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Willis Formalism of Anharmonic Temperature Factors for a General Potential and its Application in the Least-Squares Method

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Abstract

Willis treatment of anharmonic temperature factors including up to fourth-order terms has been generalized and incorporated into a conventional full-matrix least-squares program. The temperature factor $T(\mathbf{S})$ including the anharmonic vibration effect is formulated in the general case using Willis's method. $T(\mathbf{S})$ is based on the Cartesian coordinates defined by the three principal axes of the harmonic thermal ellipsoid. The simultaneous refinement of the parameters in $T(\mathbf{S})$ with the conventional parameters in crystallography, which are based on the crystal lattice system, is possible. In order to introduce $T(\mathbf{S})$ into conventional full-matrix least-squares programs, some other relations were also derived, such as that between crystallographic symmetry and $T(\mathbf{S})$, and that among parameters due to point symmetry of the atom, and so on. The present method was applied to the K and two F atoms in KCuF_3 crystals at 296 K with the point symmetries of the sites 422 , $42m$ and $mm2$, respectively, and Al and O atoms in $\alpha\text{-Al}_2\text{O}_3$ crystals at 2170 K with the point symmetries 3 and 2, respectively. The features of the potentials of atoms in KCuF_3 crystals correspond very well to the peaks on the difference-Fourier maps. After the correction for anharmonic vibration, the difference-Fourier map around each atom became flat. It indicates that in an accurate electron density study the anharmonic vibration effect is not negligible and the Willis method works effectively.

Introduction

Studies on anharmonic vibration have been mainly performed by neutron diffraction, since the constant value of the neutron cross section prevents steep diminution in intensities of high-angle reflexions, and since no interaction between aspherical thermal vibrations of nuclei and aspherical electron distribution favors the neutron diffraction study. However, recent advances in X-ray diffraction have made it possible to observe a large number of high-angle reflexions accurately. In the recent X-ray study of KCuF_3 (Tanaka & Marumo, 1982), it was shown that the interaction between the two asphericities was not so severe. And the peaks of the anharmonic vibration appeared on a difference-Fourier map after the removal of those of the aspherical electron distribution. Thus, the main difficulties in the X-ray study of anharmonic vibration in crystals where covalency of bonds does not play a significant role are believed to be overcome. It has become highly necessary and desirable to modify the harmonic temperature-factor formalism to that of the general temperature factor (GTF), which includes the effects of anharmonic vibration of atoms.

Assuming a crystal to be an assembly of independent oscillators, several authors formulated the GTF by taking the ensemble average of the one-particle potential (OPP). Willis (1969) expressed the OPP as a power-series expansion and formulated the GTF for atoms with cubic point symmetries. Kurki-Suonio,

Merisalo & Peltonen (1979) expanded the OPP by spherical harmonics and other functions depending on the crystal symmetry. They formulated the GTF and derived various relations necessary for its general use. In these two methods, the OPP is divided into harmonic and anharmonic parts, we call them V_h and V_a , respectively, and a temperature factor is calculated assuming V_a is smaller than $k_B T$, where k_B and T are Boltzman's constant and the temperature of the system, respectively. Accordingly, these methods are not available for a large anharmonic OPP. In order to avoid the difficulty Matsubara (1975*a,b*) expressed $T(\mathbf{S})$ as the exponent of the cumulant expansion

$$T(\mathbf{S}) = \langle \exp(2\pi i \mathbf{S} \cdot \mathbf{u}) \rangle = \exp \left[\sum_{n=1}^{\infty} \frac{\langle (2\pi i \mathbf{S} \cdot \mathbf{u})^n \rangle}{n!} \right],$$

where $\langle \rangle$ means an average over \mathbf{u} , a displacement vector, and \mathbf{S} is a scattering vector. $\langle (2\pi i \mathbf{S} \cdot \mathbf{u})^n \rangle$ is calculated by taking the ensemble average of the OPP.

Johnson's (1969) formalism is based on statistics and is completely different from the others. He expanded the characteristic function of an arbitrary trivariate probability density function in terms of cumulants. The first and second cumulants correspond to positional parameters and harmonic temperature factors, respectively. The third and the fourth cumulants provide an estimate of the 'skewness' and 'kurtosis' of the probability density function, respectively. Thus aspherical electron distribution due to bonding as well as the anharmonic vibration effect is involved in these terms in X-ray studies.

Johnson's formalism is the most general one and free from any kinetic constraints. It is thus free from any restrictions in the OPP expansion methods. However, clear and straightforward interpretation of the calculated cumulants is rather difficult owing to its generality and its independence of kinematical models. In the OPP expansion method by Willis, the calculated OPP exhibits directions along which an atom can vibrate easily in crystals. It is this property that makes the Willis method attractive and important. Since anharmonic vibration of atoms is expected to be continuously enhanced when a temperature becomes higher or approaches a phase transition point (Sakata, Harada, Cooper & Rouse, 1980), Willis's method is applicable to studies on precursory phenomena of diffusion and phase transition in crystals. When the anharmonic vibration becomes so large that the OPP expansion methods cannot be applied, Matsubara's method for high-symmetry atoms, or Johnson's method, should be employed. Since in most of the electron-density studies anharmonic vibration is usually small, the Willis method is the most suitable one for these studies.

Willis's method has been applied in many studies of anharmonic vibration of atoms, as summarized in Table 1. However, its application has been limited to

atoms with cubic symmetries. The exceptions are the studies on Ag atoms in α -AgI crystals (Hoshino, Sakuma & Fujii, 1977) and in β -Ag₃SI crystals (Sakuma & Hoshino, 1980), on O atoms in BaTiO₃ crystals (Tanaka, Shiozaki & Sawaguchi, 1979) and on Cu atoms in KCuF₃ crystals (Tanaka & Marumo, 1982). The directions of the principal axes of the harmonic ellipsoid are coincident with those of lattice vectors due to symmetry restrictions in the studies on the Ag and the O atoms, while in the study on KCuF₃ crystals performed by the present method they are not coincident. Whiteley, Moss & Barnea (1978) extended the Willis method by introducing the integral I ,

$$I = \int_{-\infty}^{\infty} x^n \exp(-ax^2 - bx + i\gamma x) dx \\ = (i^n \sqrt{\pi}/2^n a^{(n+1)/2}) \exp[(b - i\gamma)^2/4a]$$

