Statistical Approaches for the Treatment of Anharmonic Motion in Crystals. I. A Comparison of the Most Frequently Used Formalisms of Anharmonic Thermal Vibrations

By Udo H. Zucker and Heinz Schulz

Max-Planch-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7 Stuttgart 80, Federal Republic of Germany

Dedicated to Professor Dr Heinz Jagodzinski on the occasion of his 65th birthday

Abstract

Several statistical approaches to anharmonic motion are known, but there exists no comparison between different formalisms. Therefore the most common formalisms (potential, Edgeworth and Gram–Charlier expansions and α formalism) are compared with each other in part I of this series of papers. Mathematical shortcomings of the potential and Edgeworth expansions may lead to doubtful interpretations of the corresponding probability densities and the potentials. The α formalism works inefficiently in conventional crystallographic refinement programs; it tends to converge badly and its computation is very time consuming. The best results of all are obtained for the Gram–Charlier expansion, which can be easily expanded to tensors up to sixth rank.

1. Introduction

In elastic scattering experiments using X-rays and neutrons the Bragg diffraction data are influenced by thermal motion of the atoms in the crystal. These effects cannot in general be calculated using lattice dynamics because of their complexity. A possible alternative is provided by a statistical approach to the analysis of thermal vibrations.

To outline the main features of statistical models we shall summarize the relations between the quantities temperature factor, probability density, and potential energy. Then a discussion of the anharmonic models most frequently used will be given.

2. Temperature factor, probability density and potential energy*

At $T = 0$ K, omitting zero-point vibrations an atom is fixed at its equilibrium position. With increasing

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* We have written a detailed introduction to these quantities which is part of the description to our program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1982).

temperature it starts to vibrate around its equilibrium position. The frequency depends on the interactions which try to bring the atom back to the equilibrium position and can therefore be described by a potential energy. The potential energy determines the probability of a certain displacement.

The relation between the probability density $p(\mathbf{x})$ and the effective one-particle potential $V(\mathbf{x})$ can be determined from statistical thermodynamics (Willis, 1969).

$$p(\mathbf{x}) = \{\exp[-V(\mathbf{x})/(kT)]\}/Z. \tag{1}$$

$k =$ Boltzmann's constant,

$$Z = \iiint \exp[-V(\mathbf{x})/(kT)]\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z,$$

$\mathbf{x} =$ displacement vector. We can calculate Z if we set the energy of the equilibrium position $\mathbf{x}_0$ of the atom to zero. We get a formula which is important for practical evaluations.

$$V(\mathbf{x}) = -kT \ln[p(\mathbf{x})/p(\mathbf{x} = \mathbf{x}_0)]. \tag{2}$$

In diffraction experiments, however, we measure the temperature factor $t(\mathbf{Q})$, which is the Fourier transform of the probability density function (Willis & Pryor, 1975).

In the following we discuss expressions for p, t, and V for anharmonic motion. The parameters of the temperature factor can be fitted to intensities measured in reciprocal space. A direct physical interpretation of these parameters is difficult, but is not necessary because we will be able to compute the corresponding probability density functions (p.d.f.). The disadvantages of the p.d.f. (temperature dependence, not comparable with macroscopic quantities) are nearly removed by using the effective potentials, which is shown in part II of this series of papers (Zucker & Schulz, 1982).

3. Formalisms of anharmonic motion

Any deviations from a normal distribution (harmonic model; Willis & Pryor, 1975) is called anharmonicity.

In a statistical approach we do not try to investigate the reasons for these deviations, but try to find a mathematical expression, which enables us to describe the anharmonic p.d.f. In principle there are three ways of extending the harmonic model to an anharmonic model. We can expand the expression of t, p, or V of the harmonic model for anharmonicity. If we restrict ourselves to expansions in terms of tensors, we always get expressions which are valid for each point symmetry and for each oblique crystal coordinate system.

3.1. Expansion of the potential

Several authors (Willis, 1969; Matsubara, 1975) have used a power series expansion of the potential. So far, calculations have only been made for special site symmetries. This expansion has the disadvantage that the partition function Z (equation 1) does not exist, that means the p.d.f. is not integrable from $-\infty$ to $+\infty$ (Scheringer, 1977a). This may lead to an unphysical potential for distinct numerical parameters. Such potentials were published, for example by Hoshino & Sakuma (1980) and discussed by Perenthaler, Schulz & Beyeler (1981).

