s. of (22) in terms of a restricted Hamiltonian (the so-called potential-based or physical approach); the second is by formally expanding the l.h.s. of (22) in terms of moments or cumulants as given in (23) and (24) (so-called statistical approach). There is little to choose on general grounds in the case of the thermal DWF and both may be transferred into each other after the completed analysis. The limited applicability of one or the other is caused by mathematical short-comings as discussed in § 5. In the case of a static DWF a potential-based treatment makes no sense physically and a statistical approach appears more appropriate (Kuhs, 1983).

Potential-based formalisms

As discussed in § 3 there is no way to retrieve the information on interatomic coupling from an analysis of the thermal DWF despite the fact that it is influenced by correlated atomic motions. Consequently the atomic potential obtained from a crystallographic structure analysis has only a limited physical significance. This potential has been called the isolated-atom-potential (IAP) or one-particle-potential (OPP) and is the potential which an atom would experience on the average if all other atoms were located with a probability given by their respective p.d.f.'s at an arbitrary position, thus excluding the explicit effect of correlated displacements (see also Scheringer, 1987). The OPP takes the same form as the crystal potential given in (9) with all indices β, γ, ... and l, l', l'', ... dropped. Equation (22) then reads

$$T_\alpha(\mathbf{Q}) = [\int\exp(i\mathbf{Q}\mathbf{u}_\alpha) \times\exp[-V_\alpha^{\rm OPP}(\mathbf{u}_\alpha)/(k_BT)]\,d\mathbf{u}_\alpha/Z_\alpha^{\rm OPP} \qquad (33)$$

where $Z_\alpha^{\rm OPP}$ is the one-particle partition function

$$Z_\alpha^{\rm OPP} = \int\exp[-V_\alpha^{\rm OPP}(\mathbf{u})/(k_BT)]\,d\mathbf{u}. \qquad (34)$$

Clearly such a potential is governed by the point-group symmetry of its averaged environment; this restricts to zero some terms which are allowed in the full crystal Hamiltonian (see *e.g.* Mair, 1985).

The OPP approach has been chosen to fit experimental data by Dawson & Willis (1967) and Willis (1969) and was first formulated for cubic point-group symmetries. More recently it has been generalized by Tanaka & Marumo (1983) to any point-group symmetry including terms up to fourth order. The generalized OPP is given by

$$V_{\rm gnrl}^{\rm OPP}(\mathbf{u}) = V_{\rm har}^{\rm OPP}(\mathbf{u}) + \gamma_{ijk}^{\rm OPP}u^iu^ju^k + \delta_{ijkl}^{\rm OPP}u^iu^ju^ku^l \qquad (35)$$

with $\gamma_{ijk}^{\rm OPP}$ and $\delta_{ijkl}^{\rm OPP}$ being the third- and fourth-order anharmonic parameters, which are defined in an orthogonal coordinate system. The evaluation of the corresponding thermal DWF is done by approximating the anharmonic part of the OPP in (33) by

$$\exp[-V_{\rm anh}^{\rm OPP}(\mathbf{u})/(k_BT)] = 1 - V_{\rm anh}^{\rm OPP}(\mathbf{u})/(k_BT) \qquad (36)$$

in order to obtain closed algebraic expressions and a subsequent solution of the resulting Fourier integrals. Of course, the thermal DWF may also be calculated by numerical Fourier transformation (8*a*) of the atomic p.d.f., which is classically obtained from the Boltzmann function (here and in the following the atom label α is dropped)

$$\text{p.d.f.}(\mathbf{u}) = \exp[-V^{\rm OPP}(\mathbf{u})/(k_BT)]/Z^{\rm OPP} \qquad (37)$$

with $Z_{\rm OPP}$ as given in (34). In the quantum regime $V_{\rm gnrl}^{\rm OPP}$ in (33) has to be replaced by the corresponding one-particle Hamiltonian (Mair & Wilkins, 1976).

Other general formulations of the OPP model have been given by Coppens (1978), Kurki-Suonio, Merisalo & Peltonen (1979) and Scheringer (1985*a*). Coppens suggested the OPP of (35) expressing [within the approximation of (36)] the temperature factor by means of (reciprocal-space) Hermite polynominals $G^{ijk}\ldots(\mathbf{Q})$ (Erdelyi, 1953), which are contragredient with the crystal base vectors

$$\begin{aligned} T_{\text{gnrl}}(\mathbf{Q}) = T_{\text{har}}(\mathbf{Q})[1 - i\gamma_{ijk}^{\text{OPP}}G^{ijk}(\mathbf{Q}) \\ + \delta_{ijkl}^{\text{OPP}}G^{ijkl}(\mathbf{Q})]. \end{aligned} \tag{38}$$

$\gamma_{ijk}^{\text{OPP}}$ and $\delta_{ijkl}^{\text{OPP}}$ are covariant tensor components of the potential parameters. The idea was taken up later by Scheringer (1985*a*) who pointed out that this formulation avoids the tedious calculation of Fourier integrals. To express (38) he proposed a moment expansion of $T(\mathbf{Q})$ [see (23)] to circumvent the direct use of the clumsy Hermite polynomials in a least-squares routine. An equivalent formulation by means of a cumulant expansion of $T(\mathbf{Q})$ [see (24)] has been proposed by Mair (1980); for a comparison of the two approaches see Mackenzie & Mair (1985). Kurki-Suonio, Merisalo & Peltonen (1979) proposed the use of symmetrized harmonic oscillator wave functions expressed by means of polynomials* $H'_{ijkl}\ldots(\mathbf{u})$ to describe the anharmonic modulations of the OPP

$$V_{\text{gnrl}}^{\text{OPP}}(\mathbf{u}) = V_{\text{har}}^{\text{OPP}}(\mathbf{u})[1 - \gamma_{ijk}^{\text{FIV}}H'_{ijk}(\mathbf{u}) + \delta_{ijkl}^{\text{FIV}}H'_{ijkl}(\mathbf{u})]. \tag{39}$$

The expansion may be given conveniently only in Cartesian coordinates (or spherical and cylindrical coordinates) and yields with the approximation of (36)

$$\begin{aligned} T_{\text{gnrl}}(\mathbf{Q}) = (1/P)\,T_{\text{har}}(\mathbf{Q})[1 - \gamma_{ijk}^{\text{FIV}}H'_{ijk}(\mathbf{Q}) \\ + \delta_{ijkl}^{\text{FIV}}H'_{ijkl}(\mathbf{Q})]. \end{aligned} \tag{40}$$

Owing to the Fourier invariance (FIV) of $H'(\mathbf{Q})$ the corresponding p.d.f.($\mathbf{u}$) assumes an identical form to (40) merely replacing $H'(\mathbf{Q})$ by $H'(\mathbf{u})$. P is a normalization factor containing contributions from all even-order higher-order terms.

From the above-mentioned formulations, only the Willis approach with its variants has been routinely used in crystallographic work (for a list see Tanaka & Marumo, 1983). Although a great deal of useful work has been done in the past, the OPP approach in general suffers from the limited applicability in the case of stronger anharmonicities, which will be discussed further in § 5. This limitation led Matsubara (1975*a*, *b*) to propose a formalism based on the so-called cumulant expansion of the harmonic DWF, which in fact is a statistical treatment discussed in the following.

