

Symmetry of Terms in the Temperature Factor for Bragg Diffraction of X Rays or Neutrons*

S. L. Mair

Division of Chemical Physics, CSIRO,
P.O. Box 160, Clayton, Vic. 3168.

Abstract

Terms in the anharmonic Debye-Waller factor, taken as a perturbation about the harmonic case to second order in the van Hove ordering parameter, are classified according to the point-group symmetry of the vibrating atom. The classification is valid for a fully interacting (many-body) crystal potential. It is pointed out that certain terms, which are symmetry-allowed for such a general crystal potential, are excluded if an effective one-particle potential is employed.

1. Introduction

Perturbation expansions of the Debye-Waller factor (DWF) (or temperature factor) are frequently used in the analysis of accurate X-ray and neutron diffraction data (for some recent examples see Moss *et al.* 1980 and Kontio and Stevens 1982). The DWF may then be parametrized in terms of quadratic, cubic, quartic etc. coefficients of the vibrational potential of the crystal.

The perturbation expressions are generally in the form of moment or cumulant expansions, or some variant of these (see Zucker and Schulz 1982, and references therein; Mair 1980*a*), conversion from one form to the other being readily made. In this paper it is convenient to use the cumulant expansion form, although a moment expansion is considered as an example in Section 5*b*. Then the various classes of term in the DWF may most readily be summarized as diagrams (Cowley 1963; Mair 1980*b*), whose topology reflects their structure. It is the purpose of this paper to, firstly, show what these diagrams represent, and then to relate them to the point-group symmetry of the site of the atom under consideration.

2. Many-body and Effective One-particle Hamiltonians

We start with the definition of the temperature factor or DWF as the ensemble average $\langle \exp(i \mathbf{Q} \cdot \mathbf{u}) \rangle_H$, where \mathbf{u} is the displacement of the atom under consideration from its reference position and \mathbf{Q} is the scattering vector. The ensemble average is taken with respect to the vibrational Hamiltonian H for the crystal. By omitting the kinetic energy terms, which integrate out in the ensemble average, the many-body

* Dedicated to Dr A. McL. Mathieson on the occasion of his 65th birthday.

Hamiltonian may be given as a Taylor expansion about the positions corresponding to the minimum in the potential Φ as (Born and Huang 1954; see also Mair and Wilkins 1981)

$$H = \frac{1}{2!} \sum_{jk; \alpha\beta} \Phi_{jk; \alpha\beta}^{(2)} u_{j; \alpha} u_{k; \beta} + \frac{\lambda}{3!} \sum_{jkl; \alpha\beta\gamma} \Phi_{jkl; \alpha\beta\gamma}^{(3)} u_{j; \alpha} u_{k; \beta} u_{l; \gamma} + \frac{\lambda^2}{4!} \sum_{jklm; \alpha\beta\gamma\delta} \Phi_{jklm; \alpha\beta\gamma\delta}^{(4)} u_{j; \alpha} u_{k; \beta} u_{l; \gamma} u_{m; \delta}, \quad (1)$$

to order λ^2 in the van Hove ordering parameter λ , which is later set to unity (van Hove *et al.* 1961; see also Mair 1980a). Here $u_{j; \alpha}$ is the α th cartesian component of the displacement of the j th atom and the $\Phi_{jk...; \alpha\beta...}^{(n)}$ are the n th derivatives of the potential with respect to the $u_{j; \alpha}$, $u_{k; \beta}$ etc. All terms with $n > 2$ are treated as small anharmonic perturbations.

In the effective one-particle potential (OPP) approach, which is frequently used to define the anharmonic temperature factor (first used by Dawson *et al.* 1967), the Hamiltonian H is replaced by a sum over the effective OPPs ϕ_j :

$$H = \sum_j \phi_j,$$

where, omitting the subscript j ,

$$\phi = \frac{1}{2!} \sum_{\alpha\beta} \phi_{\alpha\beta}^{(2)} u_{\alpha} u_{\beta} + \frac{\lambda}{3!} \sum_{\alpha\beta\gamma} \phi_{\alpha\beta\gamma}^{(3)} u_{\alpha} u_{\beta} u_{\gamma} + \frac{\lambda^2}{4!} \sum_{\alpha\beta\gamma\delta} \phi_{\alpha\beta\gamma\delta}^{(4)} u_{\alpha} u_{\beta} u_{\gamma} u_{\delta}. \quad (2)$$

The $\phi_{\alpha\beta...}^{(n)}$ in equation (2) are n th derivatives of the OPP ϕ , with respect to u_{α} , u_{β} etc.

