The Identification of Phonon–Phonon Interactions in Anharmonic Crystals by X-Ray Diffraction Data *

A. G. Tsarkov and V. G. Tsirelson

Department of Physics, Mendeleev Institute of Chemical Technology, Moscow, Russia

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The effect of anharmonic atomic vibrations on the elastic scattering of X-rays by a crystal is treated by time-independent perturbation theory. The complete expression for the anharmonic temperature factor (TF) in the high-temperature limit is presented for atoms in general positions. The phonon–phonon interactions in an anharmonic crystal may be identified with X-ray diffraction data by using various temperature and scattering vector $\boldsymbol{q}$ dependencies of different anharmonic contributions to the TF. The expression for the intensity of elastic scattering by an anharmonic crystal contains an additional factor – the anharmonic cross-term. This term has to be taken into account for obtaining the unbiased thermal parameters of fourth order in $|\boldsymbol{q}|$ from X-ray diffraction data.

Key words: Lattice vibrations; Anharmonicity; Phonon–phonon interactions; Temperature factor; X-ray diffraction.

1. Introduction

For interpreting the structural information derived from X-ray diffraction data the direct problem of X-ray diffraction by a crystal has to be solved taking into account thermal atomic vibrations. The Debye–Waller theory [1] achieves this by assuming harmonicity of atomic thermal vibrations. However, strictly speaking the harmonic approximation is not valid even at absolute zero because of the zero-point vibrations [2]. Besides, the properties of some crystals (for example, ferroelectrics, superionics, high-temperature superconductors and others) have to be discussed by taking into account the anharmonicity of thermal atomic vibrations even at low temperatures.

Within the framework of the theory of lattice dynamics, anharmonic effects in X-ray scattering by crystals (as in other physical phenomena [3]) are treated by two main methods: (i) time-independent perturbation theory [4–9] and (ii) the Green-function formalism [10, 11]. Perturbation theory is the basis of both methods. It allows to treat an anharmonic crystal as a system of (weakly) interacting phonons. Then the small anharmonic terms in the expansion of the crystal potential in terms of atomic displacements from their equilibrium positions describe just phonon–phonon interactions in such a crystal. The lifetime of interacting phonons is finite and their energy is not equal to that of harmonic (non-interacting) phonons. Therefore, the transition from the harmonic approximation to the anharmonic one results in changing the intensity of the thermal diffuse X-ray scattering (TDS) (inelastic scattering of X-rays by phonons) and, hence, also that of elastic scattering.

The anharmonic effects in the TDS were investigated in detail in our previous work [9]. The anharmonic contributions to the temperature factor (TF) has been given in the general case (for atoms in sites of arbitrary symmetry and at any temperature) by the Green-function method [10, 11] and also in the special case (for atoms in centro-symmetric sites) by Kashiwase [6] by using time-independent perturbation theory. There are some differences between the results of [6, 10, 11].

In this work we discuss the effect of anharmonic atomic vibrations on the elastic scattering of X-rays by a crystal, special attention being paid to treating and interpreting the anharmonic effects in the TF. The expressions for the intensity of elastic scattering and the anharmonic TF are presented below without a detailed derivation, which was given in [8].

2. Theory and Results

The solution of the problem of X-ray diffraction in the general anharmonic approximation for thermal

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Reprint requests to Prof. Dr. Vladimir G. Tsirelson, Mendeleev Institute for Chemical Technology, Miusskaja pl. d. 9, Moskva-125190, Russia.

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atomic vibrations can be obtained by Kashiwase's approach [6] when the following approximations are used. (i) The intensity of scattered X-rays is considered within the framework of the kinematic scattering theory; the adiabatic approximation and the convolution approximation [12] are used. (ii) Anharmonic effects are considered using time-independent perturbation theory. The terms up to second order in the anharmonicity order parameter λ are taken into account (the anharmonic part of the lattice Hamiltonian is presented by $W = \lambda \cdot \Phi_3 + \lambda^2 \cdot \Phi_4$, where Φ_3 and Φ_4 are terms of third and fourth order in the anharmonic crystal potential expansion in terms of atomic displacements; λ is equated to unity at the end of calculation). (iii) Anharmonic effects are discussed in the high-temperature limit ($T > \Theta_{\mathrm{D}}$, Θ_{D} is the characteristic Debye temperature) where the anharmonic effects are expected to be largest.