3.2. Edgeworth expansion

Johnson (1969) published a generalized structure factor equation including anharmonic motion. He used the approximation of Edgeworth to describe the deviations of an experimental p.d.f. from the harmonic form. The corresponding temperature factor can be fitted easily to the measured intensities and is therefore the most frequently applied formalism.

Besides this practical argument Scheringer (1977b) reported the Edgeworth expansion to be the best description for deviations of a real p.d.f. from harmonicity. He deduced this by comparing the Edgeworth expansion with expressions of lattice dynamical calculations. He mentioned, however, that due to mathematical shortcomings even this description can lead to physically meaningless potentials.

In the following we examine the main properties of the Edgeworth expansion, which are important for the description of anharmonic motion. In part I we shall show that the Edgeworth series is hard to handle in practice. In part II we shall show that the Edgeworth expansion does not give the best fit to experimental data.

The anharmonic p.d.f. in the Edgeworth expansion* is given by (using Einstein's sum convention)

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* Equation (3) should not be confused with equation (5), which is also called the Edgeworth expansion. To avoid misunderstandings we shall call equation (5) the Edgeworth approximation.

$$p_E(\mathbf{x}) = \exp\left(D_p a^p + \frac{1}{2} D_p D_q b^{pq} - \frac{1}{3!} D_p D_q D_r c^{pqr} + \frac{1}{4!} D_p D_q D_r D_s d^{pqrs} - \cdots\right) p_{\text{harm}}(\mathbf{x}), \quad (3)$$

where

$$p_{\text{harm}}(\mathbf{x}) = \frac{[\det(\mathbf{g})]^{1/2}}{(2\pi)^{3/2}} \exp[-\tfrac{1}{2}g_{mn}(x^m - x_0^m)(x^n - x_0^n)],$$

$\det(\mathbf{g}) = $ determinant of $\mathbf{g}$, and

$$D_p = \frac{\partial}{\partial x^p}.$$

One can make the assumption that the mean and the dispersion of $p_E(\mathbf{x})$ should be given by $p_{\text{harm}}(\mathbf{x})$, because for vanishing unharmonicity the anharmonic p.d.f. should tend to the harmonic part. Therefore the tensors $\mathbf{a}$ and $\mathbf{b}$ of (3) are omitted.

The corresponding temperature factor is given by

$$t_E(\mathbf{h}) = t_{\text{harm}}(\mathbf{h}) \exp\left[\frac{(2\pi i)^3}{6} c^{pqr} h_p h_q h_r + \frac{(2\pi i)^4}{24} d^{pqrs} h_p h_q h_r h_s + \cdots\right]$$

$$t_{\text{harm}}(\mathbf{h}) = \exp(2\pi i \mathbf{h} \mathbf{x}_0) \exp(-\beta^{pq} h_p h_q) \quad (4)$$

$(\boldsymbol{\beta} = 2\pi^2 \boldsymbol{\sigma}; \boldsymbol{\sigma} = \mathbf{g}^{-1})$, $\mathbf{h} = $ reciprocal-lattice vector.

Equation (3) is an exponential function with differential operators in its argument and it cannot be evaluated numerically without any approximations. One approximation is given by Edgeworth (1905), which we call Edgeworth approximation. He expanded the exponent in a Taylor series, rearranged the terms and omitted some because of statistical considerations. (Edgeworth did his calculations only for an univariate distribution.)

The approximation is expanded to three dimensions by Johnson (1969). His result is given in equation (5) of his paper. He pointed out that the Edgeworth approximation (which contains differential operators) can be reformulated using trivariate Hermite polynomials, which is advantageous for numerical calculations (Johnson, 1970). One gets

$$P_E(\mathbf{x}) = \{1 - \tfrac{1}{6}c^{pqr} H_{pqr}(\mathbf{x}) + [\tfrac{1}{24}d^{pqrs} H_{pqrs}(\mathbf{x}) + \tfrac{1}{72}c^{pqr} c^{lmn} H_{pqrlmn}(\mathbf{x})]\} p_{\text{harm}}(\mathbf{x}) + \text{residue},* \quad (5)$$

where $H_{n_1 n_2 \ldots n_m}(\mathbf{x})$ is a trivariate Hermite polynomial of order m. Equation 5 is valid in each oblique crystal coordinate system and does not have to be transformed into a Cartesian coordinate system as mentioned by Johnson (1970).

