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## Determining Skewness in Atomic Probability Density Functions for Non-centrosymmetric Structures

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### Abstract

Skewness in atomic probability density functions can be represented by odd-order cumulants in the Edgeworth expansion about a Gaussian distribution, or by odd-order quasi-moments in the Gram–Charlier expansion. In the case of the Edgeworth expansion it is known that the absolute values of some odd-order cumulants cannot be determined from Bragg reflection data for non-centrosymmetric structures – because these cumulants affect only the phases of the calculated structure factors and not their magnitudes. It is shown that, in general, this problem is imposed by the form of the Edgeworth expansion and can be avoided by using the Gram–Charlier expansion instead. An example is given of the refinement of third-order quasi-moments for the non-centrosymmetric phase of  $\text{PbTiO}_3$ , using neutron-diffraction data collected at the Institut Laue–Langevin, Grenoble.

Many interesting phenomena are manifested in departures of atomic probability density functions (p.d.f.'s) from a purely harmonic form; and the anharmonicity of p.d.f.'s can be investigated with accurate high-resolution X-ray or neutron diffraction data. A widely used method of modelling anharmonicity in least-squares structure refinements is based on the Edgeworth expansion of the p.d.f. (Johnson & Levy, 1974), which gives the following form for the structure

factor up to sixth-order terms (Kuhs, 1983):

$$F_{\text{EW}}(\mathbf{h}) = \sum_i b_i \exp [i(2\pi x_i h_j - K_i^{jkl} h_j h_k h_l + K_i^{jklmn} h_j h_k h_l h_m h_n) - (\beta_i^{jk} h_j h_k - K_i^{jklm} h_j h_k h_l h_m + K_i^{jklmno} h_j h_k h_l h_m h_n h_o)], \quad (1)$$

where the summation is over the atoms in the unit cell (the repeated-index summation convention is assumed for the indices  $j, k, l, \dots$ ),  $b_i$  are the atomic scattering lengths (form factors for X-rays),  $x_i^j$  and  $\beta_i^{jk}$  are the positional parameters and the harmonic thermal parameters, and  $K_i^{jkl\dots}$  are the anharmonic parameters. These last are known as cumulants. The odd-order cumulants model antisymmetric anharmonicity, or 'skewness', in the p.d.f.; and the even-order cumulants model symmetric anharmonicity, or 'kurtosis'. In practice, it is usually sufficient to include only the third- and fourth-order cumulants in a structure refinement, and it is rarely, if ever, warranted to attempt to refine terms higher than sixth order. Though generally effective, this approach to anharmonicity suffers the serious limitation that it is possible to determine only the *relative* magnitudes of odd-order cumulants whose signs are not reversed by the space-group operations (Hazell & Willis, 1978). This is because increasing or decreasing such a cumulant by the same amount for all atoms – as the symmetry then permits – alters the phase but not the magnitude of the calculated structure factors [see (1)].

This problem has been recognized for some time. It was noted and explained by Duckworth, Willis & Pawley in 1970 for the particular case of the  $K^{123}$  cumulants in hexamethylenetetramine\* ( $C_6N_4H_{12}$ ): the authors could obtain only values relative to a  $K^{123}$  set arbitrarily to zero for the C atom. The same indeterminacy of the  $K^{123}$  cumulant was encountered more recently by Moss, McMullan & Koetzle (1980) in their investigation of anharmonicity in zincblende (ZnS).† Hazell & Willis (1978) gave general consideration to this aspect of refining third-order cumulants (and, implicitly, other odd orders) for non-centrosymmetric structures and – as follows from above – they concluded that *all* the odd-order cumulants of one atom in the structure have to be kept fixed in the ultimate case of space group  $P1$ . They made the further important observation that the arbitrariness lies in the refinement, and not in the structure itself: different absolute magnitudes of these odd-order cumulants, with the same relative magnitudes, correspond to *physically different* crystal structures. For example, in studying ZnS the problem is precisely to determine whether the skewness represented by the  $K^{123}$  cumulant is on the Zn atom, the S atom, or both (Moss *et al.*, 1980). If it is the case that some (or all) of the odd-order anharmonicity affects only the phases of structure factors, a severe – and crystallographically perplexing – limitation is placed on the application of diffraction methods to the study of anharmonic distributions of all kinds. Although Hazell & Willis (1978) explicitly addressed only the cumulant, or Edgeworth, expansion approach to anharmonicity, their closing remarks appear to suggest that the problem is intrinsic to crystallographic refinement in general: certainly that is the construction that has been widely placed on the matter. But we shall argue that this is a false conclusion to draw: in general, the *magnitudes* of structure factors (and hence the measured intensities) are affected by the absolute as well as relative magnitudes of all the asymmetric (odd-order) anharmonicity.