Statistical formalisms

The physical relevance of the OPP parameters is fairly limited since they essentially give information on the soft and hard directions of atoms in a crystal structure. Thus another less artificial approach, which in addition turns out to be less restrictive, merits a detailed discussion. It has been introduced by Johnson (1969, 1970) and is based on a differential expansion of the atomic Gaussian p.d.f:

$$\begin{aligned} \text{p.d.f.}_{\text{gnrl}}(\mathbf{u}) = \text{p.d.f.}_{\text{har}}(\mathbf{u})[1 - C^iD_i + (1/2!)C^{ij}D_iD_j \\ -(1/3!)C^{ijk}D_iD_jD_k \\ +(1/4!)C^{ijkl}D_iD_jD_kD_l - \ldots + \ldots] \end{aligned} \tag{41}$$

where $C^i\ldots$ are tensorial coefficients (and thus valid in any metric) and $D = \delta/\delta u$ denotes a differential operator. The Nth derivative D^N of a trivariate Gaussian p.d.f. is a polynomial of degree N in $\mathbf{u}$; these polynomials are known as Hermite polynomials* $H_N(\mathbf{u})$ and are defined as

$$\begin{aligned} H_{ijk\ldots n}(\mathbf{u})\ \text{p.d.f.}_{\cdot\text{har}}(\mathbf{u}) \\ = (-1)^N(\delta^N/\delta u^i\delta u^j\delta u^k\ldots\delta u^n)\ \text{p.d.f.}_{\cdot\text{har}}(\mathbf{u}). \end{aligned} \tag{42}$$

They are evaluated by summing over all permutations of $i, j, k, \ldots, n$ for all polynomial terms (Johnson & Levy, 1974; Zucker & Schulz, 1982).

The retention of first- and second-order anharmonic terms in (41) is common practice in statistics and has also been suggested for crystallographic use (Johnson, 1969). In this treatment a conventional harmonic least-squares refinement yields the mean and the standard deviation of the harmonic p.d.f. The first- and second-order anharmonic terms are obtained as shifts of mean and standard deviation from the conventional values in a structure refinement including higher-order terms. However, in practice the first- and third- as well as the second- and fourth-order terms are often highly correlated and an independent estimate of each cannot be obtained. Thus the first- and second-order anharmonic terms are usually set to zero (to form a so-called standardized anharmonic p.d.f.). This means that, in a higher-order refinement, the mean and the standard deviation of the harmonic part include the anharmonic shifts of atomic position and dispersion respectively and have lost the universal meaning which they have in a purely harmonic case. The refined first-order term corresponds now to the three-dimensionally time-space averaged position (the so-called mean) and

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* There are two different types of Hermite polynomials. The first, denoted $H'_{ijkl}\ldots$ (and the one of interest here), is encountered in solutions of Schrödinger's equation for a harmonic oscillator potential. The second, denoted $H_{ijkl}\ldots$, is frequently used in statistics to generalize a Gaussian p.d.f. (see below); the $H_{ijkl}\ldots$ do not possess the property of Fourier invariance in contrast to the $H'_{ijkl}\ldots$.

* See previous footnote.

usually does not coincide any longer with the maximum of the p.d.f., which is found at the so-called mode position. When it comes to the calculation of interatomic distances (using specific mechanistic models) yet another position may be introduced, which corresponds to the equilibrium position at a given temperature along a given direction (one-dimensional time-space average as discussed in § 6). In general this position is different again from either mean or mode position.

There are different ways of expressing the tensorial coefficients in (41). In statistics they are defined *via* generating functions. A generating function is a characteristic function (in the terminology of statistics) and is just the Fourier transform of the p.d.f. The tensorial coefficients may now be expressed in terms of moments μ of the p.d.f. ($\mathbf{u}$). The moment generating function [given in (23)] is reformulated for this purpose as

$$M(\mathbf{Q}) = \sum_{N=0}^{\infty} (i^N/N!) Q_i Q_j Q_k \dots Q_n \mu^{ijk\dots n}. \quad (43)$$

Thus $\mu^{ijk\dots n}$ is the coefficient of $Q^N/N!$ in the Fourier transform of the atomic p.d.f. (which is assumed to be fairly Gaussian) and hence the moments may also be expressed by

$$\mu^{ijk\dots n} = \int u^i u^j u^k \dots u^n \text{ p.d.f.}(\mathbf{u})\, d\mathbf{u}. \quad (44)$$

The moments $\mu^{ijk\dots n}$ may be expressed in terms of cumulant $\kappa^{ijk\dots n}$ (and *vice versa*) as defined in (24). In standardized form one obtains (Kendall & Stewart, 1977)

$$\begin{aligned}
\mu^{i} &= \kappa^{i}\\
\mu^{ij} &= \kappa^{ij}\\
\mu^{ijk} &= \kappa^{ijk}\\
\mu^{ijkl} &= \kappa^{ijkl} + 3\kappa^{ij}\kappa^{kl}\\
\mu^{ijklm} &= \kappa^{ijklm} + 10\kappa^{ijk}\kappa^{lm}\\
\mu^{ijklmn} &= \kappa^{ijklmn} + 15\kappa^{ijkl}\kappa^{mn}\\
&\quad + 10\kappa^{ijk}\kappa^{lmn} + 15\kappa^{ij}\kappa^{kl}\kappa^{mn}.
\end{aligned} \quad (45)$$

In some way the cumulants seem a better measure of anharmonicity as they are free from trivial contributions of lower-order terms. The cumulant generating function $K(\mathbf{Q})$ is easily deduced from (24) and is given as

$$\begin{aligned}
K(\mathbf{Q}) &\equiv \exp[M(\mathbf{Q})]\\
&= \exp\left[\sum_{N=1}^{\infty} \kappa^{ijk\dots n}(i^N/N!) Q_i Q_j Q_k \dots Q_n\right].
\end{aligned} \quad (46)$$

This exponential series in $\mathbf{Q}$ yields the temperature factor (given up to fourth order)

$$\begin{aligned}
T_{\text{EW}}(\mathbf{Q}) = T_{\text{har}}(\mathbf{Q}) \exp[&-i\gamma^{ijk}_{\text{EW}} Q_i Q_j Q_k\\
&+ \delta^{ijkl}_{\text{EW}} Q_i Q_j Q_k Q_l]
\end{aligned} \quad (47)$$

with γ^{ijk}_{EW} and $\delta^{ijkl}_{\text{EW}}$ as cumulants* of order three and four respectively and $T_{\text{har}}(\mathbf{Q})$ containing the cumulant of second order (while the first cumulant corresponds to the atomic position in the structure-factor equation). The label EW denotes an Edgeworth series defined in real space, which is chosen according to statistical practice. Another approach known in statistics as a quasi-moment expansion turns out to be even more useful in crystallographic applications. Here the tensorial coefficients are expressed in terms of quasimoments $\tilde{\mu}_{ijk\dots n}$ which are defined by the generating function $\tilde{M}(\mathbf{Q})$ (Kuznetsov, Stratonovich & Tikhonov, 1960),

$$\begin{aligned}
\tilde{M}(\mathbf{Q}) &\equiv \exp[\tfrac{1}{2}\langle(\mathbf{Q}\cdot\mathbf{u})^2\rangle]\\
&\quad \times \left[\sum_{N=0}^{\infty} \tilde{\mu}_{ijk\dots n}(i^N/N!) Q_i Q_j Q_k \dots Q_n\right],
\end{aligned} \quad (48)$$

with the corresponding temperature factor given (up to sixth order) as

$$\begin{aligned}
T_{\text{GC}}(\mathbf{Q}) = T_{\text{har}}(\mathbf{Q})[1 &- i\gamma^{ijk}_{\text{GC}} Q_i Q_j Q_k + \delta^{ijkl}_{\text{GC}} Q_i Q_j Q_k Q_l\\
&+ i\varepsilon^{ijklm}_{\text{GC}} Q_i Q_j Q_k Q_l Q_m\\
&- \zeta^{ijklmn}_{\text{GC}} Q_i Q_j Q_k Q_l Q_m Q_n]
\end{aligned} \quad (49)$$

and γ^{ijk}_{GC} *etc.* as tensorial quasimoments*; the label GC denotes Gram–Charlier series, which is the name given in statistics to the real-space counterpart.