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* In the Edgeworth approximation the terms in square brackets are omitted if the tensor of fourth rank is not determined.

Trivariate Hermite polynomials are tabulated up to fourth order in *International Tables for X-ray Crystallography* (1974).*

Johnson (1969) named the difference function $[p_E(\mathbf{x}) - p_{\text{harm}}(\mathbf{x})]$ a skew map, if tensors of fourth and higher rank are omitted. The function was called skew, because it is antisymmetric in the approximation of Edgeworth. Using the exact expression of $p_E(\mathbf{x})$ the term $c^{pqr} H_{pqr}(\mathbf{x})$ is really antisymmetric, whereas the next omitted term $c^{pqr} c^{lmn} H_{pqrlmn}(\mathbf{x})$ is symmetric. This means that the corresponding temperature factor truncated after the third-rank tensor mainly describes antisymmetric thermal motion, but also contains small symmetric parts.

As a remark we mention that with a restriction to tensors up to fourth rank a sixfold probability-density modification cannot be described, if the tensor of third rank has to be omitted because of centric site symmetry (for example 6/*mmm*).

Johnson (1969) published another series approximation, which he called an extended Edgeworth expansion. This approximation is a rearrangement of equation (3), where the mean and the dispersion of the complete p.d.f. are separated into harmonic and anharmonic parts. This arrangement is based on statistical arguments stated by Wallace (1958).

Johnsons result is given by (6), using our nomenclature.

$$p_{\text{ext}}(\mathbf{x}) = \{1 + a^p H_p(\mathbf{x}) + \tfrac{1}{6}c^{pqr} H_{pqr}(\mathbf{x})$$
$$+ [\tfrac{1}{2}(b^{pq} + a^p a^q) H_{pq}(\mathbf{x}) + \tfrac{1}{6}(a^p c^{qrs}$$
$$+ \tfrac{1}{4}d^{pqrs}) H_{pqrs}(\mathbf{x}) + \tfrac{1}{72}c^{pqr} c^{lmn} H_{pqrlm}(\mathbf{x})]\}$$
$$\times p_{\text{harm}}(\mathbf{x}, \mathbf{x}_h, \mathbf{g}_h) + \text{residue}. \qquad (6)$$

The variables $\mathbf{x}_h$, $\mathbf{g}_h$ are the mean and the dispersion of the real p.d.f., whereas $(\mathbf{a} + \mathbf{x}_h)$, $(\mathbf{b} + \mathbf{g}_h)$ are the mean and the dispersion calculated by refining (3).† Johnson (1969) suggested that $\mathbf{x}_h$ and $\mathbf{g}_h$ should be evaluated as unbiased estimates by a conventional harmonic least-squares refinement. Our refinements of structures with large anharmonicites, however, show that the assumption of unbiased estimates for $\mathbf{x}_h$ and $\mathbf{g}_h$ can fail (part II). Least-squares methods applied to refinements of parameters tend to minimize the sum of all effects and therefore the parameters of a harmonic refinement partially describe anharmonic effects as well. The magnitude of this influence is in general unpredictable and therefore the extended p.d.f. can be very inexact.

An important point is that equations (3) and (6) are

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* As far as we know no program has been published which can calculate equation (5) for general site symmetries. Therefore we have written a program, which is part of our program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1982). (The general forms of trivariate Hermite polynomials of fifth and sixth order are tabulated in Appendix 1.)

