

The Anharmonic Temperature Factor in Crystallographic Structure Analysis*

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Abstract

The most widely used formalisms to describe anharmonicity and disorder in crystallographic structure refinements are presented and their properties are reviewed. Their limitations are discussed and their range of applications is indicated. A comparative study on the lattice anharmonicity in ZnS using different models is presented. The importance of measuring Bragg intensity data sufficiently far in reciprocal space is stressed. Some indications concerning the interpretation of the results are given and the decorrelation of electronic and atomic deformations is briefly discussed.

1. Introduction

The progress made over the last few years in establishing both experimental and analytical procedures to obtain high quality Bragg intensity data allows one to detect finer and finer details of atomic and electronic density distributions in crystalline materials. The usual spherical atom form factors to describe the electron distribution around an atom, as well as the harmonic description of atomic thermal motions, is less and less commensurate with the quality of Bragg intensity data. This has been widely recognised and a variety of formalisms is available to describe deviations of the atomic and electronic densities due to anharmonicity or atomic disorder and charge redistributions respectively. In this paper we will attempt to discuss the treatment of anharmonicities and disorder in atomic density distributions and compare some of the more widely used formalisms.

The gaussian atomic probability density distributions resulting from harmonic thermal motions are modified to a variable degree by intrinsic anharmonicity (especially at higher temperatures), by curvilinear motion due to molecular or atomic vibrations or by static and dynamic atomic disorder. Most of the formalisms are in fact suitable to deal with all the aforementioned aspects of non-harmonic deformations. A distinction between e.g. intrinsic anharmonicity and atomic disorder is not always easy to make and usually has to be done via a study of the temperature dependence. In the following we will therefore use the term non-harmonicity in a general sense meaning any deviation of the atomic probability density function (pdf) from a gaussian distribution.

* Paper presented at the International Symposium on Accuracy in Structure Factor Measurement, held at Warburton, Australia, 23–26 August 1987.

2. Formalism

The formulation of a general description of non-harmonic thermal motion should have a sound physical base built into a manageable mathematical apparatus. The lattice dynamical expression of the Debye–Waller factor $DW(\mathbf{h})$ describing the reduction of Bragg intensities due to thermal motion is given in the unit cell approach as

$$DW(\mathbf{h}) = \exp\left(-\frac{1}{2} N^{-1} \sum_k m_k^{-1} \sum_{j\mathbf{q}} |2\pi \mathbf{h} \cdot \mathbf{e}(k|j\mathbf{q})|^2 E_j(\mathbf{q})/\omega_j^2(\mathbf{q})\right), \quad (1)$$

i.e. the exponential of all lattice modes of vibration with polarisation \mathbf{e} , energy E and frequency ω of all n particles k in the unit cell weighted with their mass m and the number of unit cells N in the crystal. Although $DW(\mathbf{h})$ is the quantity one observes in a Bragg scattering experiment, there is no way to extract unique information about the lattice modes by evaluating this expression. Moreover, the double summation is impracticable for any more general application; therefore the Debye–Waller factor is usually split into the different atomic contributions and no longer defined in a simple way. One obtains the atomic temperature factor

$$T_k(\mathbf{h}) = \exp\left(-\frac{1}{2} N^{-1} m_k^{-1} \sum_{j\mathbf{q}} |2\pi \mathbf{h} \cdot \mathbf{e}(k|j\mathbf{q})|^2 E_j(\mathbf{q})/\omega_j^2(\mathbf{q})\right). \quad (2)$$

Furthermore, the lattice modes give rise to an actual distribution of displacements \mathbf{u} , the thermodynamic average of which defines the atomic temperature factor

$$T_k(\mathbf{h}) = \langle \exp(-2\pi i \mathbf{h} \cdot \mathbf{u}_k) \rangle_{\text{thermodynamic}}. \quad (3)$$

Assuming that the electron cloud follows instantly the nuclear displacement, which seems well justified at least for the inner electrons and small displacements, this expression holds in the same way for X-ray and neutron Bragg scattering experiments. What is lost by the introduction of independent atoms (Einstein oscillators) is the direct information on the correlated motion of two atoms. However, the interaction modes are contained in the displacement tensors \mathbf{U} and affect the magnitude of their components (Scheringer 1972):

$$\mathbf{U} = E_j N^{-1} \sum_{\mathbf{q}} \mathbf{L}^{-1}(\mathbf{q}), \quad (4)$$

where \mathbf{L} is the (not mass adjusted) dynamical matrix. Thus, information on the interatomic repulsions and attractions is accessible by an analysis of the displacement tensors of second and higher order.

The thermodynamic average in (3) is usually expressed in terms of a potential, which is, as a consequence of the approximations made to arrive at (3), a one-particle potential (OPP) or isolated atom potential (IAP). In the classical limit one obtains the atomic temperature factor as a mean over all displacements \mathbf{u} of the atom k in the potential V , each displacement weighted by its thermodynamic probability:

$$T_k(\mathbf{h}) = \int \exp(-V_k/k_B T) \exp(2\pi i \mathbf{h} \cdot \mathbf{u}_k) d^3 \mathbf{u} / \int \exp(-V_k/k_B T) d^3 \mathbf{u}. \quad (5)$$

Assuming that in a quantum system the potential (including its anharmonic components) remains unchanged, the corresponding pdf may be obtained by a perturbation calculation of the (anharmonic) OPP density matrix (Mair and Wilkins 1976; Kara and Merisalo 1982).