Table 1. List of analyses with Willis's method

Compounds	Atoms*	Methods†	References
Fluorite	O(43m)	N	Dawson, Hurley & Maslen (1967)
		N	Rouse, Willis & Pryor (1968)
CaF ₂	F(43m)	N	Dawson, Hurley & Maslen (1967)
		N	Rouse, Willis & Pryor (1968)
		X	Cooper (1970b)
		N	Cooper & Rouse (1971)
BaF ₂	F(43m)	X	Strock & Batterman (1972)
		N	Cooper, Rouse & Willis (1968)
		N	Willis (1969)
Mg ₂ Si	Mg(43m)	X	Cooper (1970a)
		N	Cooper & Rouse (1971)
SrF ₂	F(43m)	N	Mair & Barnea (1971)
		N	Mair, Barnea, Cooper & Rouse (1974)
		N	Prager & Harvey (1975)
		N	Prager & Harvey (1975)
AuGa ₂	Ga(43m)	N	Prager & Harvey (1975)
		N	Prager & Harvey (1975)
Diamond	Si(43m)	N	Dawson & Willis (1967)
		X	Roberto & Batterman (1970)
		N	Keating, Nunes, Batterman & Hastings (1971)
Ge	Ge(43m)	N	Dawson & Willis (1967)
Rocksalt	K, Cl(43m)	X	Willis (1969)
		N	Cooper & Rouse (1973)
Zinc blende	Zn, S(43m)	N	Cooper, Rouse & Fuess (1973)
		N	Cooper, Rouse & Fuess (1973)
		N	Harada, Suzuki & Hoshino (1976)
		N	Sakata, Hoshino & Harada (1974)
CuCl	Cu, Cl(43m)	N	Moss, McMullan & Koetzle (1980)
		N	Moss, McMullan & Koetzle (1980)
Wurtzite	Cd, Se(3m)	N	Whiteley, Moss & Barnea (1978)
		N	(see text)
Perovskite	Ba, Ti(m3m), O(4/mmm)	X	Tanaka, Shiozaki & Sawaguchi (1979)
		X	Tanaka, Shiozaki & Sawaguchi (1979)
Others	Ag(42m)	N	Hoshino, Sakuma & Fujii (1977)
		N	Sakuma & Hoshino (1980)
		X	Tanaka & Marumo (1982)
		X	Present study
		X	Present study
VAI _{10.42}	Al(43m)	X	Kontio & Stevens (1982)
		X	Tanaka & Marumo (1983)
α -Al ₂ O ₃	Al(3), O(2)	X	Tanaka & Marumo (1983)
		X	Tanaka & Marumo (1983)

* Point symmetries of investigated atoms are listed in parentheses.

† X: X-ray diffraction; N: neutron diffraction.

$$\times H_n[(\gamma + ib)/2\sqrt{a}],$$

where H_n is the n th-order Hermite polynomial of complex argument. Atoms in wurtzite-type ZnTe with the point symmetry $3m$ were studied by them. Kurki-Suonio, Merisalo & Peltonen (1979) applied their method to Zn crystals with the point symmetry $\bar{6}m2$. However, these methods are not simple and cannot be easily applied to a general case. Thus it is highly desirable to generalize the Willis method and to allow every crystallographer the routine use of it. The GTF of atoms at a general position was derived by Coppens (1978). The purpose of the present study is to formulate the GTF with the Willis treatment, which is performed independently from Coppens and to present basic relations necessary to incorporate the GTF into a conventional least-squares program.

Theoretical

Choice of basis coordinates

Now we deal with the GTF including anharmonic vibration effects following the Willis (1969) treatment. The first problem is how to choose basis coordinates by which temperature factors can be conveniently expressed. We choose the Cartesian coordinates with three axes parallel to the principal axes of the harmonic thermal ellipsoid; this is because the GTF can be formulated analytically on the coordinate following the Willis treatment, variables based on it can be refined simultaneously with the other variables based on the crystal-lattice system (see Appendix 1), and site-symmetry restrictions on anharmonic parameters are expressed for all 32 point symmetries in a simple way without losing generality.

Formalism of GTF

Assuming that an atom in a crystal vibrates independently of the other atoms, we can express the potential V of an atom in terms of the displacement vector \mathbf{u} from the equilibrium position as follows. \mathbf{u} is defined on the basis of the Cartesian coordinate system cited in the preceding paragraph.

$$\begin{aligned} V = & V_0 + \sum_i b_i u_i^2/2 + \sum_{i,j} c_{ijj} u_i u_j^2 + c_{123} u_1 u_2 u_3 \\ & + \sum_{i \leq j} q_{iijj} u_i^2 u_j^2 + \sum_{i \neq j} q_{iiij} u_i^3 u_j \\ & + \sum'_i q_{iijk} u_i^2 u_j u_k. \end{aligned} \quad (1)$$

Hereafter, \sum'_i means summation over i under the condition that subscripts i, j and k are different from each other. The u_i 's are the components of the displacement vector \mathbf{u} . There are ten c_{ijk} 's and fifteen q_{ijkl} 's. From now on we take the n -dimensional column vector as a matrix with n rows and 1 column. It is

convenient to express \mathbf{u} on the basis of the crystal-lattice system and we call it $\mathbf{u}'_c = (u'_1, u'_2, u'_3)'$; ' means a transposed matrix. \mathbf{u} is expressed by \mathbf{u}_c as

$$\mathbf{u} = \mathbf{A} \mathbf{u}_c \quad (2)$$

and

$$\mathbf{A} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{i}, \mathbf{b} \cdot \mathbf{i}, \mathbf{c} \cdot \mathbf{i} \\ \mathbf{a} \cdot \mathbf{j}, \mathbf{b} \cdot \mathbf{j}, \mathbf{c} \cdot \mathbf{j} \\ \mathbf{a} \cdot \mathbf{k}, \mathbf{b} \cdot \mathbf{k}, \mathbf{c} \cdot \mathbf{k} \end{pmatrix} \quad (3)$$

or

$$\mathbf{A}^{-1} = \begin{pmatrix} \mathbf{a}^* \cdot \mathbf{i}, \mathbf{a}^* \cdot \mathbf{j}, \mathbf{a}^* \cdot \mathbf{k} \\ \mathbf{b}^* \cdot \mathbf{i}, \mathbf{b}^* \cdot \mathbf{j}, \mathbf{b}^* \cdot \mathbf{k} \\ \mathbf{c}^* \cdot \mathbf{i}, \mathbf{c}^* \cdot \mathbf{j}, \mathbf{c}^* \cdot \mathbf{k} \end{pmatrix},$$

where \mathbf{i}, \mathbf{j} and \mathbf{k} are the unit vectors along the principal axes of the thermal ellipsoid, \mathbf{a}, \mathbf{b} and \mathbf{c} , and $\mathbf{a}^*, \mathbf{b}^*$ and \mathbf{c}^* are lattice vectors and reciprocal-lattice vectors, respectively. V is rewritten for the convenience of computing facilities as follows.