It is easily seen by comparing (47) and (49) that both expressions are identical if all terms up to infinity are included (by virtue of the identity $\exp(i\mathbf{Q}) = \sum (i\mathbf{Q})^N/N!$). For a finite series, however, the cumulants of order N carry implicit information on contributions of order N^2, N^3 *etc.* in contrast to the quasi-moments; in the Gram–Charlier temperature factor (49) these contributions have to be introduced explicitly. The important advantage of the Gram–Charlier formulation is its straightforward calculation of the corresponding p.d.f:

$$\begin{aligned}
\text{p.d.f.}_{\text{GC}}(\mathbf{u}) = \text{p.d.f.}_{\text{har}}(\mathbf{u})[1 &+ (1/3!)\gamma^{ijk}_{\text{GC}} H_{ijk}(\mathbf{u})\\
&+ (1/4!)\delta^{ijkl}_{\text{GC}} H_{ijkl}(\mathbf{u})\\
&+ (1/5!)\varepsilon^{ijklm}_{\text{GC}} H_{ijklm}(\mathbf{u})\\
&+ (1/6!)\zeta^{ijklmn}_{\text{GC}} H_{ijklmn}(\mathbf{u})].
\end{aligned} \quad (50)$$

Owing to the implicit higher-order terms in the Edgeworth temperature factor the exact evaluation

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* The tensorial cumulants and quasimoments of different order are designated with greek letters for better distinction. They sometimes contain numerical factors of powers of 2π corresponding to the transformation of $\mathbf{Q}$ into $2\pi\mathbf{H}$.

of the corresponding p.d.f. is practically impossible and may be done only in an approximate way.

$$\begin{aligned}\text{p.d.f.}_{\text{EW}}(\mathbf{u}) = \text{p.d.f.}_{\text{har}}(\mathbf{u})[1 &+ (1/3!)\gamma^{ijk}_{\text{EW}}H_{ijk}(\mathbf{u}) \\ &+ (1/4!)\delta^{ijkl}_{\text{EW}}H_{ijkl}(\mathbf{u}) \\ &+ (10/6!)\gamma^{ijk}_{\text{EW}}\,\gamma^{lmn}H_{ijklmn}(\mathbf{u})] \qquad (51)\end{aligned}$$

is the form suggested by Edgeworth (1905) on the basis of statistical arguments on the relative importance of higher-order terms (which may or may not be valid in a specific case under consideration). In this approximation the quasimoments and cumulants are related by

$$\begin{aligned}&\gamma^{ijk}_{\text{GC}} = \gamma^{ijk}_{\text{EW}} \quad \delta^{ijkl}_{\text{GC}} = \delta^{ijkl}_{\text{EW}} \\ &\zeta^{ijklmn}_{\text{GC}} = \zeta^{ijklmn}_{\text{EW}} + (10/6!)\gamma^{ijk}_{\text{EW}}\gamma^{lmn}_{\text{EW}}.\end{aligned} \qquad (52)$$

Owing to the tensorial character of cumulants and quasimoments any symmetry restrictions are easily introduced in the least-squares procedure. The constraints have been tabulated by Johnson & Levy (1974) up to fourth order and Kuhs (1984) up to eighth order.

The statistical approach is well suited to cope not only with lattice anharmonicity but also with any higher-order static displacements and in fact has been used for a description of a variety of disordered crystallographic structures (Kuhs, 1983). Finally, it should be mentioned that the tensorial coefficients of the statistical approach may be transformed into OPP parameters by equating terms of equal **Q** dependency (*e.g.* Kontio & Stevens, 1982) and thus exhibit a well defined temperature dependency as expected from lattice dynamics (and in contrast to some statements in the literature). Thus, the square root of the third-order terms and the cube root of the fourth-order terms are expected to be proportional to the absolute temperature in the classical regime. Furthermore an OPP may always be calculated with the aid of the Boltzmann function (37) as

$$V^{\text{OPP}}(\mathbf{u}) = -k_BT\{\ln[\text{p.d.f.}(\mathbf{u})] - \ln[\text{p.d.f.}(\mathbf{u}=\mathbf{o})]\}. \qquad (53)$$

The question now arises whether all approaches presented in this section perform equally well. This is discussed best by considering some important limitations inherent in the different formalisms.

5. Limitations

There are different limitations to all formalisms discussed in the previous section. Some of them are of a fundamental nature, while others are imposed by more practical considerations. A discussion of these limitations may be found in the literature (Kuhs, 1988*a*) and is repeated here in a more concise form.

Mathematical restrictions

The series expansions with tensorial coefficients used in a generalized DWF are mathematically complete and cannot be extended to give a better approximation to the true DWF, which is the Fourier transform of the Boltzmann p.d.f. (= the true atomic p.d.f.) or of the corresponding quantum expression. Of course there is no guarantee that the generally well justified assumptions made in deriving the formalisms (perturbation of the OPP or Gaussian p.d.f.) automatically lead to an appropriate description of the physical situation. Likewise it is a matter of belief that a more flexible model automatically gives a better approximation to the truth, a case which can be decided upon only by comparison with experimental data. A model, however, must always fulfil certain conditions to be useful for a general description of anharmonic systems. Divergencies in both real- and reciprocal-space expressions must not occur as they are unphysical. Likewise, the p.d.f. should be positive definite everywhere to be physically meaningful. In addition, exact Fourier transformability would be a useful feature; however, it is not essential as numerical Fourier transformations are well within the reach of present day computing facilities. The performance of the different approaches relative to these points will be discussed. The approximation exp $(-x) \simeq 1 - x$ made in all generalized OPP formalisms obtained by a perturbation treatment limits their validity to relatively small anharmonicities if only a limited number of terms in included, and often makes them unsuitable for the description of disordered systems. However, problem-specific potential shapes may be introduced and treated in an exact manner (*e.g.* Mair, 1982, 1983). The ambiguity in the Fourier transforms of the generalized OPP formalisms as they are found in the literature (*e.g.* Willis, 1969; Kontio & Stevens, 1982; Tanaka & Marumo, 1983; Scheringer, 1985*a*) is not of a fundamental nature but is due to the omission of higher-order terms, which may or may not be important in a given case. The full expression for the anharmonic OPP temperature factor up to second order in the perturbation treatment is given by Mackenzie & Mair (1985). The knowledge of the Fourier transform (exact to a given order in the perturbation) is important in the interpretation of results obtained by a crystallographic least-squares refinement. It is exactly known for the OPP formalisms and the Gram–Charlier approach but is not available in a closed form for the Edgeworth case as has been discussed in the previous chapter. This suggests the use of the Gram–Charlier rather than the Edgeworth series even when the latter gives a better fit to the observations due to the implicit higher-order terms.