The argument can be presented diagrammatically for a simple non-centrosymmetric two-dimensional structure containing two atoms,  $A$  and  $B$ , in a primitive oblique cell (space group  $p1$ ). Suppose that the  $A$  atom has a skewed anharmonic p.d.f. that can be represented by convoluting the atom's harmonic thermal motion with a triangular distribution of scattering density; and for simplicity suppose, further, that both

atoms have the same harmonic thermal motion. The structure can then be drawn with the common harmonic component omitted from both p.d.f.'s, as in Fig. 1(a). The corresponding Patterson function is as shown in Fig. 1(b). Let the best Edgeworth-expansion fit to the skewed p.d.f. (up to fourth-order terms) be obtained with third-order cumulant values  $K_A^{jkl}$ .

Now consider the same structure, but with the anharmonicity on the  $B$  atom instead, such that its p.d.f. is fitted with third-order cumulant values  $-K_A^{jkl}$  – equal and opposite to those of atom  $A$  in Fig. 1. This structure and its Patterson function are depicted in Fig. 2.

Clearly the two structures are distinguishable provided the p.d.f.'s in structure I (Fig. 1a) have a different form from those in structure II (Fig. 2a). This simply requires  $|b_A| \neq |b_B|$ , as in the figures (which have  $b_A = 2b_B$ ). But the distinction cannot be captured by the cumulant model, because the model of structure I can be transformed to the model of structure II just by subtraction of  $K_A^{jkl}$  from the third cumulants of both atoms – which alters only the phases in equation (1), as already explained. (This is a two-dimensional analogue of the indeterminacy encountered in, for example, the ZnS study referred to above.) However, it can be seen that the Patterson

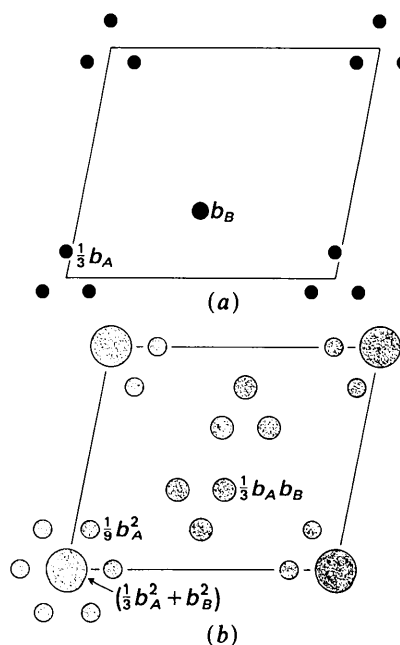


Fig. 1. (a) A hypothetical two-dimensional structure in space group  $p1$  with two atoms per unit cell, and (b) its Patterson function. The atoms,  $A$  and  $B$ , have scattering lengths  $b_A$  and  $b_B$ , respectively, and  $b_A$  is taken to be  $2b_B$ . Only the anharmonic component of the atomic p.d.f.'s is shown: thus atom  $A$  has the skewed anharmonicity obtained by convoluting its harmonic thermal motion with the triangular distribution shown in (a), while atom  $B$  has purely harmonic thermal motion (taken to be the same as that of atom  $A$ ). In both parts of the figure the 'peaks' are shown with areas in proportion to their relative weights.

\* 1,3,5,7-Tetraazatricyclo[3.3.1.1<sup>3,7</sup>]decane.