† In equation (4) the dispersion is given by σ, whereas the mean is given by $\mathbf{x}_0$.

approximations of one unique p.d.f. Because there is no formula to estimate the residues of both expressions, we can roughly estimate the goodness of the approximations by computing numerical results of both approximations (part II). If the difference between both series is large one cannot decide in general which approximation is better and therefore we deduce that the residue of at least one expression is too large. The statistical considerations of Wallace (1958), who favoured the extended Edgeworth approximations may not be valid if one uses the first few terms of the expansions and if there are large errors in the calculation of $\mathbf{x}_h$ and $\mathbf{g}_h$.

3.3. *The Gram–Charlier expansion*

The Gram–Charlier expansion has been used in statistics for a long time. Johnson & Levy (*International Tables for X-ray Crystallography*, 1974) suggested the expansion as an expression for anharmonic motion. [The expression of this series is given in equation (1) on p. 316 of *International Tables for X-ray Crystallography* (1974)].

The corresponding temperature factor is given by

$$t_G(\bar{h}) = t_{\text{harm}}(\bar{h}) \left[1 + \frac{(2\pi i)^3}{6!} c^{pqr} h_p h_q h_r \right.$$
$$\left. + \frac{(2\pi i)^4}{4!} d^{pqrs} h_p h_q h_r h_s + ... \right]. \qquad (7)$$

We point out that the Gram–Charlier expansion and the Edgeworth expansion are identical if an infinite number of terms are used.

In statistics various authors (for example Wallace, 1958) investigated which expansion should be preferred. Most of them found that the Edgeworth expansion should be the better because a tensor in the exponent of an exponential function includes parts of tensors of higher rank. (All considerations were made in one dimension only.) The above cited argument may not be valid if we use only the first few terms of the expansions and in this case we cannot say in general which expansion should be preferred. The performance of different expansions has to be compared by their applications. In most cases, the Gram–Charlier expansion gave much better results (for example see part II) and only in cases of moderate anharmonicity was the performance of the two expansions equal. [Up to now these formalisms have been applied to the ionic conductors Li_3N (part II), Ag_3SI (Perenthaler, Schulz & Beyeler, 1981), $CuTeBr$ (Bachmann, Rabenau, Kreuer & Schulz, 1981), PbF_2 (Schulz, Perenthaler & Zucker, 1981), Ag_2S, $LiAlSiO_4$, $LiKSO_4$, Cu_6PS_5Br, Cu_6PS_5I (all unpublished)].

The Gram–Charlier expansion can easily be implemented in conventional crystallographic computing programs. Using Hermite polynomials up to sixth order we can determine thermal vibrations of each crystallo-

graphic point symmetry, because an n-rank tensor of (7) can describe an n-fold density modification.

The positivity of the p.d.f. can be controlled by calulating it around the position of the atom in the unit cell. The corresponding potential exists, if in addition to the positivity of the p.d.f. the harmonic part of (7) is positive definite.

With our program system *PROMETHEUS* (Zucker *et al.*, 1982) we can refine the temperature factor of (7) up to tensors of sixth rank. Our investigations show in contrast to the presumption of Johnson (1970) that fifth- and sixth-rank tensors can significantly improve structure refinements of large anharmonicity (compare with part II). Widely distributed densities caused by very flat potentials like those in Ag_3SI (Perenthaler & Schulz, 1981) could only be fitted satisfactorily by including fifth- and sixth-rank tensors, whereas these densities were unrefineable in the harmonic approximation.

3.4. *The α formalism (quasi-orthogonal expansion model)*

The α formalism of C. K. Johnson was first mentioned by Cava, Reidinger & Wuensch (1980). Johnson (1980) published a report including a discussion of the α formalism. A parameter, called α, is introduced for each atom to reduce correlations between the atomic coordinates and the tensor of third rank as well as between the tensors of second and fourth rank.