If considered necessary these higher-order terms (usually of sixth order) may be introduced explicitly in a Gram–Charlier formulation. Real and reciprocal-space divergencies as well as the condition of positive definiteness of the p.d.f. turn out to be a severe mathematical limitation of all formalisms presented here and their respective range of applicability has to be assessed carefully. Divergent series expansions have no exact Fourier transforms. A theorem by Marcinkiewicz (1938) states that even a convergent exponential series with terms higher than second order can never be the Fourier transform of a p.d.f. in the mathematical sense because such a p.d.f. always has negative regions. This theorem has been extended to three dimensions and imaginary terms by Gromes (Scheringer, 1985*b*). Thus inspection of (47) immediately rules out the Edgeworth form of the temperature factor as a mathematically acceptable Fourier transform of (51). If one tolerates small negative regions in the p.d.f. one may however accept the Edgeworth formulations (Scheringer, 1985*b*) for practical work. Much more problematic is the divergency of the Edgeworth series in reciprocal space (37) as it affects directly the least-squares-refinement procedure. Owing to its exponential form, divergencies always occur in the presence of higher-order terms at finite $\mathbf{Q}$. This means that inclusion of data at higher $\mathbf{Q}$ will increasingly invalidate the results in contrast to first expectations and it is only due to the limited range of experimental observations that the Edgeworth approach has been successful in the past. Moreover, owing to the exponential form of (47), strongly anharmonic or disordered systems cannot be modelled because the temperature factor of such a system is negative at higher values of $\mathbf{Q}$ ('out-of-phase' scattering). A similar situation with respect to positive definiteness arises for the OPP p.d.f.'s (Mackenzie & Mair, 1985). The inverse Fourier transform of the OPP temperature factor is only an approximation of the exact Boltzmann p.d.f. given formally in (37).* Either the corresponding temperature factor given in (38) is divergent (Scheringer, 1985*a*) or the resulting p.d.f. is not everywhere positive definite. Good agreement with the exact Boltzmann p.d.f. is obtained only for weak anharmonicities and can never be fully achieved. A possible way out is to express the temperature factor of the exact Boltzmann p.d.f. by numerical Fourier transformation. The mathematical limitations in the case of the Gram–Charlier approach are not of a fundamental nature. Of course there exist parameter combinations which yield a locally negative p.d.f., but the negative definiteness apparently is not of intrinsic mathematical nature if only a limited number of terms is included. Conditions for positive definiteness have been discussed by Kuhs (1983) and Scheringer (1988); the negative volume of the Gram–Charlier p.d.f. is found to be always smaller than for the corresponding Edgeworth case. It seems acceptable to allow for slightly negative volumes in the p.d.f. at least as long as they are commensurable with the experimental error. It is worth mentioning that in the Gram–Charlier case divergencies in reciprocal space do not occur, nor do restrictions concerning the out-of-phase scattering exist. Thus it appears that the Gram–Charlier approach is the most flexible and least mathematically restricted way to describe generalized atomic displacements in crystal structures of all formalisms presented here.

Phase indeterminacy

The different mathematical expressions for the Edgeworth and the Gram–Charlier temperature factor [(47) and (49) respectively] have led to a controversy as to whether the Gram–Charlier approach allows us to overcome the indeterminacy of the phase in the structure-factor equation on including odd-order terms for acentric structures (Nelmes & Tun, 1987, 1988; Hansen, 1988). Certainly the mathematical form of the Gram–Charlier temperature factor allows for intensity changes, while the Edgeworth expression only gives rise to a phase shift. Thus the magnitude of certain terms in acentric structures cannot be refined in this case: Hazell & Willis (1978) have established rules specifying which terms have to be kept fixed in the least-squares refinement. As the Gram–Charlier and the Edgeworth series are identical if all terms up to infinity are included, this indeterminacy also holds for the limiting Gram–Charlier temperature factor. The truncated Gram–Charlier series formally does not suffer from indeterminacy in a mathematical sense. However, in the case of small anharmonicities the difference between the Gram–Charlier and the Edgeworth cases is very small [corresponding to the difference between $\exp(-\gamma)$ and $1-\gamma$] and almost singular normal equation matrices occur in the Gram–Charlier least-squares refinement preventing a meaningful determination of the odd-order terms in question. It is only in the case of disorder involving out-of-phase scattering that convergent refinements may be obtained. It is remembered that out-of-phase scattering may also be modelled by introducing split-atom positions, which similarly are allowed to be freely refined as long as one atom in the unit cell is (arbitrarily) kept fixed. In all other cases structure refinements will be near divergency and addition of higher powers of the odd-order terms in the Gram–Charlier temperature factor [corresponding to the approximation of $\exp(-\gamma)$ by a Taylor-series expansion] will further destabilize the structure refinements. Probes other than diffraction (*e.g.* light scattering) have to be used

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* The exact Boltzmann p.d.f. is obtained with the unknown, yet to be established, OPP. The OPP in the form of (35) is not an exact approximation of the true OPP as discussed above.

to establish the relative importance of ambiguous terms in the crystal potential for acentric structures.

The case of X-rays

The formal separation of atomic form factor and DWF as expressed in (6) needs some discussion. Clearly in the case of neutrons this separation is straightforward as the nuclear form factor is a constant. The situation is different for X-rays and some interference of the parameters describing asphericity in electron densities with the ones describing non-Gaussian atomic p.d.f.'s is expected in a least-squares refinement. Indeed, there is a close mathematical resemblance of the formalisms used for the two effects. The main difference is that electronic asphericities like multipole deformations mainly concern the valence electrons while anharmonic deformations affect the whole atom. Thus the sensitive range in reciprocal space is generally at lower **Q** for multipole deformations and measurements to **Q** values as high as possible are always indicated. As the sensitive range for anharmonic deformations is linked to the magnitude of thermal motion (as discussed below) one may improve the separation by working at low temperatures and a temperature-dependent study will help to clarify the interference between charge distribution and anharmonic effects. Yet a complete separation can never be achieved when considering only one of the two effects as has been shown by Mallison, Koritsansky, Elkaim, Li & Coppens (1988). If electronic charge asphericity and anharmonic thermal motion (or disorder) are suspected to exist together for the same atom, a sufficient decorrelation may however be obtained by a combined refinement of multipole and anharmonic parameters. One should also be aware of the fact that isotropic anharmonic modulations may be correlated with the radial part of the electronic charge distribution. In case of doubt independent information on the anharmonicity must be gained from a neutron diffraction study. Neutron diffraction remains in general the best way of establishing the anharmonic DWF except possibly in cases where extremely weak reflections carry all information on anharmonicity. The dynamic range of neutron diffraction is certainly much smaller than what is available on modern synchrotron sources, yet this is partially offset by the gain at high angles due to the constant form factor and the complete insensitivity to the charge distribution of the nuclear interaction of the neutrons.