$$V = V_0 + \mathbf{u}' \mathbf{B} \mathbf{u}'/2 + \mathbf{u}' \mathbf{C} \mathbf{v} + c_{123} u_1 u_2 u_3 + \mathbf{v}' \mathbf{Q} \mathbf{w},$$

where \mathbf{v}' and \mathbf{w}' are the (1,3) and (1,6) matrices with the form (u_1^2, u_2^2, u_3^2) and $(u_1^2, u_2^2, u_3^2, u_2 u_3, u_3 u_1, u_1 u_2)$, respectively. \mathbf{B}, \mathbf{C} and \mathbf{Q} are matrices with the forms

$$\begin{aligned} \mathbf{B} &= \begin{pmatrix} b_1 & 0 & 0 \\ 0 & b_2 & 0 \\ 0 & 0 & b_3 \end{pmatrix}, & \mathbf{C} &= \begin{pmatrix} c_{111} & c_{122} & c_{133} \\ c_{211} & c_{222} & c_{233} \\ c_{311} & c_{322} & c_{333} \end{pmatrix}, \\ \mathbf{Q} &= \begin{pmatrix} q_{1111} & q_{1122} & q_{1133} & q_{1123} & q_{1131} & q_{1112} \\ 0 & q_{2222} & q_{2233} & q_{2223} & q_{2231} & q_{2212} \\ 0 & 0 & q_{3333} & q_{3323} & q_{3331} & q_{3312} \end{pmatrix}. \end{aligned}$$

The GTF is evaluated by taking the ensemble average of the potential in the classical limit,

$$\begin{aligned} T(\mathbf{S}) &= \langle \exp(2\pi i \mathbf{S} \cdot \mathbf{u}) \rangle \\ &= \int \exp(-V/k_B T) \exp(2\pi i \mathbf{S} \cdot \mathbf{u}) \mathbf{u} \\ &\quad \times [\int \exp(-V/k_B T) \mathbf{u}]^{-1}, \end{aligned} \quad (4)$$

where $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$. From (2), $\mathbf{S} \cdot \mathbf{u}$ is expressed in terms of \mathbf{u} as follows.

$$\begin{aligned} \mathbf{S} \cdot \mathbf{u} &= hu_1^c + ku_2^c + lu_3^c \\ &= \mathbf{h}' \mathbf{u}_c \\ &= \mathbf{h}' \mathbf{A}^{-1} \mathbf{u}, \end{aligned}$$

where $\mathbf{h}' = (h, k, l)$. If we put $\mathbf{H}' = (H_1, H_2, H_3) = 2\pi \mathbf{h}' \mathbf{A}^{-1}$, $\mathbf{S} \cdot \mathbf{u}$ becomes

$$\mathbf{S} \cdot \mathbf{u} = \mathbf{H}' \mathbf{u}/2\pi. \quad (5)$$

Following the Willis method, $T(\mathbf{S})$ is derived (see Appendix 2),

$$T(\mathbf{S}) = \exp\left(-\sum_i H_i^2 U_i/2\right) \{1 - (\xi_r - \eta_r + \zeta_r) - i(\xi_i - \eta_i)\}/(1 - \xi_r), \quad (6)$$

where

$$\xi_r = 3 \sum_i Q_{iii} U_i^2 + \sum_{i < j} Q_{ijj} U_i U_j,$$

$$\eta_r = 6 \sum_i Q_{iii} H_i^2 U_i^3 + \sum_{i < j} Q_{ijj} (H_i^2 U_i^2 U_j + H_j^2 U_i U_j^2) + 3 \sum_{i \neq j} Q_{ijj} H_i H_j U_i^2 U_j + \sum_i' Q_{ijk} H_j H_k U_i U_j U_k,$$

$$\zeta_r = \sum_i Q_{iii} H_i^4 U_i^4 + \sum_{i < j} Q_{ijj} H_i^2 H_j^2 U_i^2 U_j^2 + \sum_{i \neq j} Q_{ijj} H_i^3 H_j U_i^3 U_j + \sum_i' Q_{ijk} H_i^2 H_j H_k U_i^2 U_j U_k,$$

$$\xi_i = 3 \sum_i C_{iii} H_i U_i^2 + \sum_{i \neq j} C_{ijj} H_i U_i U_j,$$

$$\eta_i = \sum_i C_{iii} H_i^3 U_i^3 + \sum_{i \neq j} C_{ijj} H_i H_j^2 U_i U_j^2 + C_{123} H_1 H_2 H_3 U_1 U_2 U_3.$$

For U_i 's, C_{ijk} 's and Q_{ijk} 's, see Appendix 2. The imaginary part of $T(\mathbf{S})$ originates from the third-order terms of u_i 's in the potential V in (1). ξ_r, η_r, ζ_r and ξ_i, η_i are dependent on harmonic components U_i 's and are proportional to $k_B T$, $(k_B T)^2$ and $(k_B T)^3$, respectively. ζ_r is independent of \mathbf{S} . Denoting the harmonic temperature factor $\exp(-\sum_i H_i^2 U_i/2)$ as $T_h(\mathbf{S})$, we express $T(\mathbf{S})$ as

$$T(\mathbf{S}) = T_h(\mathbf{S})[T_q(\mathbf{S}) + iT_c(\mathbf{S})],$$

where

$$T_q(\mathbf{S}) = (1 - \xi_r + \eta_r - \zeta_r)/(1 - \xi_r)$$

$$T_c(\mathbf{S}) = (-\xi_i + \eta_i)/(1 - \xi_r).$$

As seen in (6), all the terms in ξ_r, η_r and ζ_r are of even powers of H_i and those in ξ_i and η_i are odd powers of H_i . Accordingly, $T_c(\mathbf{S})$ of the other Friedel pair changes its sign, while $T_q(\mathbf{S})$ does not.

In order to introduce $T_h(\mathbf{S})$ into least-squares programs based on the crystal-lattice system, we must derive the relation between U_i 's and U_{ij} 's defined in the conventional harmonic temperature factor $T_0(\mathbf{S})$ as

$$T_0(\mathbf{S}) = \exp\{-2\pi^2[h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2(hka^* b^* U_{12} + hla^* c^* U_{13} + klb^* c^* U_{23})]\} \\ = \exp(-2\pi^2 \mathbf{h}' \mathbf{N} \mathbf{U}_0 \mathbf{h}), \quad (7)$$

where \mathbf{N} is the diagonal matrix with reciprocal-lattice constants, a^*, b^* and c^* , as diagonal elements and \mathbf{U}_0 is the conventional thermal vibration tensor. $T_h(\mathbf{S})$ is expressed in the same way,

$$T_h(\mathbf{S}) = \exp(-\mathbf{H}' \mathbf{U}_h \mathbf{H}/2) \\ = \exp(-2\pi^2 \mathbf{h}' \mathbf{A}^{-1} \mathbf{U}_h \mathbf{A}^{-1'} \mathbf{h}), \quad (8)$$

where \mathbf{U}_h is the diagonal matrix with diagonal elements U_1, U_2 and U_3 , respectively. From (7) and (8),

$$\mathbf{A}^{-1} \mathbf{U}_h \mathbf{A}^{-1'} = \mathbf{N} \mathbf{U}_0 \mathbf{N}$$

or

$$\mathbf{U}_h = \mathbf{A} \mathbf{N} \mathbf{U}_0 \mathbf{N} \mathbf{A}' \\ = \mathbf{M} \mathbf{U}_0 \mathbf{M}',$$

where $\mathbf{M} = \mathbf{A} \mathbf{N}$.