There is a second more direct access to a general non-harmonic temperature factor. It has been proved (Marshall and Lovesey 1971) that the structure factor for any form of the atomic density distribution in a crystal is the Fourier transform of the average density in the unit cell. This means that one may express the atomic temperature factor as the Fourier transform of the averaged atomic probability density pdf_k:

$$T_k(h) = \int \text{pdf}_k(u) \exp(2\pi i h \cdot u_k) d^3 u. \quad (6)$$

The two expressions (5) and (6) for the atomic temperature factor are starting points for a generalised treatment of non-harmonicity in thermal motions. Formalisms derived from (5) we call potential-based, in contrast to probabilistic formalisms derived from (6). One may expect that the potential-based formalisms are more closely related to quantities of physical meaning and indeed this is found to be the case. On the other hand, the description of statically disordered systems in terms of an anharmonic potential certainly means over-interpreting the results and a purely statistical approach seems to be more appropriate in this case. Ultimately there are ways of transforming the results of a potential-based formalism into a probabilistic description and vice versa, so that there is little to choose between the two approaches on general grounds. Rather, one has to be concerned with the limitations of any given formalism for the specific problem under consideration, and this will be discussed in Section 4.

The determination of non-harmonicity in atomic thermal motions usually involves a crystallographic least-squares refinement procedure. Therefore, a parametrisation of the non-harmonicity is needed, which furthermore should allow the introduction of constraints in order to obey the point group symmetry of the atom position under consideration. The parametrisation of (5) is usually obtained via an expansion of the potential in powers of the displacement u :

$$V_{\text{gnrl}}(u) = V_{\text{har}}(u) + V_3(u) + V_4(u) + \dots \quad (7)$$

This approach has been chosen by Willis (1969) and formulated for cubic point group symmetries. Recently (Tanaka and Marumo 1983) this formalism has been generalised to treat anharmonicity up to fourth order in any point group symmetry:*

$$V_{\text{gnrl}}(u) = V_{\text{har}}(u) + \gamma_{ijk} u^i u^j u^k + \delta_{ijkl} u^i u^j u^k u^l, \quad (8)$$

with γ_{ijk} and δ_{ijkl} being the third and fourth order anharmonic potential parameters which are defined in an orthogonal coordinate system. The evaluation of the corresponding temperature factor involves the solution of Fourier integrals. Another formulation has been suggested by Scheringer (1985*a*), which circumvents the tedious

* Here and in the following the repeated index summation rules are assumed. Note that the index k for the atom under consideration has been dropped, since an IAP situation is assumed.

calculation of those integrals. The temperature factor is expressed as

$$T_{\text{gnrl}}(\mathbf{h}) = T_{\text{har}}(\mathbf{h}) \{ 1 - i^3 A_{ijk} \sigma^{ijk}(\mathbf{h}) - i^4 A_{ijkl} \sigma^{ijkl}(\mathbf{h}) \}, \quad (9)$$

where G^{ijk} are Hermite polynomials of the scattering vector \mathbf{h} , which are contravariant in the crystal base vectors, while A_{ijk} and A_{ijkl} are the third and fourth order tensor components defined in the crystallographic axis system and used to describe the anharmonic potential; they may be transformed into the conventional anharmonic potential parameters γ and δ .

The parametrisation of (6) is usually done via a differential expansion of the gaussian probability density function:

$$\begin{aligned} \text{pdf}_{\text{gnrl}}(\mathbf{u}) = \text{pdf}_{\text{har}}(\mathbf{u}) \{ & 1 - C^i D_i + (1/2!) C^{ij} D_i D_j \\ & - (1/3!) C^{ijk} D_i D_j D_k + (1/4!) C^{ijkl} D_i D_j D_k D_l + \dots \}, \end{aligned} \quad (10)$$

where $C^{i\dots}$ are tensorial coefficients and D denotes a differential operator. The function is expressed in terms of Hermite polynomials, which are covariant in the crystal base vectors,

$$(-D)^r \text{pdf}_{\text{har}}(\mathbf{u}) = H_r(\mathbf{u}) \text{pdf}_{\text{har}}(\mathbf{u}). \quad (11)$$

Two formulations of the general pdf given in (10) are known in statistics and both have been applied to describe non-harmonicity in the thermal smearing. To minimise correlation problems in a least-squares refinement, the non-harmonic first and second order terms are omitted. Johnson (1969) suggested the use of the Edgeworth (EW) expansion (up to fourth order):

$$\begin{aligned} \text{pdf}_{\text{EW}}(\mathbf{u}) = \text{pdf}_{\text{har}}(\mathbf{u}) \{ & 1 + (1/3!) \gamma_{\text{EW}}^{ijk} H_{ijk}(\mathbf{u}) \\ & + (1/4!) \delta_{\text{EW}}^{ijkl} H_{ijkl}(\mathbf{u}) + (10/6!) \gamma_{\text{EW}}^{ijk} \gamma_{\text{EW}}^{lmn} H_{ijklmn}(\mathbf{u}) \}. \end{aligned} \quad (12)$$