Experimental limitations

For a successful determination of higher-order terms in the DWF it is important to be aware of some restrictions imposed by the quality and the extent of the Bragg intensity data; the general disclaimer concerning X-ray data has been discussed already in the previous sections. It is remembered that the relative changes of the p.d.f. due to anharmonicity or disorder at small displacements are a few per cent of the total probability density in most cases. At larger displacements the relative changes become increasingly greater, but the influence on the Bragg intensity data becomes less important. The relative effect of anharmonicity or disorder on the DWF is increasing with Q, however the greatest absolute change of the DWF is expected at some finite value of **Q**. It may be calculated by taking the derivatives of the generalized DWF expressions (Kuhs, 1988*a*) and is given in the Gram–Charlier case by

$$Q_n = 2n^{1/2}(2\pi)^{-1/2}(2\ln 2)^{1/2}\langle u^2\rangle^{-1/2} \qquad (54)$$

where n is the order of the anharmonic terms and $\langle u^2\rangle$ is the mean square displacement of the atom in the direction of interest. As a rule of thumb the data collection has to be extended at least out to Q_n for refining successfully terms of order n. Many attempts to determine higher-order terms in the DWF appear to have failed because the data set was not measured at sufficiently high resolution, rather than because of deficiencies in the models or the quality of the data. Evidently the quality of the data has to be commensurate with the size of the anharmonic effect to be investigated. Thus higher-order terms are easily established in strongly anharmonic systems like fast ionic conductors and need considerably better quality data in materials with strong covalent or ionic bonding. The level at which higher-order terms are meaningful should be monitored by calculating difference Fourier maps together with the corresponding error maps. Often the large number of independent higher-order terms, especially in low-symmetry structures, has been considered as a drawback to all the formalisms. However, the increased dynamic range of modern X-ray and neutron diffractometers in general allows a sufficient number of independent data to be collected by going to smaller wavelengths (see Kuhs, 1988*b*) and thus to overdetermine the problem by a factor of five to ten even when fourth-order terms are considered. Moreover, insignificant terms may be set to zero and 'chemical' constraints on the different tensor components could be introduced thus reducing the number of freely refined parameters. With such precautions meaningful higher-order terms may be obtained from any crystalline material as has been demonstrated by an increasing number of publications.

6. Aids in the interpretation

The purpose of a diffraction experiment is to obtain a better understanding of the physics or chemistry of a material. How can one extract the relevant information from the large number of higher-order terms established by a least-squares-refinement procedure?

There are several ways to condense the wealth of information into numbers related to physical quantities of interest or into maps of immediate evidence, and some of them will be discussed in this section. The first step of the analysis must be the assessment of the significance of the results obtained. The minimal requirement is that the improvement in the quality of fit by the addition of anharmonic terms satisfies statistical tests. The refinement process itself should be controlled closely as the high parameter correlations typically encountered between terms of order n and $n+2$ may lead to spurious results; it is often necessary to add higher-order terms in several steps before all parameters can be freely refined. These precautions are vital as very often the refined anharmonic parameters are not highly significant. Before far-reaching conclusions are drawn it is wise to repeat the analysis with an independently measured data set. An important check on the consistency of the results is performed by a calculation of the p.d.f. (or the OPP) from the least-squares estimated parameters. Strongly negative regions of the p.d.f. or divergencies in the OPP especially near the atomic positions are unphysical and the refined parameters must be considered as unreliable. There is good evidence that such results are in general not due to deficiencies in the model, but rather due to deficiencies (*e.g.* systematic errors) in the data (Kuhs, 1988*a*). As mentioned in the previous section one may tolerate negative regions far from the atomic position if they are considered as insignificant. Likewise, divergencies or unboundedness of the OPP are not a serious problem as long as they occur in regions of real space insignificantly populated at the temperature of the diffraction experiment. Thus the errors in the p.d.f. or OPP have to be established. This has not been done very often in the past as it is cumbersome to do analytically. A Monte-Carlo technique allows for a mathematically exact and yet easily realizable calculation of the variances (and also the covariances) of a p.d.f. map. Details of this method are given in the Appendix. The inspection of the p.d.f. together with its error p.d.f. immediately shows the significant features due to higher-order terms of the DWF, the action of which in real space is not easily predicted otherwise. The calculation and display of p.d.f. or OPP maps is usually a very efficient way of presenting the results in a digestible way. As the anharmonic modulations are usually small, it is more appropriate to display the anharmonic deformation densities $\text{p.d.f.}_{\text{def}}$ (or the disorder deformation densities in the case of a static DWF) together with error maps instead of the total $\text{p.d.f.}_{\text{gnrl}}$:

$$\text{p.d.f.}_{\text{def}}(\mathbf{u}) = \text{p.d.f.}_{\text{gnrl}}(\mathbf{u}) - \text{p.d.f.}_{\text{har}}(\mathbf{u}). \qquad (55)$$

When pure third- or pure fourth-order contributions are displayed they are called skew and kurtosis maps respectively. Of course, Fourier maps may also be used; they suffer, however, from series-termination effects and necessitate a complete set of data, which is not always reliably available.

The full information content of the anharmonic terms (which should be given in units of Å rather than as dimensionless quantities* to allow for a better comparison) may be condensed to provide single numbers for a discussion of the underlying physics. A very useful operation in this respect is a tensor contraction (see *e.g.* Hamermesh, 1962; Pach & Frey, 1964). Invariants of a higher-order tensor of rank N with N even (it is recalled that many anharmonic models operate with tensorial coefficients as discussed in § 4) are obtained by full contraction with the components of the real-space metric tensor g_{ij}

$${}^N I_0 = g_{ij} g_{kl} \ldots g_{mn} \beta^{ijkl\ldots mn}. \qquad (56)$$

${}^N I_0$ is also called the trace of a tensor of rank N. In a similar way, vector invariants of odd-rank tensors may be calculated

$${}^N v^i = g_{jk} \ldots g_{mn} \beta^{ijk\ldots mn} \qquad (57)$$

where v^1 is called the 23 trace (*etc.*). The scalar invariant ${}^N I_0$ gives a global number for even-order anharmonic terms: in the case of a Gram–Charlier treatment negative values indicate flatness of the p.d.f. or, more specifically, disorder in the case of a static DWF, while positive values indicate peakedness of the p.d.f. compared with a Gaussian distribution. Likewise, the vector ${}^N v^i$ gives the direction of the maximal skewness of the p.d.f. (which can be related to the atomic shift vectors in the case of structural phase transitions). Partial contraction is sometimes useful in order to access directional aspects of generalized p.d.f.'s. The elements of the second-order tensor ${}^N d^{ij}$ obtained by the contraction

$${}^N d^{ij} = g_{kl} \ldots g_{mn} \beta^{ijkl\ldots mn} \qquad (58)$$

from the full fourth- or sixth-order tensor reveal the directions of peakedness or flatness in the p.d.f. It may be useful in some cases to expand the contracted tensor in order to quantify the higher-order anisotropy

$$\tilde{\beta}^{ijkl\ldots mn} = {}^N I_0 [(N+1)!]^{-1} P(g^{ij} g^{kl} \ldots g^{mn}) \qquad (59)$$

where P is a permutation operator for full interchange of indices and g^{ij} *etc.* is a component of the reciprocal-space metric tensor. The higher-order anisotropy is then given as

$$\Delta\beta^{ijkl\ldots mn} = \beta^{ijkl\ldots mn} - \tilde{\beta}^{ijkl\ldots mn} \qquad (60)$$

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* The least-squares programs in general operate with dimensionless quantities $\beta^{ijk\ldots n}$. They may be transformed according to

$$u^{ijk\ldots n} = [N!/(2\pi)^N] \beta^{ijk\ldots n} |\mathbf{a}^i|^{-1} |\mathbf{a}^j|^{-1} |\mathbf{a}^k|^{-1} \ldots |\mathbf{a}^n|^{-1}$$

(no summation) into quantities of units Å^N; $\mathbf{a}^i$ *etc.* are reciprocal-lattice vectors.

(no summation). Equation (59) also allows parameter constraints to be derived for higher-order tensors in the case of imposed isotropy or second-order anisotropy. This may be useful in order to reduce the number of freely refined parameters.

The higher-order moments μ_N of the total p.d.f. in a certain direction **u** are obtained numerically as

$$\mu_N(\mathbf{u}) = \int \mathbf{u}^N \text{ p.d.f.}(\mathbf{u}) \, du \qquad (61)$$

and may be further analysed in terms of coefficients of skewness and kurtosis (Kuhs, 1988*a*). $\mu_1(\mathbf{u})$ gives the shift of the atomic position from the refined value and may be used in certain cases (assuming a specific model of coupled motion) to get a better estimate of the bond distance.