The effective OPP can be thought of as a mean field at the particular atom due to all the other atoms in the crystal. The parameters $\phi_{\alpha\beta...}^{(n)}$ of the OPP are essentially independent of temperature, after the minor effects of thermal expansion of the lattice are taken into account (see e.g. Mair *et al.* 1974), and so the OPP is useful for understanding the vibrational properties of the crystal. Strong temperature dependence in the OPP parameters may, however, occur for highly anharmonic, strongly coupled thermal vibration; for example, near a structural phase transition (Mair 1982) in which case the OPP formalism is of more limited use.

3. Cumulant Expansion and Diagrams for the DWF

The expansion of the ensemble average for the DWF, when written as a cumulant expansion, is given by (Kendall and Stuart 1958)

$$\langle \exp(i \mathbf{Q} \cdot \mathbf{u}) \rangle_H = \exp \{ \langle i \mathbf{Q} \cdot \mathbf{u} \rangle_{\text{cum}} + (1/2!) \langle (i \mathbf{Q} \cdot \mathbf{u})^2 \rangle_{\text{cum}} + (1/3!) \langle (i \mathbf{Q} \cdot \mathbf{u})^3 \rangle_{\text{cum}} + (1/4!) \langle (i \mathbf{Q} \cdot \mathbf{u})^4 \rangle_{\text{cum}} + \dots \}, \quad (3)$$

and the cumulants $\langle \dots \rangle_{\text{cum}}$ may be defined in terms of the moments of the distribution.

Here the moments correspond to expectation values, or ensemble averages, of the form $\langle X \rangle_H$. Each cumulant in equation (3) gives rise to classes of terms in the DWF with a characteristic structure and for each class this structure can be represented by a single diagram. [For example, as discussed in Section 5, the fourth and fifth terms in equation (4) are represented by the same diagram.] The diagrams should be considered as just a useful device, allowing one to summarize a potentially rather complicated set of terms. To order λ^2 there are eight possible diagrams and the corresponding expressions have been presented explicitly by Mair (1980*b*) for the general case of a many-body crystal Hamiltonian and also for the special case of an effective OPP. The expressions by Mair (1980*b*) are valid in the quantum régime and results for the classical régime are obtained by taking the high-temperature limit (see Table 1 of Mair 1980*b*). Note that the diagrams are the same over the whole temperature range.


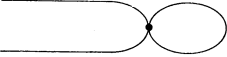
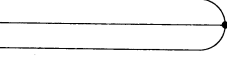
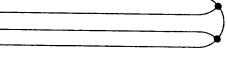
Diagram	Factor of order $(iQ_\alpha)^p$	Factor of type $\Phi^{(n)}$
	$i^2 Q_\alpha Q_\beta$	harmonic (special case)
	$i^2 Q_\alpha Q_\beta$	$\times \Phi^{(4)}$
	$i^3 Q_\alpha Q_\beta Q_\gamma$	$\times \Phi^{(3)}$
	$i^4 Q_\alpha Q_\beta Q_\gamma Q_\delta$	$\times \Phi^{(3)} \Phi^{(3)}$

Fig. 1. Some examples giving the form of factors occurring in the numerators of terms belonging to a class represented by a particular diagram. For an effective OPP model, the $\Phi^{(n)}$ become $\phi^{(n)}$ (see below for definitions of n and p).

It is unnecessary to reproduce all the terms in the DWF here, since all terms in the class represented by any single diagram obey the same symmetry classification, as set out in Section 4 below. It is only necessary to be able to identify the class of terms corresponding to each diagram, which may be done by following the procedure:

(a) The number p of horizontal lines at the left of the diagram gives the power of iQ_α in the DWF and reveals the origin of the diagram as the p th cumulant in equation (3).