The terms γ_{EW}^{ijk} and $\delta_{\text{EW}}^{ijkl}$ are the cumulants of rank 3 and 4. If all terms up to infinity are included the Edgeworth expansion is not different from the Gram-Charlier (GC) expansion, which has been preferred for reasons discussed later by several authors (Zucker and Schulz 1982; Kuhs 1983; Scheringer 1985*b*). The Gram-Charlier series (up to sixth order) is given as

$$\begin{aligned} \text{pdf}_{\text{GC}}(\mathbf{u}) = \text{pdf}_{\text{har}}(\mathbf{u}) \{ & 1 + (1/3!) \gamma_{\text{GC}}^{ijk} H_{ijk}(\mathbf{u}) \\ & + (1/4!) \delta_{\text{GC}}^{ijkl} H_{ijkl}(\mathbf{u}) + (1/5!) \epsilon^{ijklm} H_{ijklm}(\mathbf{u}) \\ & + (1/6!) \zeta_{\text{GC}}^{ijklmn} H_{ijklmn}(\mathbf{u}) \}. \end{aligned} \quad (13)$$

The terms γ_{GC}^{ijk} and $\delta_{\text{GC}}^{ijkl}$ are the quasi-moments of rank 3 and 4, which are related to the cumulants by

$$\begin{aligned} \gamma_{\text{GC}}^{ijk} &= \gamma_{\text{EW}}^{ijk}, & \delta_{\text{GC}}^{ijkl} &= \delta_{\text{EW}}^{ijkl}, \\ \zeta_{\text{GC}}^{ijklmn} &= \zeta_{\text{EW}}^{ijklmn} + (10/6!) \gamma_{\text{EW}}^{ijk} \gamma_{\text{EW}}^{lmn}. \end{aligned} \quad (14)$$

The Fourier transform of (13) is known exactly and given by

$$T_{GC}(h) = T_{har}(h) \{ 1 - (4/3)\pi^3 i \gamma_{GC}^{ijk} h_i h_j h_k \\ + (2/3)\pi^4 \delta_{GC}^{ijkl} h_i h_j h_k h_l + (4/15)\pi^5 i \epsilon_{GC}^{ijklm} h_i h_j h_k h_l h_m \\ - (4/45)\pi^6 \zeta_{GC}^{ijklmn} h_i h_j h_k h_l h_m h_n \}, \quad (15)$$

while the Fourier transform of (12) is exact only under certain conditions concerning the relative importance of the terms in (11) (Kuks 1983):

$$T_{EW}(h) = T_{har}(h) \exp \{ -i \gamma_{EW}^{ijk} h_i h_j h_k + \delta_{EW}^{ijkl} h_i h_j h_k h_l \}. \quad (16)$$

This is the first reason why the Gram–Charlier series should be preferred over the Edgeworth series for general applications. Both the EW and the GC series are valid in any crystal metric. The symmetry restrictions of the thermal tensor components are tabulated in the literature (Johnson and Levy 1974; Kuhs 1984).

Yet another approach to describe non-harmonicity in thermal smearing exists: the Fourier-invariant (FIV) formalism as proposed by Kurki-Suonio *et al.* (1979). It is based on the Boltzmann function in a similar way to the other potential-based formalisms, but it uses symmetrised harmonic oscillator wavefunctions instead of the potential expansion given in (7). The expansion in cartesian coordinates reads in real space as

$$\text{pdf}_{FIV}(u) = (1/P) \text{pdf}_{har}(u) \{ 1 - \gamma_{ijk}^{FIV} H_{ijk}(u) + \delta_{ijkl}^{FIV} H_{ijkl}(u) \}, \quad (17)$$

where P is a normalisation factor containing all even order non-harmonic terms. This normalisation assures that the second order terms (contained in pdf_{har}) maintain their usual meaning and are not merely second order terms in a series expansion, as are the quadratic terms in the EW and GC expansion. Due to the Fourier invariance the expression for the temperature factor assumes a similar form:

$$T_{FIV}(h) = (1/P) T_{har}(h) \{ 1 - \gamma_{ijk}^{FIV} H_{ijk}(h) + \delta_{ijkl}^{FIV} H_{ijkl}(h) \}. \quad (18)$$

This formalism is valid for any crystal metric as long as a local cartesian coordinate system is used as reference for the oscillator eigenfunctions.

3. Limitations

There is a series of limitations to all the formalisms discussed in Section 2. Some of them are of a fundamental nature, while others are imposed by more practical considerations. The approximation $e^{-x} \approx 1 - x$ made in all potential-based formalisms limits their validity to relatively small non-harmonicities and makes them less suitable for the description of disordered systems. There is some ambiguity in the Fourier transformation of the OPP formalism, which means that a unique formulation of the corresponding temperature factor cannot be given (Mair 1980; Scheringer 1985a). The relative importance of the higher order terms determine whether one or another formulation is preferable, which makes a straightforward interpretation difficult. The exact Fourier-transformability certainly has some advantages in the

interpretation of results obtained in a crystallographic least-squares refinement. The ambiguity in the Fourier transform of the EW series has been mentioned in Section 2. Even if in some cases the EW temperature factor expression (16) gives a better fit to the data than any other formalism (and there is some evidence that under special circumstances this could be so), one is left with only an approximate probability density function after the Fourier transformation (12). The exact Fourier transforms are known for the GC series (equations 13 and 15) and the FIV formalism (equations 17 and 18).