All manipulations described above are helpful to gain some insight into the physical origin of anharmonic atomic displacements, mainly because they clarify directional aspects. Those aspects are often buried under the large number of independent tensor components, which in turn may have been a deterrant to including an anharmonic DWF altogether.

7. Future work

From the preceding discussion it emerges that a sound base, both theoretically and experimentally, has been established for a detailed investigation of anharmonic behaviour in the crystalline state by diffraction methods. Still, such an analysis is not yet straightforward for a variety of reasons. On the experimental side considerable effort is needed to obtain diffraction data of highest quality. Multiple diffraction effects need to be surveyed closely in cases where weak reflections carry the crucial information on higher-order displacement parameters. While the effect of uncorrected thermal diffuse scattering on the harmonic DWF is reasonably well known, the effect on higher-order terms has not yet been studied in a systematic way. It is not likely to be negligible. Thus, in addition to the generally applied corrections to Bragg intensity data, both the effects of multiple diffraction and thermal diffuse scattering should be considered in studies of the anharmonic DWF. Generally, single-crystal studies give the best results, however neutron powder diffraction work has been shown to give significant answers at least for strongly anharmonic systems (*e.g.* Yude, Boysen & Schulz, 1990).

Some topics of interest for future experimental work will probably be the study of the anharmonic DWF near phase transitions and especially near the melting transition, where no high-quality data are available at all. Temperature stabilities of a few hundredths of a degree over long periods necessary to perform such work are now routinely available on several four-circle diffractometers. It must be remembered that lattice anharmonicity and/or positional disorder in the solid phase are ingredients of most theories of melting and much could be learned from diffraction experiments on the role both of them play for the melting transition. In more classical fields of structure analysis involving anharmonic displacement parameters, as in the study of fast ionic conductors or molecular crystals, work will certainly continue. The latter will profit from a general inclusion of higher-order terms (especially of third order), possibly constraint in so-called **TLS** models of thermal motion. This could help to get more realistic interatomic distances, even if a more thorough analysis of the higher-order terms is not carried out. The mathematical formulation for this approach was worked out a long time ago (Prince & Finger, 1973). It is only a matter of applying it in least-squares structure refinements.

With respect to theory a variety of analytical approaches is available to calculate anharmonic interactions in general and the anharmonic DWF in particular starting from interatomic potentials or force constants. For weakly anharmonic systems perturbative approaches seem fully satisfactory, while strongly anharmonic systems usually are treated with renormalized harmonic models with residual anharmonic corrections. Crystals near ferroelectric phase transitions, fast ionic conductors, rotationally disordered solids and quantum crystals are typical examples of strongly anharmonic systems. It is likely that crystals near the melting point also behave in a strongly anharmonic fashion, yet the lack of experimental data prevents a definite statement on this point. The abovementioned computational procedures are applicable in practice only to simple crystal structures. More complicated systems may be analysed by Monte-Carlo or molecular-dynamics simulations, again based on assumed or calculated interatomic potentials, usually effective pair potentials. But, even then, due to the large number of possible atomic interactions, some simplifying assumptions still have to be made. Monte-Carlo or molecular-dynamics simulations provide m.s.d.'s and higher-order displacement parameters directly, which can be used for a comparison with crystallographic results.

It appears that comparisons between theoretical and experimental DWF's will be fruitful in several respects. For simple systems (like metals or ionic solids) a very detailed cross-check of theory and experiment may be performed, possibly calling for even further improved experimental data or a revision of current theories. Unfortunately this has been rarely done in the past, possibly because the results are sometimes not directly comparable. The experimentally obtained cumulants, quasi-moments or OPP parameters have often to be expressed in terms of anharmonic contributions to the DWF obtained in theoretical calculations, a transformation which could be done straightforwardly, if not analytically, then at least numerically. For more complicated systems the experimental results obtained in a diffraction experiment are more accurate at present than the results of theoretical calculations, a fact which could be used as a guide for improvements in the theory. Again this does not seem to happen very often, probably because the crystallographic community and theoretical physicists working in this field are not in close contact with each other. It should be mentioned in this context that experimental techniques other than diffraction are frequently used to study anharmonicity on the atomic level, the more prominent ones being IR and Raman spectroscopy, inelastic neutron scattering and EXAFS. These methods are extremely useful in many cases as they give very accurate information on specific anharmonic interactions. However, none of these methods allows us to locate straightforwardly the individual anharmonic contributions of all atoms in arbitrary directions and the analysis of more complicated systems becomes increasingly difficult. It is the advantage of diffraction techniques that they provide useful data almost routinely on the anharmonic DWF even in the most complicated crystal structures. There is no reason why anharmonic motions of structural units in large molecules of biological interest could not be analysed on the basis of good-quality diffraction data.

In considering the static DWF, the situation on the theoretical side seems to be less favourable for reasons discussed in § 3. It appears that an adequate theory has yet to be worked out for the specific problem under investigation. It also appears that studies of the diffuse scattering should accompany the analysis of the static DWF whenever possible. There is clearly a need for more work to be done in this field on such different materials as disordered molecular crystals, non-stoichiometric compounds, alloys, metal hydrides and minerals with variable chemical composition. This will eventually give experimental access to the force fields near defect lattice sites or at least it will provide more realistic interatomic distances and angles in these systems.

It is hoped that the state of affairs presented in this work is helpful to the reader interested in venturing into a certainly intricate, but undoubtedly very revealing, field of solid-state research.

APPENDIX

Monte-Carlo error estimation for density maps

The calculation of errors in p.d.f. maps is of crucial importance for assessing the significance of higher-order modulations in real space. The least-squares-estimated quantities used in the p.d.f. calculation are the harmonic displacement parameters, which enter as components of **P**, the inverse of the dispersion matrix **U**, into the Hermite polynomials, see (16), and the components of the higher-order displacement tensors, which enter as coefficients in (39), (50) or (51). The resulting expressions are fairly lengthy and an error calculation including parameter correlations (which are often >0.90) is very cumbersome. One seeks to calculate the variance $\text{p.d.f.}^{1\sigma}(\mathbf{u})$ around the mean $\overline{\text{p.d.f.}}(\mathbf{u})$:

$$\begin{aligned}\text{p.d.f.}^{1\sigma}(\mathbf{u}) &\equiv \langle[\overline{\text{p.d.f.}}(\mathbf{u})-\text{p.d.f.}(\mathbf{u})]^2\rangle\\ &= \int_{p_1}\int_{p_2}\dots\int_{p_n}[\text{p.d.f.}(p_1,p_2,\dots p_n,\mathbf{u})]^2\\ &\quad\times J(p_1,p_2,\dots,p_n)\,\mathrm{d}p_1\,\mathrm{d}p_2\dots\mathrm{d}p_n \qquad (A1)\end{aligned}$$

where $J(p_1,p_2,\dots,p_n)$ is the joint probability density function for all parameters. A mathematically correct way to evaluate the multiple integral is by Monte-Carlo simulation. The Monte-Carlo (MC) method allows us to include easily the full variance-covariance matrix **V** of the least-squares estimation of the n refined parameters p. The parameters taken into consideration may be restricted to the atom of interest or may include all refined parameters. The following steps need to be taken:

(1) Generation of random numbers R. There is a variety of random number generators on almost any computer, although not all perform equally well (see James, 1980). A generator of the multiplicative congruential type providing pseudo-random numbers R in the range $0\le R<1$ is generally sufficient for our purpose