Generalized structure factor

As Dawson (1967) pointed out, 'both at-rest charge distribution and nuclear smearing function due to thermal vibration may be non-centrosymmetric and hence they may be complex', the imaginary part of a temperature factor originates from the third-order non-centrosymmetric terms as shown in (6). Since the temperature factor of an atom at a symmetry-related position, as well as the scattering factor, are not necessarily the same as those of an atom at the original position, the generalized structure factor $F(\mathbf{S})$ is expressed as follows.

$$F(\mathbf{S}) = \sum_j^J a_j \sum_s^S f_{js}(\mathbf{S}) T_{js}(\mathbf{S}) \exp[2\pi i \mathbf{S} \cdot \mathbf{r}_{js}], \quad (9)$$

where $f_{js}(\mathbf{S})$ and $T_{js}(\mathbf{S})$ are the aspherical scattering factor and the temperature factor, respectively, of the j th atom at the s th symmetry-related position. J and S are the number of atoms in the asymmetric unit and the number of symmetry operations, respectively. $f_{js}(\mathbf{S})$ is expressed including the effects of anomalous dispersion as follows.

$$f_{js}(\mathbf{S}) = f_{js}^c(\mathbf{S}) + \Delta f_j' + [f_{js}^a(\mathbf{S}) + \Delta f_j''], \quad (10)$$

where superscripts c and a refer to the centrosymmetric and antisymmetric components, respectively. From (8), (9) and (10), we obtain

$$F(\mathbf{S}) = \sum_j^J a_j \sum_s^S [A_{js}(\mathbf{S}) + iB_{js}(\mathbf{S})],$$

where

$$A_{js}(\mathbf{S}) = [f_{js}^c(\mathbf{S}) + \Delta f_j'] \alpha_{js}^u - [f_{js}^a(\mathbf{S}) + \Delta f_j''] \beta_{js}^u, \\ B_{js}(\mathbf{S}) = [f_{js}^c(\mathbf{S}) + \Delta f_j'] \beta_{js}^u + [f_{js}^a(\mathbf{S}) + \Delta f_j''] \alpha_{js}^u, \quad (11) \\ \alpha_{js}^u = T_{js}^c \alpha_{js} - T_{js}^a \beta_{js}, \\ \beta_{js}^u = T_{js}^c \beta_{js} + T_{js}^a \alpha_{js},$$

Table 3. Symmetry restrictions on Q_{ijk}

* indicates symmetry-permitted independent parameters. $n_i i' j' k'$ in the column Q_{ijk} means that Q_{ijk} is equal to $Q_{i' j' k'}$, multiplied by n_i . N_{ind} is the number of independent parameters. Point symmetries with the same symmetry restrictions are put together in a row. For details, see text.

Point symmetry	Q_{1111}	Q_{1122}	Q_{1133}	Q_{2222}	Q_{2233}	Q_{3333}	Q_{1123}	Q_{1131}	Q_{1112}	Q_{2223}	Q_{2231}	Q_{2212}	Q_{3323}	Q_{3331}	Q_{3312}	N_{ind}
$1, \bar{1}$	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	15
$2(u_3 \parallel 2),$ $m(u_3 \perp m),$ $2/m(u_3 \parallel 2)$	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	9
$222, mm2,$ mmm	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	6
$4, 4, 4/m$	*	*	*	1111	1133	*	*	*	*	*	*	-1112	*	*	*	5
$422, 4mm,$ $42m, 4/mmm$	*	*	*	1111	1133	*	*	*	*	*	*	*	*	*	*	4
$3, \bar{3}$	*	2.1111	*	1111	1133	*	-3.2223	*	*	*	*	-3.1131	*	*	*	5
$32(u_1 \parallel 2),$ $3m(u_1 \perp m),$ $3m(u_1 \perp m)$	*	2.1111	*	1111	1133	*	-3.2223	*	*	*	*	*	*	*	*	4
$6, \bar{6}, 6/m,$ $622, 6mmm$ $6m2, 6/mmm$	*	2.1111	*	1111	1133	*	*	*	*	*	*	*	*	*	*	3
$23, m3, 432,$ $43m, m3m$	*	*	1122	1111	1122	1111	*	*	*	*	*	*	*	*	*	2

Restrictions are easily found from the fact that the potential energy in (1) is invariant under the operations of the point symmetry. They are summarized in Tables 2 and 3 for C_{ijk} 's and Q_{ijk} 's, respectively. The number of independent parameters in these tables are identical to those tabulated by Johnson (1969). However, restrictions are not the same as those tabulated by Johnson or those in *International Tables for X-ray Crystallography* (1974) since Johnson's formalism is based on the crystal-lattice system, and the present one is based on the Cartesian coordinate system described in the foregoing discussion.

In our least-squares program *LINKT80* (available on request) written by one of the authors (KT), one of the axes which has the largest directional cosine with the lattice vector \mathbf{a} or \mathbf{b} is assigned as u_1 or u_2 , respectively. Principal axes u_1 , u_2 and u_3 of harmonic thermal ellipsoids of atoms with triclinic, monoclinic or orthorhombic point symmetries are determined and assigned unequivocally from harmonic temperature factors. Those of atoms with cubic point symmetries are taken to be parallel to the lattice vectors. However, in the cases of tetragonal, trigonal and hexagonal point symmetries, we cannot determine u_1 and u_2 uniquely, while the u_3 axis is coincident with the main rotation axis X or rotational inversion axis \bar{X} . u_1 and u_2 axes for atoms with such point symmetries as X , \bar{X} and X/m (X is 3, 4 or 6) can be chosen to take any directions perpendicular to the main axis. As for the other tetragonal, trigonal and hexagonal point symmetries, u_1 and u_2 axes should be parallel to the diad rotation axis or perpendicular to the mirror plane which is parallel to the u_3 axis. ($u_i \parallel 2$) or ($u_i \perp m$) in the first column of

Tables 2 and 3 means that the u_i axis is parallel to the diad rotation axis or perpendicular to a mirror plane, respectively. The restrictions in the tables are valid for this special assignment of the u_i axis.