Some further important restrictions are found when one analyses the convergency behaviour of the different series expansion. It has been shown by Scheringer (1985*a*) that series expansions of the Boltzmann function are always divergent. This restricts the range of interpretation to the lower excited levels of the OPP. Similar divergencies may occur in probabilistic formalisms when one is trying to calculate the OPP from the obtained pdf via the Boltzmann function.* Certain combinations of parameters give a slightly negative pdf with a resulting divergency in the OPP. Although in these cases the pdf is not defined in a mathematical sense (a pdf must be integrable and everywhere positive), it still may form a good approximation to the true density distribution in the crystal. Often slightly negative values of a pdf are encountered in regions of low atomic density where the sensitivity of Bragg intensity data is small anyhow. If necessary, more rigorous conditions on the pdf or the potential (global positivity or boundness) may be imposed by fitting some appropriate function to the result obtained from a crystallographic experiment. One should note that even if no divergencies occur some spurious features may be obtained at larger displacements. Any interpretation therefore has to be restricted to a range commensurate with the extent and quality of the Bragg intensity data and to thermal displacements not too far from the atomic positions.

Much more problematic are divergencies encountered in reciprocal space expressions, because there they affect directly the result of the least-squares refinement procedure. It should be stressed that the Fourier transform of the EW series due to its exponential form is always divergent; an example of this is shown in Fig. 1. The extension of data to higher scattering angles will increasingly invalidate the results obtained. Moreover, the stronger the non-harmonicities, the lower are the values of $\sin \theta / \lambda$ at which the divergency will occur. This gives a very strong argument for abandoning the use of the EW series to describe non-harmonic thermal motions. Moreover, the exponential form assumed by the Fourier transform of the EW series (16) does not allow highly disordered systems to be modelled, because the temperature factor $T(h)$ of such a system is negative at certain scattering angles h . On the other hand, the Fourier transform of the GC series (15) is quite flexible in its ability to reproduce the features of a disordered system, as shown in Fig. 2. Specific models are necessary in the case of the potential-based formalisms to model systems with pronounced disorder (Mair 1983*a*, 1983*b*).

Apart from the limitations inherent in the formalisms, there are restrictions imposed by the quality and the extent of the Bragg intensity data. The relative changes of the pdf (or the potential) at small displacements are a few per cent of the total density in most cases. At higher displacements the relative changes become increasingly greater,

* In the case of low temperatures (relative to the Debye temperature), the corresponding quantum expression has to be used.

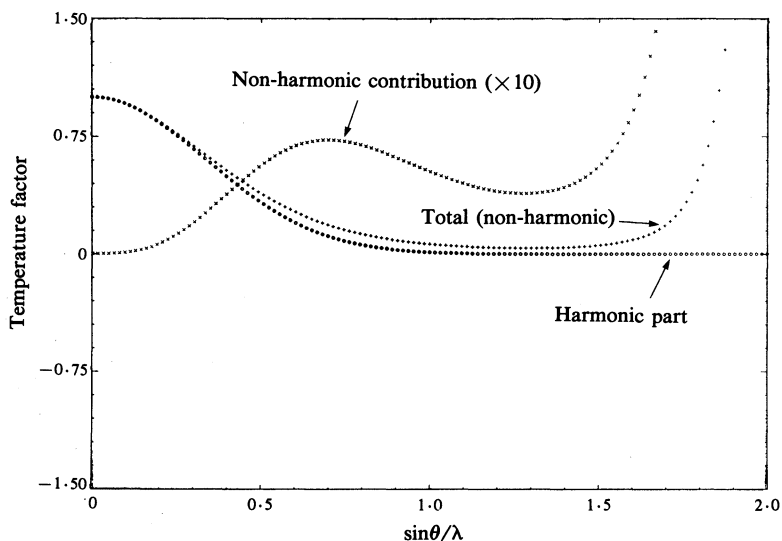


Fig. 1. Divergent temperature factor (Fourier transform of the Edgeworth series) in ZnS at 1300 K along the [111] direction as a function of $\sin \theta/\lambda$. Shown are the harmonic part, the total (non-harmonic) temperature factor and the non-harmonic contribution (exaggerated by a factor of 10).