(2) Generation of Gaussian-distributed numbers R^G. A computationally very efficient way of producing R^G is by the method of Box & Muller (1958), which produces a pair of pseudo-random numbers

$$R_1^G=(-2\ln R_1)^{1/2}\cos(2\pi R_2) \qquad (A2a)$$

$$R_2^G=(-2\ln R_1)^{1/2}\sin(2\pi R_2). \qquad (A2b)$$

(3) Generation of correlated random numbers R^C. This is achieved with the aid of the 'square-root' method (see James, 1980). The vector of dimension n of Gaussian-random numbers is modified by the lower-triangular matrix **C**

$$\mathbf{R}^C=\mathbf{C}\cdot\mathbf{R}^G. \qquad (A3)$$

The matrix **C** is calculated from the variance-covariance matrix **V** with the following recursive procedure (James, 1980):

$$C_{i1}=V_{i1}/V_{11}^{1/2} \quad 1\le i\le n \qquad (A4a)$$

$$C_{ii}=\left|V_{ii}-\sum_{k=1}^{i-1}C_{ik}^2\right|^{1/2} \quad 1<i\le n \qquad (A4b)$$

$$C_{ij}=\left(V_{ij}-\sum_{k=1}^{j-1}C_{ik}C_{jk}\right)\bigg/C_{jj} \quad 1<j<i\le n. \qquad (A4c)$$

(4) Modification of the parameters $p_1\dots p_n$ with the n-dimensional array of correlated random numbers $\mathbf{R}^c$

$$\mathbf{p}^{MC}=\mathbf{p}+\mathbf{R}^c. \qquad (A5)$$

(5) Calculation of the p.d.f. with the modified parameters.

(6) Accumulation of the deviations for each pixel **u** for the p.d.f. map. It has been found that 10 000 MC steps are sufficient to obtain convergency in all cases (usually 1000 MC steps suffice). It is possible to accumulate positive and negative deviations separately, however the 1σ root-mean-square deviations $\text{p.d.f.}^{1\sigma}(\mathbf{u})$ seem to be a good number for most purposes. The results may be displayed in an $m\sigma$ confidence map for anharmonic (or disorder) deformation densities $\text{p.d.f.}_{\text{def}}(\mathbf{u})$, see (55):

$$\text{p.d.f.}_{\text{def}}^{m\sigma\text{ confidence}}(\mathbf{u}) = \text{p.d.f.}_{\text{def}}(\mathbf{u}) - \operatorname{sgn}[\text{p.d.f.}_{\text{def}}(\mathbf{u})] \times m\ \text{p.d.f.}_{\text{def}}^{1\sigma}(\mathbf{u}) \qquad (A6)$$

where sgn is the sign function.

If it appears interesting one could also calculate the covariances between two pixels $\mathbf{u}_1$ and $\mathbf{u}_2$ of the map with the same procedure. The MC method presented here may also be used to calculate the errors in other least-squares filtered maps (*e.g.* multipole deformation densities). An MC calculation of this type has been included in a new version of the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

References

Ashcroft, N. W. & Mermin, N. D. (1976). *Solid State Physics*, ch. 25. New York: Holt, Rinehart and Winston.

Bauer, G. S. (1979). In *Treatise on Materials Science and Technology*, Vol. 15, edited by G. Kostorz, pp. 291-336. New York: Academic Press.

Binder, K., Meissner, G. & Mais, H. (1976). *Phys. Rev. B*, **13**, 4890-4898.

Bloch, F. (1932). *Z. Phys.* **74**, 295-335.

Born, M. (1942). *Rep. Prog. Phys.* **9**, 294-333.

Box, G. E. P. & Muller, M. E. (1958). *Ann. Math. Stat.* **29**, 610-611.

Bruce, A. D. & Cowley, R. A. (1981). *Structural Phase Transitions.* London: Taylor and Francis.

Choquard, P. (1967). *The Anharmonic Crystal.* New York: W. A. Benjamin.

Coppens, P. (1978). In *Electron and Magnetization Densities in Molecules and Crystals*, edited by P. Becker, pp. 521-543. New York: Plenum Press.

Cowley, R. A. (1968). *Rep. Prog. Phys.* **31**, 123-165.

Dawson, B. (1967). *Proc. R. Soc. London Ser. A*, **298**, 255-263, 264-288, 379-394.

Dawson, B. (1975). In *Advances in Structure Research by Diffraction Methods*, Vol. 6, edited by W. Hoppe & R. Mason. Oxford: Pergamon Press.

Dawson, B. & Willis, B. T. M. (1967). *Proc. R. Soc. London Ser. A*, **298**, 307-315.

Dederichs, P. H. (1973). *J. Phys. F*, **3**, 471-496.

Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Phys. Chem.* **92**, 856-867.

Edgeworth, F. Y. (1905). *Proc. Cambridge Philos. Soc.* **20**, 36-141.

Erdelyi, A. (1953). *Higher Transcendental Functions*, Vol. 11. New York: McGraw-Hill.

Fujii, K. & Matsubara, T. (1987). *Prog. Theor. Phys.* **78**, 177-179.

Glyde, H. R. & Klein, M. L. (1971). *Crit. Rev. Solid State Sci.* **2**, 181-254.

Hahn, H. & Ludwig, W. (1961). *Z. Phys.* **161**, 404-423.

Hamermesh, M. (1962). *Group Theory and its Applications to Physical Problems.* Reading, MA: Addison-Wesley.

Hansen, N. K. (1988). *Acta Cryst.* A**44**, 1097.

Hazell, R. G. & Willis, B. T. M. (1978). *Acta Cryst.* A**34**, 809-811.

Hüller, A. & Press, W. (1979). *Acta Cryst.* A**35**, 876-880.

James, F. (1980). *Rep. Prog. Phys.* **43**, 1145-1189.

Johnson, C. K. (1969). *Acta Cryst.* A**25**, 187-194.

Johnson, C. K. (1970). In *Thermal Neutron Diffraction*, edited by B. T. M. Willis, pp. 132-160. Oxford Univ. Press.

Johnson, C. K. & Levy, H. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 311-336. Birmingham: Kynoch Press. (Present distributer Kluwer Academic Publishers, Dordrecht.)

Kanzaki, H. (1957). *J. Phys. Chem. Solids*, **2**, 24-36, 107-114.

Kendall, M. G. & Stewart, A. (1977). *The Advanced Theory of Statistics*, Vol. 1. London: Charles Griffin & Co.

Koehler, T. R. (1975). In *Dynamical Properties of Solids*, Vol. 2, edited by G. K. Horton & A. A. Maradudin, ch. 1. Amsterdam: North-Holland.

Kontio, A. & Stevens, E. D. (1982). *Acta Cryst.* A**38**, 623-629.

Krivoglaz, M. A. (1969). *The Theory of X-ray and Thermal Neutron Scattering by Real Crystals.* London: Plenum Press.

Krivoglaz, M. & Tekhonova, E. A. (1961). *Sov. Phys. Crystallogr.* **6**, 399-403.

Kuhs, W. F. (1983). *Acta Cryst.* A**39**, 148-158.

Kuhs, W. F. (1984). *Acta Cryst.* A**40**, 133-137.

Kuhs, W. F. (1988*a*). *Aust. J. Phys.* **41**, 369-382.

Kuhs, W. F. (1988*b*). *Mater. Sci. Forum*, **27/28**, 25-34.

Kuhs, W. F. & Lehmann, M. S. (1986). *Water Sci. Rev.* **2**, 1-65.