If the u_i axis is replaced by the u_j axis, we can obtain the new symmetry restrictions simply by exchanging i with j in C_{ijk} or Q_{ijk} , since the C_{ijk} 's and Q_{ijk} 's are symmetric with respect to all index permutations. For example, if the diad rotation axis of point symmetry 32 is assigned as u_2 , then the two parameters C_{111} and Q_{2223} are changed to C_{222} and Q_{1131} , respectively. Symmetry restrictions $C_{122} = -3C_{111}$ and $Q_{1123} = -3Q_{2223}$ are replaced by $C_{211} = -3C_{222}$ and $Q_{2231} = -3Q_{1131}$, respectively. The other restrictions of point symmetry 32 remain unaltered. The only exception to the axis exchange rule mentioned above is the case of point symmetry 42m. The replacement of ($u_1 \parallel 2$) by ($u_2 \parallel 2$) does not change the restriction. However, if it is replaced by ($u_1 \perp m$), then the independent parameter C_{123} is changed to C_{311} which is equal to $-C_{322}$ due to symmetry restriction.

Example of the analysis

(a) KCuF_3 crystals*

Since small anharmonic vibrations of atoms can be treated most properly by the Willis method, its

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38449 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

application to an electron density study is an interesting topic. The results can be interpreted easily by comparing them with difference density maps. In the previous paper (Tanaka & Marumo, 1982), the GTF of the Cu atom with the point symmetry mmm in crystals of $KCuF_3$ (space group $I4/mcm$) was determined at 296 K. GTF's of the other atoms, K, F(1) and F(2) with point symmetries 422 , $42m$ and $mm2$, respectively, were calculated as an example. The coordinates of K, F(1) and F(2) are $(0,0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{4})$ and $(0.22769,0.72769,0)$, respectively. As shown in Table 3, the K atom has six fourth-order anharmonic parameters, Q_{1111} , Q_{1122} , Q_{1133} , Q_{2222} , Q_{2233} and Q_{3333} , in which Q_{2222} and Q_{2233} are equal to Q_{1111} and Q_{1133} , respectively. u_1 , u_2 and u_3 axes were taken to be parallel to the a , b and c axes, respectively. F(1) has one third-order and three fourth-order independent parameters. u_1 , u_2 and u_3 axes were selected for both atoms to be parallel to $\mathbf{a} + \mathbf{b}$, $-\mathbf{a} + \mathbf{b}$ and \mathbf{c} , respectively. These parameters were refined simultaneously by fixing harmonic temperature factors. Parameter interactions between harmonic and anharmonic parameters were severe, while those between anharmonic parameters were small. The final $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_2 = \{ \sum (|F_o| - |F_c|)^2 / \sum F_o^2 \}^{1/2}$ were 0.0099 and 0.0096, respectively, for 888 reflexions with $\sin \theta / \lambda \leq 1.322 \text{ \AA}^{-1}$. R_1 and R_2 for 500 independent reflexions were 0.0077 and 0.0073, respectively. R_1 and R_2 values before the correction were 0.0084 and 0.0079, respectively, for the independent reflexions. Temperature factors of these atoms as well as that of the Cu atom were converted to the parameters of OPP in (1) and they are listed in Table 4, in which parameters with values greater than their standard deviations are marked with *. The number of reflexions perturbed by the anharmonic effect more than their statistical counting errors was 38 among 888 reflections. Perturbations in structure factors of 122 reflexions were greater than 0.1 in electron units.

Table 4. Harmonic ($\times 10^{-19} \text{ J \AA}^{-2}$) and anharmonic third-order ($\times 10^{-19} \text{ J \AA}^{-3}$) and fourth-order ($\times 10^{-19} \text{ J \AA}^{-4}$) potential parameters of atoms in $KCuF_3$ at 296 K

Values in parentheses are the e.s.d.'s.				
	Cu	K	F(1)	F(2)
b_1	6.343 (0.035)	2.650 (0.008)	1.833 (0.010)	5.442 (0.090)
b_2	4.667 (0.019)	b_1	b_1	2.062 (0.013)
b_3	7.127 (0.042)	2.828 (0.013)	5.684 (0.114)	2.055 (0.020)
c_{111}				-0.39 (0.28)*
c_{122}				-0.03 (0.26)
c_{133}				0.60 (0.27)*
c_{311}			0.56 (0.51)*	
c_{322}			$-c_{311}$	
q_{1111}	-6.30 (3.77)*	0.01 (0.15)	0.08 (0.22)	-2.30 (2.88)
q_{1122}	25.36 (4.27)*	-0.90 (0.79)*	0.96 (0.098)	6.63 (4.54)*
q_{1133}	2.33 (23.79)	0.84 (0.58)*	-3.44 (3.20)*	1.65 (4.61)
q_{2222}	-2.32 (1.66)*	q_{1111}	q_{1111}	-0.63 (0.36)*
q_{2233}	-5.96 (14.31)	q_{1133}	q_{1133}	0.78 (1.17)
q_{3333}	0.83 (2.13)	-0.33 (0.22)*	2.45 (3.17)	-0.33 (0.35)

(b) $\alpha\text{-Al}_2\text{O}_3$ crystals at 2170 K

This is an example of the application of the present method to low-symmetry atoms at high temperature. The X-ray data set has been measured and analyzed by Ishizawa, Miyata, Minato, Marumo & Iwai (1980). The experimental condition at 2170 K was too severe to collect accurate intensity data. However, the temperature was high enough for anharmonic thermal vibration to have a significant effect on intensity data.

The Al and O atoms have point symmetries 3 and 2, respectively. The u_1 , u_2 and u_3 axes of the Al atom were taken to be parallel to \mathbf{a} , $\frac{1}{2}\mathbf{a} + \mathbf{b}$ and \mathbf{c} , respectively, while the axes of the O atom were calculated from the harmonic temperature factors. The unit vectors along u_1 , u_2 and u_3 axes are

$$\mathbf{i} = 0.206\mathbf{a}$$

$$\mathbf{j} = 0.0935\mathbf{a} + 0.187\mathbf{b} - 0.0467\mathbf{c}$$

$$\mathbf{k} = 0.0739\mathbf{a} + 0.148\mathbf{b} + 0.0591\mathbf{c}$$

Since the u_1 axis is coincident with the twofold axis, $u_3 \parallel 2$ in Tables 2 and 3 is changed to $u_1 \parallel 2$. Following the axis exchange rule mentioned previously, the parameters C_{3jj} and Q_{H12} were changed to C_{1jj} and Q_{H23} , respectively. The calculated potential parameters are tabulated in Table 5. Detailed discussions of them are presented elsewhere (Tanaka & Marumo, 1983). After the correction R_1 and R_2 values were reduced from 0.035 and 0.038 to 0.033 and 0.034, respect-

Table 5. Harmonic ($\times 10^{-19} \text{ J \AA}^{-2}$) and anharmonic third-order ($\times 10^{-19} \text{ J \AA}^{-3}$) and fourth-order ($\times 10^{-19} \text{ J \AA}^{-4}$) potential parameters of atoms in $\alpha\text{-Al}_2\text{O}_3$