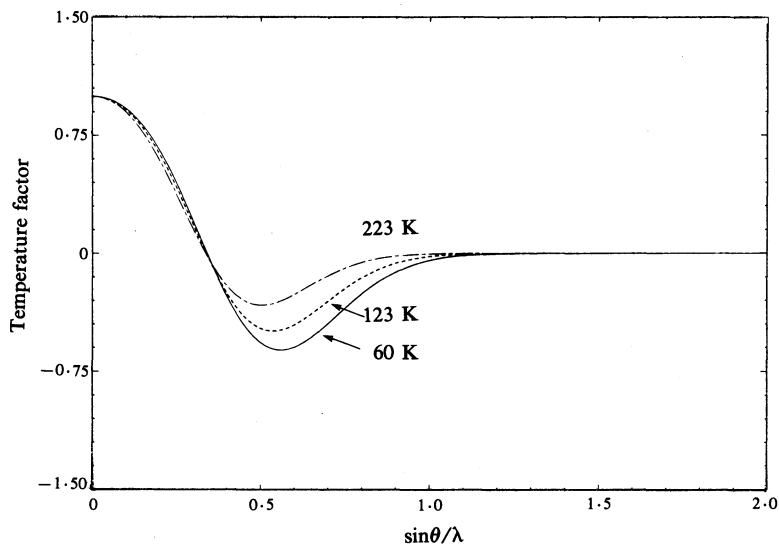


Fig. 2. Temperature factor (Fourier transform of the Gram-Charlier series) for a strongly disordered system as a function of $\sin \theta/\lambda$. Shown is the disordered hydrogen position along the hydrogen bond in ice Ih at the three temperatures indicated. The site separation is $\sim 0.75 \text{ \AA}$ and is nearly constant with temperature.

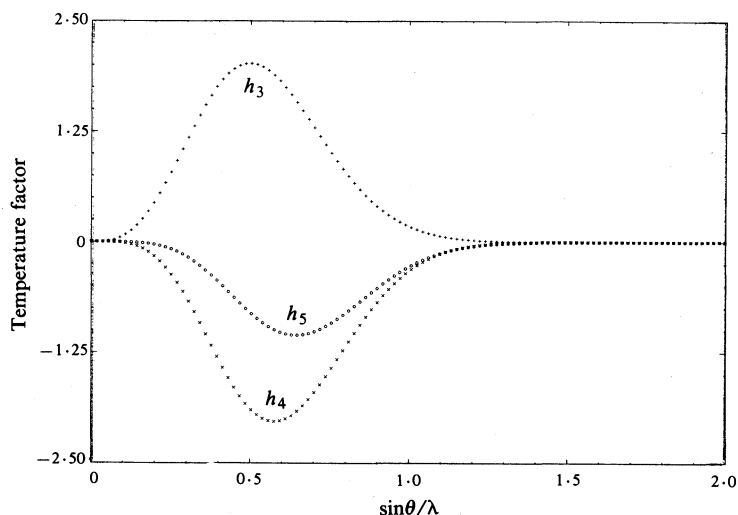


Fig. 3. Non-harmonic contribution to the total temperature factor (Fourier transform of the Gram-Charlier series) of the Cu atom in the solid ionic conductor $\text{Cu}_6\text{PS}_5\text{I}$ along the conduction channel as a function of $\sin \theta/\lambda$. Shown are the third, fourth and fifth order contributions. The positions of the maximal modifications are marked as h_n , as calculated from equation (19).

but at the same time the Bragg intensity data become less sensitive. The greatest absolute changes in the reciprocal space expression occur at some mathematically well-defined value of the scattering vector. In order to possess enough sensitivity in the refinement of terms of order n one should measure at least out to a wave vector h_n whose value increases as the order n of the non-harmonic expansion increases. The following expression holds for the GC series, but is also a reasonable approximation for other formalisms:

$$h_n = n^{\frac{1}{2}}(2\pi)^{-\frac{3}{2}}(2 \ln 2)^{\frac{1}{2}} \langle u^2 \rangle^{-\frac{1}{2}}, \quad (19)$$

where $\langle u^2 \rangle$ is the harmonic mean-square displacement of the atom and direction under consideration. The position of h_n together with the absolute non-harmonic modification is shown in Fig. 3 for the case of a strongly non-harmonic system. Note that a combination of higher order terms of different order could shift the value of h_{anh} (the maximum of the total anharmonic modification) to lower scattering angles or create even two extrema at different angles. Many attempts to refine higher order terms in atomic probability densities appear to have failed because the data set was not measured far enough in reciprocal space, rather than due to deficiencies in the formalism or the quality of the data.

Often the large number of non-harmonic terms 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, and thus to over-determine the problem by a factor of 5 to 10 even when going up to fourth order terms. Moreover, insignificant terms are usually set to zero and not varied in the final refinements. Likewise, 'chemical' constraints on the different tensor components could be easily introduced and the number of freely refined parameters reduced in this way.

4. Interpretation

In order to draw the appropriate conclusions from the result of a refinement including non-harmonic terms, the flexibility of the underlying models and their limits must be known. The discussion in the preceding section has shown that results obtained with the EW formalism have to be considered with care. Spurious results are easily obtained (especially when fourth order terms are included) and in general meaningful non-harmonic parameters are derived only for moderately non-harmonic systems.

The flexibility of all models discussed in Section 2 is considered to be sufficient at least for small deviations from harmonicity. The interplay of harmonic and non-harmonic parameters allows for a widely variable shape in the resulting densities or potentials. If necessary the flexibility may be increased by the introduction of fifth and sixth order terms (especially in disordered systems). Usually, however, the inclusion of terms up to fourth order is sufficient to describe the higher order moments of atomic displacements within the experimental accuracy.