(b) The diagram with no vertex represents the harmonic term, which is a special case, the other diagrams representing perturbations about this term.

(c) A vertex at which n lines meet corresponds to an n th derivative of the potential $\Phi^{(n)}$ (or $\phi^{(n)}$ in an OPP formulation), occurring in the numerators of the terms.

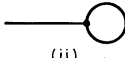
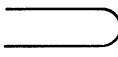
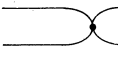
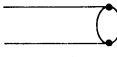
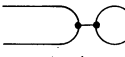
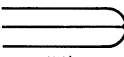
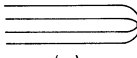
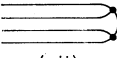
(d) If more than one vertex appears in a diagram then the corresponding derivatives of the potential are multiplied together.

Examples of the application of these rules are given for four diagrams in Fig. 1.

4. Symmetry Classification of the Diagrams

Since the DWF is a one-particle property of the system, its components are governed by the point-group symmetry of the site of the atom under consideration. Accordingly, a classification of the diagrams contributing to the DWF can be made (see Table 1) showing which diagrams are allowed for any point-group symmetry. In Table 1, the diagrams to order λ [diagrams (i), (ii) and (iii)] are shown as bold lines, the remaining diagrams being of order λ^2 . The diagrams are arranged so that those in the p th row of the table originate from the p th cumulant of equation (3).

Table 1. Symmetry classification for diagrams contributing to the DWF

Cumulant $\langle (i \cdot Q \cdot u)^p \rangle_{\text{cum}}$ $p =$	Harmonic	Anharmonic			
	Allowed point groups				
	ALL	ALL (OPP: 1, 2, m, 222, mm, 3, 32, 3m, 4, $\bar{4}$, 4mm, $\bar{4}2m$, 6, $\bar{6}$, 6mm, $\bar{6}m2$, 23, $\bar{4}3m$)	1, 2, m, 222, mm, 3, 32, 3m, 4, $\bar{4}$, 4mm, $\bar{4}2m$, 6, $\bar{6}$, 6mm, $\bar{6}m2$, 23, $\bar{4}3m$	1, 2, m, mm, 3, 3m, 4, 4mm, 6, 6mm	
1				 (ii)	
2	 (i)	 (iv)	 (vi)	 (viii)	
3			 (iii)		
4		 (v)	 (vii)		

In the general case of a many-body Hamiltonian, five diagrams [(i), (iv), (v), (vi) and (vii) in Table 1] are always allowed (to order λ^2), but for the special case of an effective OPP, two of these diagrams [(vi) and (vii)] are excluded unless the atom is at a site belonging to one of the 18 non-centrosymmetric point groups listed in Table 1. Unlike a many-body potential, the effective OPP itself is governed by the point-group symmetry of the atomic site, so that the cubic coefficients $\phi_{\alpha\beta\gamma}^{(3)}$ in equation (2) are zero if the point-group symmetry is not one of the 18 mentioned above. Since diagrams (vi) and (vii) depend on the product of two such cubic coefficients, these diagrams are zero in this case. Thus, for example, for any Bravais lattice, diagrams (vi) and (vii) are zero in an OPP formulation but nonzero for a many-body potential (see Section 5 for a particular example).

For an atom on a site belonging to one of the 10 polar point groups, two extra diagrams [(ii) and (viii)] are present in the DWF. These terms are associated with the shift of one sub-lattice with respect to another. Note that it is for this same set of point groups that the equilibrium or mean position of the atom does not correspond to that defining the minimum in the potential (Mair and Wilkins 1981).

Diagrams (ii), (viii) and (iii), which depend on $\Phi_{\alpha\beta\gamma}^{(3)}$, do not have a separate category for OPPs and many-body potentials. This is because they are only allowed for a subset [or the full set for diagram (iii)] of the 18 non-centrosymmetric point groups for which $\Phi_{\alpha\beta\gamma}^{(3)}$ is nonzero in the OPP case. Note that diagram (iii) corresponds for a diamond structure to the well-known cubic term in the temperature factor, describing motion of the atom in the four equivalent tetrahedral directions away from the nearest neighbours.