The temperature factor in the α formalism is given as

$$t_{\alpha}(\mathbf{h}) = t_{\text{harm}}(\mathbf{h}) \left[1 + \frac{(2\pi i)^3}{3!} G_{jkl}(\mathbf{h}, \alpha)c^{jkl} \right.$$

$$\left. + \frac{(2\pi i)^4}{4!} G_{jklm}(\mathbf{h}, \alpha)d^{jklm} + \text{higher orders} \right], \quad (8)$$

where

$$G_{jkl}(\mathbf{h}, \alpha) = h_j h_k h_l - \frac{\alpha}{2} P_3[(\beta^{-1})_{jk} h_l]$$

$$G_{jklm}(\mathbf{h}, \alpha) = h_j h_k h_l h_m - \frac{\alpha}{2} P_{10} [h_j h_k (\beta^{-1})_{lm}]$$

$$+ \frac{\alpha^2}{4} (\beta^{-1})_j P_3[_k(\beta^{-1})_{lm}],$$

β^{-1} = inverse of the anisotropic temperature tensor, and $\mathbf{P}_n$ = permutation tensor, which designates that the term in parentheses is to be permutated over all permutations of those indices which produce different terms.

The corresponding p.d.f. is given by Johnson (1980), but it is reformulated by us in terms of Hermite polynomials and normalized.

$$p_{\alpha}(\mathbf{x}) = \frac{p_{\text{harm}}(\mathbf{x}, \mathbf{x}_0, \mathbf{g})}{N} [1 + T_3(\mathbf{x}) + T_4(\mathbf{x})],$$

where

$$T_3(\mathbf{x}) = \frac{c^{jkl}}{3!} \{H_{jkl}(\mathbf{x}) + \alpha P_3[H_j(\mathbf{x}) g_{kl}]\}$$

$$T_4(\mathbf{x}) = \frac{d^{jklm}}{24!} \{H_{jklm}(\mathbf{x}) + \alpha P_{10}[H_{jk}(\mathbf{x}) g_{lm}]$$

$$+ \alpha^2 g_j P_3(_k g_{lm})\}$$

$$N = 1 + \frac{\alpha^2}{24} g_j P_3(_k g_{lm}) d^{jklm}; \quad \mathbf{g} = 2\pi^2 \beta^{-1}.$$

In the limit $\alpha = 0$ we get the Gram–Charlier expansion again, whereas for $\alpha = 1$ (8) is a series expansion of trivariate Hermite polynomials. But the orthogonality of the Hermite polynomials cannot be used, because in crystallography the temperature factor is fitted to a non-continuous function (the Bragg intensities) by least-squares methods. Johnson (1980) called the reduction of the correlations quasi orthogonalization, but the diminution of the correlation is based on a subtraction and should therefore, we think, not be called quasi orthogonalization, to prevent misunderstanding.

The scalar α should reduce correlations between odd- and between even-rank tensors, respectively (Johnson, 1980). We implemented the α formalism in our program system *PROMETHEUS** and applied it to several substances (for example Li_3N; part II). We found that the parameter α (for each atom) weakly reduced the correlations, but other large correlations appeared between the tensor elements and the parameter α of this atom. All refinements consumed much more computing time (compared with Edgeworth or Gram–Charlier expansion), and they converged badly if either α (of an atom) was refined and/or the second-rank tensor was large. The mathematical reasons for this behaviour are given in Appendix 2.

In general we can say that the application of the α formalism leads at most to a slightly better fit than the application of the Gram–Charlier expansion up to fourth order, because of the increasing number of parameters (one per atom). The Gram–Charlier expansion of sixth order, however, results always in fits of equal or better goodness.

4. Conclusion

For the analysis of anharmonic motion a statistical approach has to be used, because in most cases the lattice dynamical calculations cannot be carried out.

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* We mention that there are some versions of the program *BIGJO* (Johnson, undated) in use, which contain a fatal error in computing the α formalism. The error is described in Appendix 2. Appendix 2 can also be used as a guide for implementing the α formalism.

The difficulties of interpreting the parameters of the temperature factor in reciprocal space can be removed by calculating the corresponding probability densities and the effective one-particle potentials (see part II).

The mathematical shortcomings of the Edgeworth expansion and its corresponding approximations led to a doubtful interpretation of the p.d.f. and the potential.

The α formalism could remove the mathematical disadvantages of the Edgeworth expansion, but it works very inefficiently in conventional crystallographic refinement programs. The refinements tend to converge badly and they consume more computing time than the other formalisms. In general the results of the α formalism are only slightly better than the results of the Gram–Charlier expansion up to fourth-rank tensors.

The best results of all were obtained using the Gram–Charlier expansion up to tensors of sixth rank. All calculations can be carried out exactly, an implementation in crystallographic programs is easily possible.