Kurki-Suonio, K., Merisalo, M. & Peltonen, H. (1979). *Phys. Scr.* **19**, 57-63.

Kuznetsov, P. I., Stratonovich, R. & Tikhonov, V. I. (1960). *Theory Probab. Its Appl. (USSR)*, **5**, 80-97.

Leibfried, G. (1964). In *Lattice Dynamics*, edited by R. F. Wallis, pp. 237-245. Oxford: Pergamon Press.

Leibfried, G. & Ludwig, W. (1961). In *Solid State Physics*, Vol. 12, edited by F. Seitz & D. Turnbull. New York: Academic Press.

Lima, R. A. T. & Tsallis, C. (1980). *Phys. Rev. B*, **21**, 458-466.

Lovesey, S. W. (1984). *Theory of Neutron Scattering from Condensed Matter.* Oxford: Clarendon Press.

Mackenzie, J. K. & Mair, S. L. (1985). *Acta Cryst.* A**41**, 81-85.

McMahon, M. I., Nelmes, R. J., Piltz, R. O. & Kuhs, W. F. (1990). *Europhys. Lett.* **13**, 143-148.

Mair, S. L. (1980). *J. Phys. C*, **13**, 2857-2868.

Mair, S. L. (1982). *J. Phys. C*, **15**, 25-36.

Mair, S. L. (1983). *J. Phys. C*, **16**, 4811-4825, 5591-5604.

Mair, S. L. (1985). *Aust. J. Phys.* **38**, 421-426.

Mair, S. L. (1986). *J. Phys. C*, **19**, 6321-6338.

Mair, S. L. & Wilkins, S. W. (1976). *J. Phys. C*, **9**, 1145-1158.

Mallison, P. R., Koritsansky, T., Elkaim, E., Li, N. & Coppens, P. (1988). *Acta Cryst.* A**44**, 336-342.

Maradudin, A. A. & Flinn, P. A. (1963). *Phys. Rev.* **129**, 2529-2547.

Maradudin, A. A., Montroll, E. W., Weiss, G. H. & Ipatova, I. P. (1971). *Theory of Lattice Dynamics in the Harmonic Approximation. Solid State Physics*, Suppl. 3. New York, London: Academic Press.

Marcinkiewicz, J. (1938). *Math. Z.* **44**, 612-618.

Matsubara, T. (1975*a*). *J. Phys. Soc. Jpn*, **38**, 1076-1079.

Matsubara, T. (1975*b*). *Prog. Theor. Phys.* **53**, 1210-1211.

Meissner, G. & Binder, K. (1975). *Phys. Rev. B*, **12**, 3948-3955.

Metzger, H., Behr, H. & Peisl, J. (1982). *Z. Phys. B*, **46**, 295-299.

Michel, K. H. (1986). *J. Chem. Phys.* **84**, 3451-3460.

Nelmes, R. J. & Tun, Z. (1987). *Acta Cryst.* A**43**, 635-638.

Nelmes, R. J. & Tun, Z. (1988). *Acta Cryst.* A**44**, 1098.

Pach, K. & Frey, T. (1964). *Vector and Tensor Analysis.* Budapest: Terra.

PRANDL, W., HOSER, A. & BRÜCKEL, T. (1988). *Mater. Sci. Forum*, **27/28**, 35-48.
PRINCE, E. & FINGER, L. W. (1973). *Acta Cryst.* B**29**, 179-183.
SAMATHIYAKANIT, V. & GLYDE, H. R. (1973). *J. Phys. C*, **6**, 1166-1180.
SCHERINGER, C. (1980). *Acta Cryst.* A**36**, 497-499.
SCHERINGER, C. (1985*a*). *Acta Cryst.* A**41**, 73-79.
SCHERINGER, C. (1985*b*). *Acta Cryst.* A**41**, 79-81.
SCHERINGER, C. (1987). *Acta Cryst.* A**43**, 703-706, 706-710.
SCHERINGER, C. (1988). *Acta Cryst.* A**44**, 343-349.
SHUKLA, R. C. (1981). *Phys. Rev. B*, **23**, 3087-3090.
SHUKLA, R. C. & HÜBSCHLE, H. (1989). *Phys. Rev. B*, **40**, 1555-1559.
SHUKLA, R. C. & MOUNTAIN, R. D. (1982). *Phys. Rev. B*, **25**, 3649-3657.
SHUKLA, R. C. & PLINT, C. A. (1989). *Phys. Rev. B*, **40**, 10337-10344.
TANAKA, K. & MARUMO, F. (1983). *Acta Cryst.* A**39**, 631-641.
TEWARY, W. K. (1973). *J. Phys. F*, **3**, 1515-1523.
WALLER, I. (1927). *Ann. Phys.* **83**, 153-183.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 227-300.
WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
WOLFE, G. A. & GOODMAN, B. (1969). *Phys. Rev.* **178**, 1171-1189.
YUDE, Y., BOYSEN, H. & SCHULZ, H. (1990). *Z. Kristallogr.* **191**, 79-91.
ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1983). *J. Appl. Cryst.* **16**, 358.
ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* A**38**, 568-576.

Acta Cryst. (1992). A**48**, 98-103

The Ewald and Darwin Limits Obtained from the Hamilton–Darwin Energy Transfer Equations

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Abstract

There are two classic limiting solutions for the diffraction profile and integrated intensity of Bragg reflections from semi-infinite perfect crystals. These are the Ewald and Darwin solutions for the symmetric Bragg case. It is shown that exact values of these limiting solutions can be obtained with the use of three concepts: (1) the kinematic scattering from a small absorbing crystal; (2) the Hamilton-Darwin energy transfer equations; (3) the dynamic refractive index of the crystal.

1. Introduction

In 1967 Zachariasen attempted to obtain a general solution for the extinction factor in a finite perfect crystal. He used the Darwin (1922) energy transfer equations to describe the flow of the incident and diffracted beams through the crystal and made the intuitive conjecture that the coupling coefficient between the beams could be represented by the kinematic scattering cross section per unit volume from a small and perfect crystal. He did not include absorption in the small crystal and he made the approximation that the wave vectors within the crystal were the same as the wave vectors in free space. His treatment did not reproduce the classical dynamical theory solutions for the flat plate of finite thickness, which is the only case for which exact solutions are available.

Sabine (1988, 1992) showed that, with the use of Hamilton's (1957) generalization of Darwin's equations this method led to the exact Ewald ($\mu \equiv 0$, $\mu D \equiv 0$) solution for the integrated intensity in the Bragg case, but that the solution obtained for the Darwin ($\mu \simeq 0$, $\mu D \gg 0$) case was in error by a factor of one-half.

In the present work it is shown that, with the inclusion of the dynamic refractive index of the crystal and explicit allowance for absorption in the calculation of the diffraction profile of the small crystal, the conjecture by Zachariasen (1967) leads to the exact solution for both limits.

The analysis is given for neutrons for which the polarization factor is unity and, by convention, the structure factor includes the scattering length.

2. Notation

A	$=\lambda N_c\lvert F'_H\rvert T/\sin\theta_B \equiv \lambda N_c\lvert F'_H\rvert D$.
D	Average path length of the diffracted beam in the crystal.
F_H	The structure factor of the reflection whose Miller indices are HKL ($F_H = F'_H + iF''_H$).
g	$= -F''_0/\lvert F''_H\rvert$.
$\mathbf{k}$	Scattering vector in free space $[\lvert\mathbf{k}\rvert = 2(\sin\theta)/\lambda]$.
$\mathbf{K}$	Scattering vector within the crystal.

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