5. Discussion with Examples

(a) Diamond Structure

We consider first an atom in a diamond crystal, which has point-group symmetry $\bar{4}3m$. The cumulant expansion of the DWF in the high-temperature limit has been given (Mair 1980*a*, equation 14) for an OPP as

$$\begin{aligned} T(Q) = & T_0(Q) \exp\{i\phi^{(3)}(k_B T)^2 Q_1 Q_2 Q_3 / \phi^{(2)3} \\ & + (10\phi_1^{(4)} / \phi^{(2)3} - \frac{1}{2}\phi^{(3)2} / \phi^{(2)4})(k_B T)^2 Q^2 \\ & - \phi_1^{(4)}(k_B T)^3 Q^4 / \phi^{(2)4} - \phi_2^{(4)}(k_B T)^3 (Q_1^4 + Q_2^4 + Q_3^4 - \frac{3}{2}Q^4) / \phi^{(2)4} \\ & + \frac{1}{2}\phi^{(3)2}(k_B T)^3 (Q_1^2 Q_2^2 + Q_2^2 Q_3^2 + Q_3^2 Q_1^2) / \phi^{(2)5}\}, \end{aligned} \quad (4)$$

where k_B is the Boltzmann constant, T the temperature, $Q^2 = Q_1^2 + Q_2^2 + Q_3^2$, while $T_0(Q)$ is the harmonic DWF and corresponds to diagram (i) in Table 1. The anharmonic terms correspond, in order of appearance in equation (4), to diagrams (iii), (iv), (vi), (v), (v) and (vii). Note that there are two terms for diagram (v), corresponding to the two different symmetry-allowed quartic coefficients, $\phi_1^{(4)}$ and $\phi_2^{(4)}$, defined by Mair (1980*a*). Even if a full many-body potential is used, no further diagrams would contribute to $T(Q)$.

(b) Face-centred Cubic Structure

The atoms in a face-centred cubic structure are situated on sites of $m\bar{3}m$ symmetry. By using a moment expansion, the DWF in the high-temperature limit was given by Cooper and Rouse (1973) for an OPP as

$$\begin{aligned} T(q) = & T_0(Q)[1 + 10\phi^{(4)}(k_B T)^2 Q^2 / \phi^{(2)3} - \phi_1^{(4)}(k_B T)^3 Q^4 / \phi^{(2)4} \\ & - \frac{2}{3}\phi_{II}^{(4)}(k_B T)^3 \{Q_1^4 + Q_2^4 + Q_3^4 - 3(Q_1^2 Q_2^2 + Q_2^2 Q_3^2 + Q_3^2 Q_1^2)\}], \end{aligned} \quad (5)$$

where an obvious change in notation has been made and the normalization term has been cancelled out. Once again $T_0(Q)$ corresponds to diagram (i), the three remaining terms corresponding to diagrams (iv), (v) and (v) respectively. Diagrams (vi) and (vii) are not represented in equation (5), but they do occur for a many-body potential, as

shown by equation (6.11) of Maradudin and Flinn (1963). In that equation the terms correspond, respectively, to diagrams (i), (vi), (iv), (vi),(v) and (vii).

It may be seen from the above example that one consequence of using the OPP formalism is that the effective OPP coefficients $\phi^{(n)}$ do not necessarily correspond only to a sum of many-body potential coefficients $\Phi^{(n)}$, with the same value of n . In particular, refined quartic coefficients $\phi^{(4)}$ will in general represent a mixture of terms with coefficients $\Phi^{(3)}$ and $\Phi^{(4)}$ in a many-body treatment.

It would be inappropriate to pick out specific examples from the literature where the OPP approximation is of dubious validity, since all OPPs (however useful) represent a gross simplification of the dynamics of the system. Some examples of work, in which OPP coefficients up to the quartic term have been derived directly from Bragg diffraction data, are as follows: Cooper and Rouse (1973) for KCl, Mair *et al.* (1974) for SrF₂, Moss *et al.* (1980) for ZnS and Kontio and Stevens (1982) for VAl_{10,42}. For these cases, as with all applications of the OPP formalism, appropriate caution should be exercised in the interpretation of the results.

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