All calculations described in this paper can be carried out for each oblique crystal coordinate system and for each point symmetry using the program system *PROMETHEUS*, which is available on request.

APPENDIX 1

Hermite polynomials of fifth and sixth order in real space are given by

$$H_{ijklm}(\mathbf{x}) = z_i z_j z_k z_l z_m - P_{10}(g_{ij} z_k z_l z_m)$$

$$+ P_{15}(g_{ij} g_{kl} z_m)$$

$$H_{ijklmn} = z_i z_j z_k z_l z_m z_n - P_{15}(z_i z_j z_k z_k z_l g_{mn})$$

$$+ P_{45}(z_i z_j g_{kl} g_{mn}) - P_{15}(g_{ij} g_{kl} g_{mn})$$

where $z_i = g_{ij} x^k$. The tensor $\mathbf{g}$ and the permutation operator P_n are described in the paper.

APPENDIX 2

The structure-factor equation of the α formalism for N atoms in the unit cell is given by

$$F(\mathbf{h}) = \sum_{s=1}^{N} f_s(\mathbf{h}) \exp(2\pi i h_j \, x_s^j) \exp(-\beta_s^{jk} h_j h_k)$$

$$\times (1 - i\tfrac{4}{3}\pi^3 G_{jkl}(\mathbf{h}, \alpha_s) c_s^{jkl} + \ldots),$$

where f_s is the scattering factor curve for the s atom of the unit cell, $\mathbf{x}_s$ are the coordinates of the s atom of the

unit cell, and β_s is the anisotropic temperature factor. The other quantities are defined in the paper.

In conventional crystallographic programs for structure factor calculation the sum over the atoms of the unit cell is separated into a sum over the atoms in the asymmetric unit and a sum over symmetry operations:

$$F(\mathbf{h}) = \sum_{p=1}^{M} \sum_{n=1}^{L} E(p) f_p \exp\{2\pi i h_j [R_m^j(n) \, x_p^m + T^j(n)]\}$$

$$\times \exp[-h_j h_k R_l^j(n) R_m^k(n) \beta_p^{lm}]$$

$$\times (1 - i\tfrac{4}{3}\pi^3 \, G_{jkl}(\mathbf{h}, \alpha_p)$$

$$\times R_{m_1}^j(n) R_{m_2}^k(n) R_{m_3}^l(n) \, c_p^{m_1 m_2 m_3} + \ldots),$$

where $\sum_{p=1}^{m}$ means summation over all atoms of one asymmetric unit, $\sum_{n=1}^{L}$ means summation over all symmetry operations, $E(p)$ is the equipoint fraction of the pth atom, $\mathbf{T}(n)$ is the translation vector of the nth symmetry operation, and $\mathbf{R}(n)$ is the rotation matrix of the nth symmetry operation.

A tensor of rank n is transformed rather than a product of coordinates.

The rotation matrices can be applied to the Miller indices, as done in conventional crystallographic programs, for example:

$$\text{result } (n) = \beta_p^{lm}[R_l^j(n) h_j][R_m^k(n) h_k] = \beta_p^{lm} h_l^*(n) h_m^*(m),$$

where $h_f^*(n)$ transforms the Miller index of the nth symmetry operation. The transformations are now independent of the values of the tensor elements, and have therefore to be computed only once.

For the transformed third-rank tensor product however this method gives

$$\text{third order} = c_p^{m_1 m_2 m_3} \left\{ h_{m_1}^*(n) h_{m_2}^*(n) h_{m_3}^*(n) \right.$$

$$\left. - \frac{1}{(2\pi)^2} \alpha_p P_3[g_{jk} R_{m_1}^j(n) R_{m_2}^k(n) h_{m_3}^*] \right\}.$$

In this case a program has to calculate at first the inverse matrix of β to get the tensor $\mathbf{g}$ ($\mathbf{g} = 2\pi^2 \beta^{-1}$) and then it has to calculate the transformation $\mathbf{RRg}$ for each symmetry transformation. [This transformation is not carried out in some versions of the program *BIGJO* (Johnson, undated).] The transformation of the Miller indices is still necessary. These transformations have to be repeated for each reflection, because a storing of the results normally requires too much storage in a computer. This is the main reason why the α formalism is very inefficient in computing time.