Values in parentheses are the e.s.d.'s.		
	Al	O
b_1	10.22 (0.33)	10.98 (0.64)
b_2	b_1	13.15 (0.68)
b_3	11.55 (0.33)	9.34 (0.32)
c_{111}	0.03 (0.56)	4.06 (1.86)*
c_{122}	$-3c_{111}$	-4.03 (5.75)
c_{133}		-7.13 (3.27)*
c_{211}	$-3c_{222}$	
c_{222}	0.11 (0.47)	
c_{311}	0.94 (0.92)*	
c_{322}	c_{311}	
c_{333}	-0.80 (0.76)*	
c_{123}		-6.33 (6.76)
q_{1111}	1.68 (1.46)*	16.71 (9.70)*
q_{1122}	$2q_{1111}$	-117.8 (70.7)*
q_{1133}	-16.28 (12.10)*	-9.80 (33.78)
q_{2222}	q_{1111}	20.35 (17.39)*
q_{2233}	q_{1133}	13.23 (39.54)
q_{3333}	6.54 (4.78)*	0.14 (5.71)
q_{1123}	$-3q_{2223}$	-37.19 (53.30)
q_{1131}	1.91 (9.00)	
q_{2223}	-4.15 (8.59)	12.13 (33.19)
q_{2231}	$-3q_{1131}$	
q_{3323}		1.83 (21.98)

ively. The number of reflexions perturbed by anharmonic effects more than their statistical counting errors was only one out of 76 reflexions. However, perturbations in structure factors of 63 reflexions were greater than 0.1 in electron units.

Discussion

Willis's treatment assumes that the anharmonic potential V_a is much smaller than $k_B T$, and that $(V_a/k_B T)^2$ and higher terms are negligible. V_a is always larger than $k_B T$ further from an atom. However, the amplitude of the atomic vibration is limited. Thus we judge the validity of the Willis treatment from the $(V_a/k_B T)$ value at the root-mean-square displacement (r.m.s.d.) of the atom which is calculated from the harmonic temperature factor T_h . In Table 6, r.m.s.d.'s along the principal axes of the thermal ellipsoid of each atom and $V_a/k_B T$ at r.m.s.d.'s are tabulated. Apparently the assumption is valid in the present examples. The ratios of anharmonic potentials of the third-order V_c to the fourth-order V_q at r.m.s.d.'s of the F(2) atom along the u_1 axis is 1.96. It is apparent that V_c and V_q have values of the same order. Thus the assumption that V_q is negligibly small compared to V_a is not always valid.

Willis's treatment of anharmonic vibration gives us the OPP in such a manner as to reveal preferred directions of atomic vibrations. Thus in accurate studies there is a close correspondence between OPP and difference-Fourier maps. Positive peaks are observed where anharmonic potentials are negative and *vice versa*. In the examples of KCuF_3 crystals, the significant anharmonic potential of the K atom on the plane $u_3 = 0$ is $-0.90u_1^2u_2^2$ as shown in Table 4.

Table 6. The ratio of V_a to $k_B T$ at r.m.s.d. along the u_i axis from each atom

Vectors in parentheses indicate the direction of the u_i axes.

Atom	Point symmetry	Axis	R.m.s.d. (Å)	$V_a/k_B T$
Cu	<i>mmm</i>	u_1 (a + b)	0.0803	-6.41×10^{-3}
		u_2 (-a + b)	0.0936	-4.36×10^{-3}
		u_3 (c)	0.0757	6.68×10^{-4}
K	422	u_1 (a)	0.1242	5.82×10^{-5}
		u_2 (b)	0.1242	5.82×10^{-5}
		u_3 (c)	0.1202	-1.69×10^{-3}
F(1)	42 <i>m</i>	u_1 (a + b)	0.149	6.82×10^{-3}
		u_2 (-a + b)	0.149	6.82×10^{-3}
		u_3 (c)	0.141	3.10×10^{-3}
F(2)	<i>mm2</i>	u_1 (a + b)	0.0867	-9.39×10^{-3}
		u_2 (-a + b)	0.141	-6.06×10^{-3}
		u_3 (c)	0.141	-3.20×10^{-3}
Al	3	u_1 (a)	0.171	4.82×10^{-3}
		u_2 (a/2 + b)	0.171	4.82×10^{-3}
		u_3 (c)	0.161	3.52×10^{-3}
O	2	u_1	0.165	1.02×10^{-1}
		u_2 (see text)	0.151	3.53×10^{-2}
		u_3	0.179	1.87×10^{-3}

Equi-potential curves of it are two rectangular hyperbolae which correspond to the four leaves around the K atoms in Fig. 1(a). They became spherical after the correction as shown in Fig. 1(b). F(2) has four significant anharmonic parameters as shown in Table 4. The difference-Fourier map on the plane $u_3 = 0$ is depicted in Fig. 2(a). Equi-potential curves of the F(2) atom calculated from the significant anharmonic terms on the same plane are also shown in Fig. 3. To the right of the F(2) atom, a positive peak is found in Fig. 2(a) and V_a is negative around this area in Fig. 3. After the anharmonic vibration correction all these peaks became less pronounced as shown in Fig. 2(b). The F(1) atom has four significant parameters. However, they are approximately equal to their standard deviations, and the difference-Fourier map shows only a slight improvement after the correction.

Little correlation between the third- and fourth-order anharmonic parameters may be because the former is the component of the imaginary part of the temperature factor while the latter is that of the real part. As pointed out by Cooper & Rouse (1973) and Mair, Barnea, Cooper & Rouse (1974), correlation between harmonic and anharmonic parameters was so severe

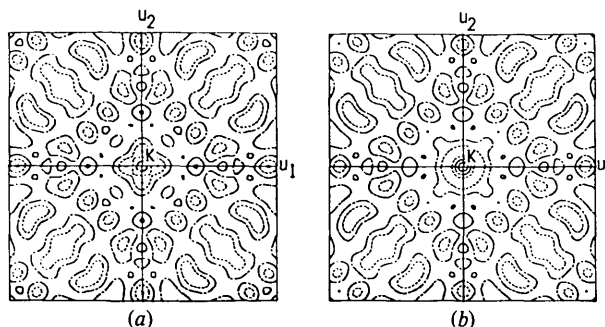


Fig. 1. Sections of the difference-Fourier map around K (a) before and (b) after the anharmonic vibration analysis. Contours are at intervals of $0.1 \text{ e } \text{Å}^{-3}$. Negative and zero contours are in broken and dashed-dotted lines, respectively.