† Yamanaka & Tokonami (1985) have recently claimed to resolve the problem in this case by the use of Fourier difference maps. But it is a false claim. Difference maps have to be based on the phases obtained in a particular structure refinement, and this is nothing more than another way of applying a particular constraint (arbitrarily) to the cumulant values. The indeterminacy remains, albeit hidden.

functions of the two structures are different (given  $|b_A| \neq |b_B|$ ), and this implies that in general there are differences in the diffracted intensities. The problem is that the cumulant model of equation (1) is insensitive to these differences.

An alternative approach to the general parameterization of anharmonic p.d.f.'s has been adopted by Zucker, Perenthaler, Kuhs, Bachmann & Schulz (1983) for their *PROMETHEUS* suite of crystallographic programs. They utilize the Gram-Charlier expansion (Johnson & Levy, 1974) which yields the following form for the structure factor up to sixth-order terms (Kuhs, 1983):

$$F_{GC}(\mathbf{h}) = \sum_i b_i \exp(2\pi i x_i^j h_j - \beta_i^{jk} h_j h_k) \\ \times [1 - (4/3)\pi^3 i C_i^{jkl} h_j h_k h_l \\ + (2/3)\pi^4 C_i^{jklm} h_j h_k h_l h_m \\ + (4/15)\pi^5 i C_i^{jklmn} h_j h_k h_l h_m h_n \\ - (4/45)\pi^6 C_i^{jklmno} h_j h_k h_l h_m h_n h_o], \quad (2)$$

where, instead of the cumulants of (1), we have the 'quasi-moments'  $C_i^{jkl\dots}$ . The relationship between this and the Edgeworth-expansion approach to the modelling of anharmonicity, and their relative advantages, have been examined in detail by Kuhs (1983). What matters for our present purposes is that the odd-order quasi-moments do not appear in a pure phase factor in (2). The magnitudes of  $F_{GC}(\mathbf{h})$  will thus depend on the *absolute* magnitudes of all the quasi-moments.

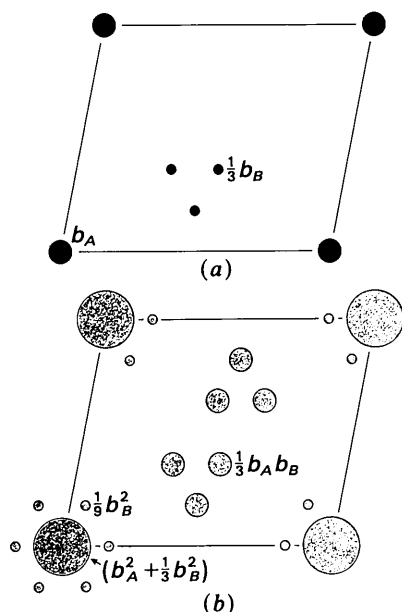


Fig. 2. The same as Fig. 1, except that atom *B* has the skewed p.d.f., while atom *A* has purely harmonic thermal motion. The skewness of atom *B*'s p.d.f. is the inverse of that shown for atom *A* in Fig. 1.

In a high-resolution neutron-diffraction study of  $\text{PbTiO}_3$ , we have encountered significant odd-order anharmonicity, and have used the data (collected at the Institut Laue-Langevin, Grenoble) to test our conclusion that the Gram-Charlier approach is one way to overcome the problem of arbitrary odd-order terms.  $\text{PbTiO}_3$  has a cubic-to-tetragonal phase transition on cooling through  $T_c = 763$  K (Shirane & Hoshino, 1951). The space group below  $T_c$  is non-centrosymmetric,  $P4mm$ , and the two cumulants  $K^{113}$  and  $K^{333}$  have to be set arbitrarily to zero (or some other value) for one of the atoms in the structure when refining with (1). In our first study of anharmonicity  $\sim 60$  K below  $T_c$  (Nelmes & Kuhs, 1985) we refined the quasi-moments of (2), with the  $C^{113}$  and  $C^{333}$  values set to zero for the Pb atom in the (mistaken) belief that this was necessary – and basing the choice of constraint on a generally held assumption that the Pb thermal motion is close to harmonic above and below  $T_c$  in  $\text{PbTiO}_3$ . However, we have since found that we can indeed refine all of the non-zero third-order quasi-moments without any constraints, using neutron-diffraction data collected out to  $(\sin \theta)/\lambda = 1.4 \text{ \AA}^{-1}$ ; and these refinements suggest that it is in fact the Pb p.d.f. that is significantly skewed below  $T_c$ . The latter point is of considerable interest in relation to recent refinements of data collected at  $T_c + 2$  K, which reveal (very unexpectedly) that the Pb atom has a highly anharmonic, and possibly disordered, p.d.f. in the cubic phase. (Details of this work will be published separately.)