The consistency of results obtained with different formalisms give some further indication of the significance of the results obtained. Comparisons have been published by several authors (Moss *et al.* 1980; Larsen *et al.* 1982; Zucker and Schulz 1982; Kuhs 1983). There are clear differences in the quality of the fits and in the densities (or potentials) obtained. A detailed discussion and comparison is beyond the scope of this paper. As an example only, some results obtained for ZnS are given in Table 1 and shown in Figs 4–6. These results should not be generalised, although they confirm once more the impression (Zucker and Schulz 1982; Kuhs 1983) that the best fit to the data is obtained by employing the GC formalism. In the rare cases where the EW formalism was more successful (especially at high temperatures), the inclusion of sixth order terms (which are implicit in the EW series) in the GC series led to an equally good or even better fit. The remaining slight differences (see Figs 4–6) in the results could indicate some inadequacy in some (or all) of the models, which however in many cases is much smaller than the magnitude of the non-harmonic deformation. It is worth noting that convergency problems were encountered in the refinements employing the FIV formalism. They mainly arise because the normalisation factor P (see equation 17) is a function of the non-harmonic even order terms; consequently, the corresponding derivatives are very lengthy and were calculated only in an approximate way by setting P equal to 1.

An important test has to be performed before any interpretation of the result is attempted—even when the refined terms seem to be significant—because strong correlations between parameters could lead to spurious results. The pdf must be positive everywhere; negative regions are tolerable only for very large displacements. Likewise, the potential obtained should not diverge or, if it does, only for large displacements outside the range seen in the diffraction experiment.

The main advantage of the potential-based formalisms is that they produce results of immediate significance. Results from the probabilistic approaches need to be translated into quantities with a more obvious physical meaning. This could be done either by directly transforming the refined tensor components into potential parameters (Kontio and Stevens 1982) or by a calculation of the potential from the Boltzmann function:

$$V(\mathbf{u}) = -k_B T \{ \ln \text{pdf}(\mathbf{u}) - \ln \text{pdf}(\mathbf{u}=0) \}. \quad (20)$$

Table 1. Results of refinement including non-harmonic terms using data on ZnS from Moss *et al.* (1980)

Parameters were refined by a full-matrix least-squares procedure where the quantity minimised was $\sum w(F_0^2 - kF_c^2)$, where k is the scale factor. An extinction parameter in the model type I with Lorentzian distribution function in the formulation of Becker and Coppens (1975) was included in the refinement. The upper entry in the table gives the weighted R factor

$$R_w = \{\sum w(F_0^2 - F_c^2)^2 / wF_0^4\}^{\frac{1}{2}},$$

with $w = 1/\sigma^2(F_0)$, and the lower entry the goodness-of-fit

$$S = \{\sum w(F_0^2 - F_c^2)^2 / (N - P)\}^{\frac{1}{2}},$$

with N the number of observations and P the number of parameters. OPP is the one-particle potential; FIV, the Fourier invariant; EW, Edgeworth; GC, Gram-Charlier; all, all fourth order terms refined; and R , only δ^{1111} refined

T^A (K)	OPP ^B	FIV _{all}	EW _R	GC _R	GC _{all}
520	0.0112	0.0112 ^C	0.0111 ^C	0.0110 ^C	0.0110 ^C
	0.51	0.50	0.51	0.51	0.51
960	0.0216	0.0230 ^C	0.0213	0.0211	0.0210
	0.85	0.89	0.83	0.82	0.81
1150	0.0371	0.0389 ^C	0.0338	0.0328	0.0300
	1.02	1.01	0.93	0.90	0.84
1300	0.0300	0.0297	0.0291	0.0299	0.0287 ^D
	0.75	0.74	0.73	0.74	0.73

A Revised temperature scale (see Moss *et al.* 1983).

B Results taken from Moss *et al.* (1980).

C Only third order terms included. The FIV refinements at 960 and 1150 K including fourth order terms were slowly diverging—damping of parameter shifts has not been tried.

D Results including sixth order terms are $R_w = 0.0268$ and goodness-of-fit of 0.70.

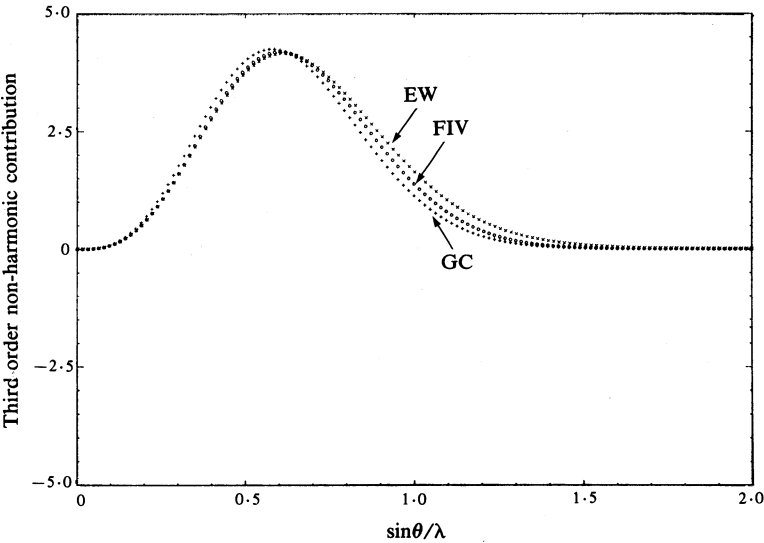


Fig. 4. Third order non-harmonic contribution to the temperature factor (multiplied by 10) in ZnS at 1300 K along [111] as a function of $\sin \theta/\lambda$. Shown are the Gram-Charlier, the Edgeworth and the Fourier-invariant results.