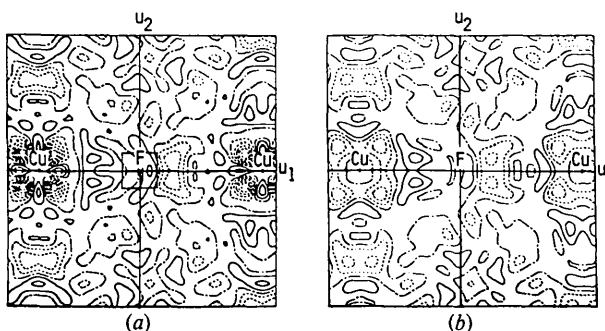


Fig. 2. The sections on the difference-Fourier map on the plane $u_3 = 0$ around F(2) (a) before and (b) after the anharmonic vibration analysis. Contours are the same as in Fig. 1. The square around the F(2) atom in (a) indicates the area, the potential of which is shown in Fig. 3.

that the simultaneous refinement of them was almost impossible, and harmonic temperature factors were fixed during the refinement. It is probable that T_h is determined including a part of the anharmonic effect as well as that of the harmonic one, and it might be the remaining anharmonic effect that is corrected for in the subsequent refinement. However, this is not a serious problem since each term in V_a except $c_{iii}u_i^3$ and $q_{iiii}u_i^4$ specifically expresses thermal vibrations along such directions as harmonic terms in T_h cannot represent. When $c_{iii}u_i^3$ and $q_{iiii}u_i^4$ are comparable to $b_i u_i^2$, the $b_i u_i^2$ are possibly refined to include a significant part of the anharmonic vibration effect. In the case of small anharmonic vibration, T_h may not be affected significantly by anharmonic effects, since fitting second-order harmonic terms to the higher-order terms, which has a much less pronounced effect, may produce many more discrepancies than those without the correction. If T_h is perturbed by anharmonic vibration significantly, new ghost peaks would be expected to appear on difference-Fourier maps. When anharmonic terms up to fourth order cannot express an atomic vibration along some special direction, fifth- or sixth-order terms should be employed. Since the potential of the O atom in Table 5 with the very low symmetry revealed ridges and valleys of the potential along lines connecting neighboring O atoms (Tanaka & Marumo, 1983), parameters up to fourth order, however, are expected to be sufficient.

Sakata & Harada (1979) pointed out in the study of CuCl crystals by neutron diffraction that parasitic peaks appear on Fourier and difference-Fourier maps without correction for anharmonic odd-order terms, since imaginary components of a temperature factor shift a phase in a structure factor. In the case of an X-ray study this problem also occurs even in crystals with a center of symmetry. $B_{js}(\mathbf{S})$ in (11) is, in this case,

$$B_{js}(\mathbf{S}) = \Delta f_{js}'' \alpha_{js}^u.$$

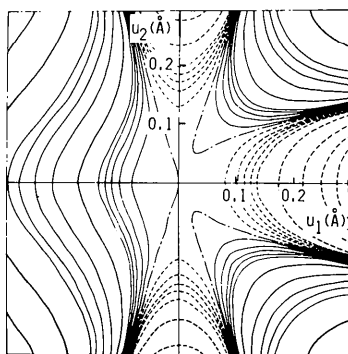


Fig. 3. Potential around F(2) on the square shown in Fig. 2(a). Contours in thin and thick lines are at intervals of 2×10^{-23} and 2×10^{-22} J, respectively. Broad lines at the extreme left on (a) are at intervals of 2×10^{-21} J. Negative and zero contours are in broken and dashed-dotted lines, respectively.

Accordingly, the phase-shift problem occurs if the dispersion effect is significant. Since $\Delta f_{js}''$ is a constant value, it is comparable to $f_{js}^c(\mathbf{S})$ and $f_{js}^a(\mathbf{S})$ in high-angle reflexions where the effect of anharmonic vibration is prominent. In studies of anharmonic vibration by X-rays, the dispersion effect should not be ignored. In fact most of the parasitic peaks in Fig. 2(a) disappeared in Fig. 2(b) after the correction.

We must add at most 25 more parameters per atom to the conventional least-squares procedure. It seems too many compared to their effect on structure factors. However, it is not necessary to use all of the symmetry-permitted parameters, since not all of the anharmonic parameters are always significant. Thus they can be omitted from the refinement. Refinement with all of the symmetry-permitted parameters and with effective parameters gave essentially the same results in the present studies on KCuF₃ and α -Al₂O₃ crystals.

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APPENDIX 1

Let us consider the case with N variables, p_1, p_2, \dots, p_N , to be refined by the least-squares method for M structure factors, F_1, F_2, \dots, F_M . We assume that n variables p_1, p_2, \dots, p_n are transformed from q_1, q_2, \dots, q_n based on another coordinate system by the linear transformation, that is

$$q_i = \sum_{k=1}^n g_{ik} p_k \quad (i = 1, 2, \dots, n). \quad (A1)$$

We define the column vectors \mathbf{p} and \mathbf{q} with elements $p_1, p_2, \dots, p_n, p_{n+1}, \dots, p_N$ and $q_1, q_2, \dots, q_n, p_{n+1}, \dots, p_N$, respectively. Then

$$\mathbf{q} = \mathbf{G}\mathbf{p}, \quad (A2)$$

where \mathbf{G} is a square matrix with elements

$$(\mathbf{G})_{ij} = \begin{cases} g_{ij} & \text{for } i \leq n \text{ and } j \leq n \\ \delta_{ij} & \text{elsewhere.} \end{cases}$$

δ_{ij} is the Kronecker delta. We assume here that there exists an inverse matrix of \mathbf{G} . Following the usual procedure, the normal equation is obtained,

$$\mathbf{D}' \mathbf{D}\mathbf{p} = \mathbf{D}' \mathbf{v}, \quad (A3)$$

where \mathbf{D} is a matrix with M rows and N columns with elements $(\mathbf{D})_{ij} = \partial F_i / \partial p_j$ and \mathbf{v} is the column vector with M elements v_1, v_2, \dots, v_M defined as the difference between observed and calculated structure factors. When $j \leq n$, $(\mathbf{D})_{ij}$ is obtained from (A1) as

$$(\mathbf{D})_{ij} = \sum_{k=1}^n (\partial F_i / \partial q_k) g_{kj}.$$

Accordingly,

$$\mathbf{D} = \mathbf{D}_q \mathbf{G}, \quad (A4)$$

where \mathbf{D}_q is a matrix with M rows and N columns with elements

$$(\mathbf{D}_q)_{ij} = \begin{cases} \partial F_i / \partial q_j & \text{for } j \leq n \text{ and } i \leq N \\ \partial F_i / \partial p_j & \text{for } j > n \text{ and } i \leq N. \end{cases}$$

Putting (A2) and (A4) into (A3), we obtain

$$\mathbf{D}'_q \mathbf{D}_q \mathbf{q} = \mathbf{D}'_q \mathbf{v}. \quad (A5)$$

It is evident that if the normal equation (A3) holds for \mathbf{p} then the normal equation (A5) holds for \mathbf{q} .