We thus reach these conclusions:

(i) The absolute magnitudes of skewness in the atomic p.d.f.'s of a non-centrosymmetric structure can be determined in principle if the structure is distinguishable from the inversion of itself. In the case of the structures in Figs. 1 and 2, where both atoms are assumed to have the same harmonic thermal motion, this condition reduces to the requirement that  $|b_A| \neq |b_B|$ ; if the two atoms had different harmonic thermal motion the structures would be distinguishable even with  $|b_A| = |b_B|$ . But it is apparent that 'distinguishability' will usually be greater the larger is the difference in magnitude of the scattering lengths (form factors).

(ii) The skewness can be determined from diffraction data of sufficient accuracy and resolution in relation to the 'distinguishability', *provided* the p.d.f.'s are not modelled in a way that treats odd-order anharmonic parameters as simply higher-order terms in the phase of the structure factor. The Gram-Charlier expansion satisfies this condition. Whilst there is no reason to suppose that the Gram-Charlier approach makes *maximal* use of the information in the diffraction data, it is clearly to be preferred over the Edgeworth expansion – in this way adding to the other general advantages of the Gram-Charlier expansion that have been expounded by Kuhs (1983).

(iii) Because the information distinguishing structures such as those in Figs. 1 and 2 will mainly reside in small intensity differences at high  $(\sin \theta)/\lambda$ , accurate determinations of absolute magnitudes for all odd-order anharmonic parameters are more likely to be achieved with neutron-diffraction techniques. A further inherent advantage of neutron diffraction is the possibility of maximizing the difference in magnitude of the scattering lengths by varying the isotopic proportions of the atoms in a structure.

Finally, a note of caution. When fourth-order terms ( $C_i^{ijklm}$ ) are included in our  $\text{PbTiO}_3$  refinements, parameter correlations arise which reduce the accuracy with which the  $C^{113}$  and  $C^{333}$  quasi-moments are determined. This highlights the need always to test for significant fourth-order terms in studies of skewness: such terms may substantially increase the demands on data accuracy and resolution relative to the intrinsic 'distinguishability' of the skewness.

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## Resolution Analyses for Mössbauer Diffraction: Resolved TDS Profiles in Silicon\*

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### Abstract

The resolution function for Mössbauer  $\gamma$ -ray scattering and the thermal diffuse scattering (TDS) near the 444 reflection in silicon have been measured with high-intensity Mössbauer radiation from the 46.48 keV transition in  $^{183}\text{W}$ . A general analysis of the resolution function has been carried out for the first time which shows that its energy and momentum components can be factored independently with the energy resolution being determined by the Mössbauer resonance. The half-widths of the momentum reso-

lution ellipsoid were measured to be 0.011, 0.11 and  $1.13 \text{ \AA}^{-1}$  in the transverse, longitudinal and vertical directions, respectively. The ratios of these half-widths are significantly different from those commonly encountered in neutron scattering. These analyses indicate that the observed broad distribution of inelastic scattering in the TDS profiles is consistent with published elastic constants for silicon.

### Introduction

Thermal diffuse scattering (TDS) is coherent inelastic scattering due to lattice vibrations in a crystalline solid. In a conventional X-ray diffraction experiment, the TDS, with energy transfer of 0–0.1 eV, is not directly separable from the Bragg scattering intensity, since these energy shifts are smaller than the 1–5 eV intrinsic energy spread of common X-ray lines. The

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