Further difficulties of the α formalism are the derivatives with respect to the elements of the second-rank tensor. The derivatives are extensive because $\mathbf{g}$ is an implicit function of β. As an approximation for this derivative, we can omit this implicit relation, but this

leads to badly converging refinements if $\alpha > 0$ or the shifts of β or β itself are large ($\alpha > 0$).

One can try to remove this difficulty by using **g** as a constant, which is calculated only once at the beginning of a refinement. This cannot be recommended because it corresponds to an increase of (at most) six parameters for each atom. A procedure which refines first the harmonic parameters for $\alpha = 0$ and then the anharmonic parameters with $\beta = $ constant can be used. But in the end all parameters must be refined together.

References

BACHMANN, R., KREUER, K. D., RABENAU, A. & SCHULZ, H. (1981) Conference on Chemistry and Physics of Sulfides, Selenides and Tellurium in Solids. Collected Abstracts.

CAVA, R. J., REIDINGER, F. & WUENSCH, B. J. (1980). Solid State Commun. 24, 411–416.

EDGEWORTH, F. Y. (1905). Proc. Cambridge Philos. Soc. 20, 36–141.

HOSHINO, S. & SAKUMA. T. (1980). J. Phys. Soc. Jpn, 48, 1036.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1969). Acta Cryst. A25, 187–194.

JOHNSON, C. K. (1970). Thermal Neutron Diffraction, pp. 132–160. Oxford Univ. Press.

JOHNSON, C. K. (1980) Thermal Motion Analysis. Report 1980 DOE/TIC-11068. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

MATSUBARA, T. (1975). Prog. Theor. Phys. 53, 1210–1211.

PERENTHALER, E. & SCHULZ, H. (1981) Solid State Ionics, 1, 335–365.

PERENTHALER, E., SCHULZ, H. & BEYELER, H. U. (1981) Acta Cryst. B37, 1017–1023.

SCHERINGER, C. (1977a). Acta Cryst. A33, 426–429.

SCHERINGER, C. (1977b). Acta Cryst. A33, 879–884.

SCHULZ, H., PERENTHALER, E. & ZUCKER, U. H. (1982). Acta Cryst. A. In the press.

WALLACE, D. L. (1958). Ann. Math. Stat. 29, 635–654.

WILLIS, B. T. M. (1969). Acta Cryst. A25, 277–300.

WILLIS, B. T. M. & PRYOR, A. W. (1975). Thermal Vibrations in Crystallography. Cambridge Univ. Press.

ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1982). PROMETHEUS. Program system for structure refinements. Submitted to J. Appl. Cryst.

ZUCKER, U. H. & SCHULZ, H. (1982). Acta Cryst. (1982). A38, 568–576.

Statistical Approaches for the Treatment of Anharmonic Motion in Crystals. II. Anharmonic Thermal Vibrations and Effective Atomic Potentials in the Fast Ionic Conductor Lithium Nitride (Li₃N)

BY UDO H. ZUCKER AND HEINZ SCHULZ

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7 Stuttgart 80, Federal Republic of Germany

Abstract

Results of X-ray diffraction experiments on lithium nitride (Li₃N) in the temperature range between 294 and 888 K show strong anharmonic effects. The deviations from harmonicity cannot be interpreted by interstitial sites or split positions. The application of an anharmonic temperature factor which is based on the Gram–Charlier expansion leads to an excellent fit of the data, whereas an anharmonic temperature factor, based on the Edgeworth series expansion, cannot fit the measurements in a satisfactory way. The corresponding anharmonic probability densities and the effective one-particle potentials are presented. The activation energy of the ionic conduction in Li₃N perpendicular to the c axis and the thermal expansion of the lattice constant are derived from the potentials. These results agree well with results obtained by other experimental techniques. Therefore it is concluded that the potentials derived from elastic scattering experiments are physically meaningful.

1. Introduction

The most commonly used structure factor formalisms for the treatment of anharmonic thermal motion in crystals has been discussed in part I (Zucker & Schulz,