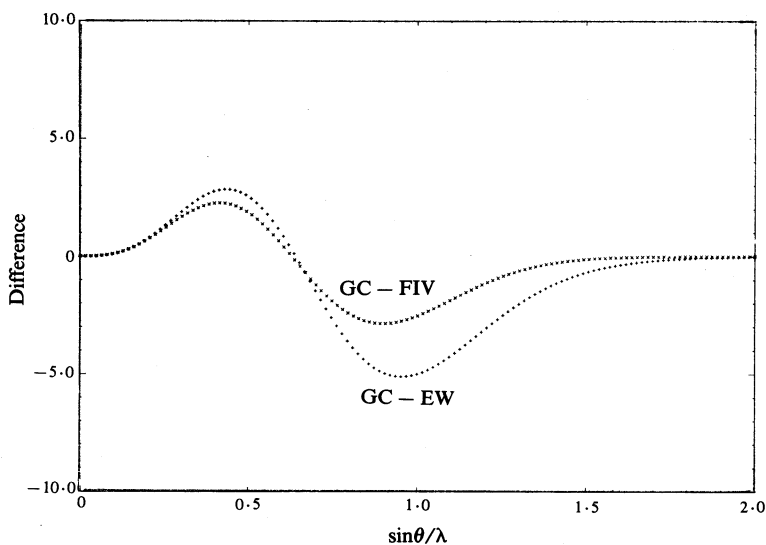


Fig. 5. Difference of the third order non-harmonic contribution (see Fig. 4) to the temperature factor (multiplied by 100) in ZnS at 1300 K for the Gram-Charlier/Edgeworth and for the Gram-Charlier/Fourier-invariant results.

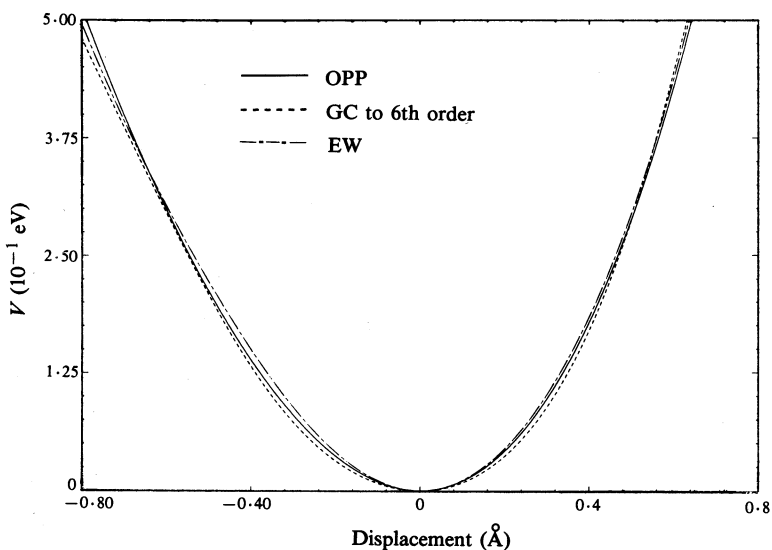


Fig. 6. (Anharmonic) one-particle potential for the Zn atom in ZnS at 1300 K along the [111] direction, showing the OPP, the Gram-Charlier up to sixth order, and the Edgeworth results.

The higher order moments μ_n of the distribution for a certain direction u are obtained by numerical integration:

$$\mu_n(u) = \int u^n \exp\{-V(u)/k_B T\} du / \int \exp\{-V(u)/k_B T\} du. \quad (21)$$

The corresponding cumulants may be calculated using a standard transformation (Kendall and Stuart 1976):

$$\begin{aligned}
k_1(u) &= \mu_1(u), \\
k_2(u) &= \mu_2(u) - \mu_1^2(u), \\
k_3(u) &= \mu_3(u) - 3\mu_2(u)\mu_1(u) + 2\mu_1^3(u), \\
k_4(u) &= \mu_4(u) - 4\mu_3(u)\mu_1(u) \\
&\quad - 3\mu_2^2(u) + 12\mu_2(u)\mu_1^2(u) - 6\mu_1^4(u),
\end{aligned} \tag{22}$$

where μ_1 gives the shift of the atomic position from the refined value along the direction u . If u is in the direction of a bond, μ_1 may be used to get a better estimate of the bond distance. Also, μ_2 gives the total mean square displacement (msd). A comparison with the harmonic msd allows the softening or hardening of the potential in the direction u to be quantified. A direct measure of the skewness of the distribution is found in k_3 and a direct measure of the kurtosis in k_4 . Similarly the skewness $S(u)$ and kurtosis $K(u)$ may be defined in terms of the moments:

$$S(u) = \mu_3(u)\mu_2^{-\frac{3}{2}}(u), \quad K(u) = \mu_4(u)\mu_2^{-2}(u) - 3. \tag{23}$$

In contrast to the refined tensorial quasi-moments (15) and cumulants (16) the quantities $S(u)$ and $K(u)$ are largely temperature independent. A change of $S(u)$ or $K(u)$ indicates a change of relative importance of the third and fourth order terms, in a similar way that a change in the potential parameters indicates a change of the potential.