Anharmonic parameters based on the crystal-lattice system and on the principal-axes system have a linear relationship to each other. The relationship among anharmonic parameters of an atom with point symmetry mmm in space group $I4/mcm$ is derived as an example. The principal axes of the thermal ellipsoid point along $\mathbf{a} + \mathbf{b}$, $-\mathbf{a} + \mathbf{b}$ and \mathbf{c} , respectively, in this case. From (2) and (3),

$$\begin{aligned} u_1 &= a(u_1^c + u_2^c) / \sqrt{2} \\ u_2 &= a(-u_1^c + u_2^c) / \sqrt{2} \\ u_3 &= cu_3^c. \end{aligned} \quad (A6)$$

From (1) and Table 3, the anharmonic potential is

$$V_a = \sum_{i \neq j} \sum q_{iijj} u_i^2 u_j^2. \quad (A7)$$

Putting (A6) into (A7), we obtain

$$\begin{aligned} V_a &= a^4(q_{1111} + q_{2222} + q_{1122})(u_1^{c4} + u_2^{c4})/4 \\ &+ a^4(3q_{1111} + 3q_{2222} - q_{1122})u_1^{c2}u_2^{c2}/2 \\ &+ a^2c^2(q_{1133} + q_{2233})(u_1^{c2} + u_2^{c2})u_3^{c2}/2 \\ &+ c^4q_{3333}u_3^{c4} \\ &+ a^4(q_{1111} - q_{2222})(u_1^{c3}u_2^c + u_1^cu_2^{c3}) \\ &+ a^2c^2(q_{1133} - q_{2233})u_1^cu_2^cu_3^{c2}. \end{aligned}$$

Thus the anharmonic parameters based on the crystal-lattice system are expressed as the linear combination of q_{iijj} 's based on the principal-axes system.

$$\begin{aligned} q_{1111}^c &= a^4(q_{1111} + q_{2222} + q_{1122})/4 \\ q_{1122}^c &= a^4(3q_{1111} + 3q_{2222} - q_{1122})/2 \\ q_{1133}^c &= a^2c^2(q_{1133} + q_{2233})/2 \\ q_{2222}^c &= q_{1111}^c \\ q_{2233}^c &= q_{1133}^c \\ q_{3333}^c &= c^4q_{3333} \\ q_{1112}^c &= a^4(q_{1111} - q_{2222}) \\ q_{2212}^c &= q_{1112}^c \\ q_{3312}^c &= a^2c^2(q_{1133} - q_{2233}) \end{aligned}$$

Accordingly six q_{iijj} 's can be refined in the usual way with the least-squares method instead of q_{1111}^c , q_{1122}^c , q_{1133}^c , q_{3333}^c , q_{1112}^c and q_{3312}^c .

APPENDIX 2

Assuming that an anharmonic potential V_a , which is equal to $\mathbf{u}' \mathbf{C} \mathbf{v} + c_{123} u_1 u_2 u_3 + \mathbf{v}' \mathbf{Q} \mathbf{w}$, is small compared with $k_B T$, the numerator M in (4) becomes, in the general case,

$$M = \exp(-V_0/k_B T) \int \exp(-V_h/k_B T) (1 - V_a/k_B T) \times \exp(i\mathbf{H}' \mathbf{u}) d\mathbf{u},$$

where V_h is a harmonic potential and equal to $\mathbf{u}' \mathbf{B} \mathbf{u}/2$. We replace $b_i/k_B T$, $c_{ijk}/k_B T$ and $q_{iijk}/k_B T$ by B_i , C_{ijk} and Q_{iijk} , respectively, and we put

$$\begin{aligned} I_i^{2n} &= \int_{-\infty}^{\infty} u_i^{2n} \exp(-B_i u_i^2/2) \cos(H_i u_i) du_i \\ I_i^{2n+1} &= \int_{-\infty}^{\infty} u_i^{2n+1} \exp(-B_i u_i^2/2) \sin(H_i u_i) du_i. \end{aligned}$$

Then M becomes

$$\begin{aligned} M &= \exp(-V_0/k_B T) \left\{ I_1^0 I_2^0 I_3^0 - i \left(\sum_i' C_{iii} I_i^3 I_i^0 I_i^0 \right. \right. \\ &+ \sum_{i \neq j} C_{ijj} I_i^1 I_j^2 I_k^0 - C_{123} I_1^1 I_2^1 I_3^1 \left. \right) \\ &- \left(\sum_i' Q_{iiii} I_i^4 I_j^0 I_k^0 + \sum_{i < j} Q_{iijj} I_i^2 I_j^2 I_k^0 \right. \\ &\left. \left. - \sum_{i \neq j} Q_{iiij} I_i^3 I_j^1 I_k^0 - \sum_i' Q_{iijk} I_i^2 I_j^1 I_k^1 \right) \right\}, \quad (A8) \end{aligned}$$

where suffixes i, j and k are different from each other. The I_i^n are evaluated as

$$I_i^0 = (2\pi/B_i)^{1/2} \exp(-H_i^2/2B_i),$$

$$I_i^1 = (H_i/B_i) I_i^0,$$

$$I_i^2 = (1/B_i - H_i^2/B_i^2) I_i^0,$$

$$I_i^3 = (3H_i/B_i^2 - H_i^3/B_i^3) I_i^0,$$

$$I_i^4 = (3/B_i^2 - 6H_i^2/B_i^3 + H_i^4/B_i^4) I_i^0.$$

Inserting I_i^n 's into (A8), we obtain

$$M = \exp(-V_0/k_B T) I_1^0 I_2^0 I_3^0 \{1 - (\xi_r - \eta_r + \zeta_r) - i(\xi_i - \eta_i)\} \quad (A9)$$

(for $\xi_{r,i}$, $\eta_{r,i}$ and ζ_r , see text). Similarly, if we replace integrals

$$\int_{-\infty}^{\infty} u_i^{2n} \exp(-B_i u_i^2) du_i$$

by J_i^{2n} ($n = 0, 1, 2$), the denominator N in (4) is evaluated as

$$N = \exp(-V_0/k_B T) \left\{ J_1^0 J_2^0 J_3^0 - \left(\sum_i' Q_{iii} J_i^4 J_j^0 J_k^0 + \sum_{i<j} Q_{ijj} J_i^2 J_j^2 J_k^0 \right) \right\}, \quad (A10)$$

where subscripts i, j and k are different from each other again. The J_i^{2n} are evaluated as

$$J_i^0 = (2\pi/B_i)^{1/2},$$

$$J_i^2 = (1/B_i) J_i^0,$$

and

$$J_i^4 = (3/B_i^2) J_i^0.$$

Putting these into (A10), N becomes

$$N = \exp(-V_0/k_B T) (8\pi^3/B_1 B_2 B_3)^{1/2} (1 - \xi_r). \quad (A11)$$

From (A9) and (A11), $T(\mathbf{S})$ is derived:

$$T(\mathbf{S}) = \exp\left(-\sum_i H_i^2 U_i/2\right) \{1 - (\xi_r - \eta_r + \zeta_r) - i(\xi_i - \eta_i)\} / (1 - \xi_r),$$

where $U_i = 1/B_i = k_B T/b_i$.

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