The modelling of systems with unresolved disorder by inclusion of higher order terms proved to be very powerful (e.g. Kuhs and Lehmann 1987). The degree of disorder (i.e. the deviations of the atomic positions from the averaged atomic site) for any direction u is well characterised by the skewness $S(u)$ (for acentric sites) and/or the kurtosis $K(u)$ (for acentric and centrosymmetric sites). Again any temperature dependency of $S(u)$ or $K(u)$ indicates a change in the degree of the disorder.

The directional aspects of the non-harmonicity are best visualised by plotting the non-harmonic deformation density maps (or disorder deformation density maps in the case of atomic disorder), i.e. the modifications of the harmonic pdf due to higher order terms:

$$\text{pdf}_{\text{def}}(u) = \text{pdf}_{\text{gnrl}}(u) - \text{pdf}_{\text{har}}(u). \tag{24}$$

The absolute magnitude of the density modifications depends on the harmonic densities. The quantity of interest is the normalised density modification, which does not show a systematic change as a function of temperature for an unchanged potential (or unchanged disorder pattern):

$$\text{pdf}_{\text{def, norm}}(u) = \text{pdf}_{\text{def}}(u) / \text{pdf}_{\text{har}}(u=0). \tag{25}$$

An example of a disorder deformation density map is given in Fig. 7.

It is worth noting that purely electronic deformations (due to bonding effects) only slightly influence the magnitude of non-harmonic deformations and vice versa. Refinements using high order X-ray data are a reasonable way to determine just the non-harmonic deformations. Cooling the sample clearly helps to separate both

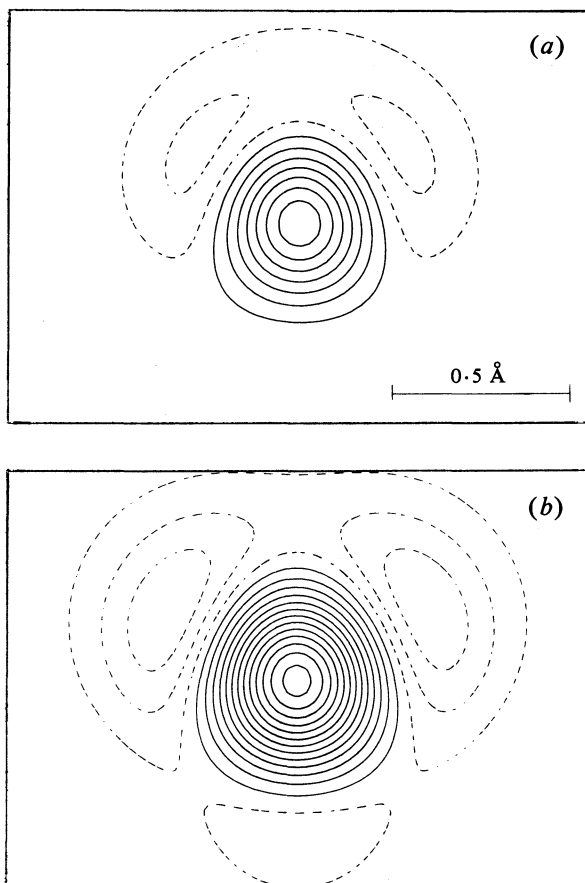


Fig. 7. Normalised disorder deformation density map of the oxygen atom in D_2O ice Ih in the molecular plane at (a) 223 K and (b) 275 K. The increase of molecular disorder on approaching the melting point is clearly seen.

effects further (compare equation 19). An improved decorrelation is usually achieved by a combined refinement of parameters describing electronic and anharmonic deformations. In some cases (e.g. lone-pair densities, strongly librating atoms,* hydrogen atoms in general), a complete decorrelation is difficult and independent information on the anharmonic deformations must be gained from neutron diffraction experiments.

5. Conclusions

All of the aforementioned formalisms to describe non-harmonicity in thermal motion have their own special features and there is some evidence that they are not equally successful in fitting Bragg intensity data. However, it is too early to

* Model calculations (Kuks 1983, unpublished) have shown that in the case of strong librations some of the total multipole scattering contributions change by up to 5% if the deformations due to the librations are not included in the model. This corresponds to population differences of up to 0.005, which is a significant change in a high quality electron density study.

make a choice in favour of one or the other. What is clearly needed is more comparative work and possibly even better data to discriminate amongst the different formalisms. Likewise, more effort should be devoted to transforming the results from probabilistic and potential-based formalisms into each other. As concerns the ease of programming, the Gram–Charlier formalism has certain advantages and indeed has been implemented in several crystallographic least-squares programs; for reasons discussed above it should be preferred over the widely used Edgeworth formalism. Programs using local cartesian coordinate systems are well suited to implement the generalised OPP formalism, but probabilistic formalisms may be inserted too. Wherever possible, several formalisms should be tried. Since the mathematical form assumed by the different approaches is different, there is no reason to believe that ultimately one of them is in general more successful than the others when dealing with different sources of non-harmonicity.

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