The stated approximations allow to obtain the following expression for the intensity of elastic scattering [6, 8]:

$$I_0 = \sum_{\mu\mu'} F_\mu^*(\boldsymbol{q})\, F_{\mu'}(\boldsymbol{q}) \exp\{-\Delta M_{\mu\mu'}(\boldsymbol{q})\} \cdot L(\boldsymbol{q}) \,, \quad (1)$$

where

$$F_\mu(\boldsymbol{q}) = f_\mu(\boldsymbol{q})\, T_\mu(\boldsymbol{q}) \exp\{i\, \boldsymbol{q}\, \boldsymbol{r}_\mu\} \,. \quad (2)$$

Here $\boldsymbol{r}_\mu$ describes the equilibrium position of the μth atom in the unit cell; $\boldsymbol{q}$ is the scattering vector; f_μ is the atomic scattering amplitude of the μth atom; $T_\mu(\boldsymbol{q})$ is the anharmonic temperature factor; $L(\boldsymbol{q})$ is Laue's interference function; $\Delta M_{\mu\mu'}$ is an anharmonic two-particle term.

Taking into account anharmonicity of thermal atomic vibrations results in changing the form of the TF (see below). Besides, the expression for the intensity of elastic scattering is found to contain an additional factor – the anharmonic cross-term $\Delta M_{\mu\mu'}$. It is caused by inelastic scattering processes and results from the interaction of phonons describing the vibrations of atoms of different kind in the unit cell [8]. We do not give the complicated expression for this term here, which has been presented for the general case (for atoms at sites of arbitrary symmetry, at any temperature) and also in the high- and low-temperature limits in [8]. The anharmonic cross-term is found to be of second order in λ and to have the following dependencies on the scattering vector $\boldsymbol{q}$ and on the temperature (in the high-temperature limit):

$$\Delta M_{\mu\mu'} = \Delta M_{\mu\mu'}(T^3, |\boldsymbol{q}|^4) \,. \quad (3)$$

Following Kashiwase [6], the anharmonic TF is presented by

$$T_\mu(\boldsymbol{q}) = \exp\{-(M_{\mathrm{a}}^\mu + M_{\mathrm{b}}^\mu + M_{\mathrm{c}}^\mu + M_{\mathrm{d}}^\mu + M_{\mathrm{e}}^\mu + M_{\mathrm{f}}^\mu + M_{\mathrm{g}}^\mu + M_{\mathrm{h}}^\mu)\} \,. \quad (4)$$

Here M_{a}^μ is the zero-order (quasiharmonic) term. The other terms describe "net" anharmonic effects, the imaginary terms M_{b}^μ and M_{c}^μ of first order in λ (equal to zero for atoms at centrosymmetric sites) and the real terms M_{d}^μ to M_{h}^μ of second order in λ resulting from four-phonon interactions and pairs of three-phonon ones, respectively. The expressions for M_{a}^μ to M_{h}^μ in the high-temperature limit are detailed in Appendix A. The corresponding expressions for arbitrary temperature are given in [8].

3. Discussion

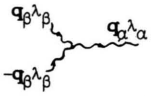
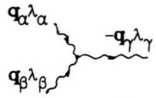
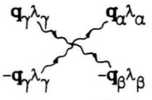
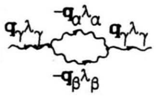
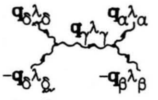
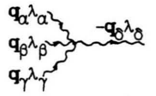
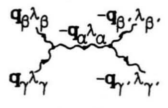
The characteristics of different contributions to the anharmonic TF exponent are given in Table 1.

In the second column of Table 1 the diagrams of phonon–phonon interactions contributing to the anharmonic TF are depicted; wavy lines that enter and leave a vertex (a region of the phonon–phonon interaction) represent phonons due to annihilation and creation processes, respectively. For each term in (4) only one of several possible diagrams is given. For each diagram the momentum conservation condition is presented. The third column indicates the order of the term in λ (the anharmonicity-order parameter). It is further shown in the table whether a term is real or imaginary, how the point-group symmetry of the atomic position affects the magnitude of a term and how the term depends on the scattering vector $\boldsymbol{q}$ and on the temperature (in the high-temperature limit).

The data in Table 1 demonstrate that the anharmonic terms in the TF exponent have different dependencies on the temperature and on the scattering vector $\boldsymbol{q}$ and can be associated with different interactions of phonons in an anharmonic crystal. As a result it is, in principle, possible to study phonon–phonon interactions by discussing thermal parameters of different order as a function of $|\boldsymbol{q}|$ from X-ray diffraction data measured at different temperatures.

Expression (3) and Table 1 show that $\Delta M_{\mu\mu'}(\boldsymbol{q})$ and M_{g}^μ, M_{h}^μ are of same order in λ and depend in the same way on the scattering vector $\boldsymbol{q}$ and on the temperature. This fact leads to an important conclusion: when the intensity of elastic scattering is expressed as a product

Table 1. Characteristics of different contributions to the anharmonic temperature factor exponent.

Term in (4)	Phonon–phonon interaction	Order in λ	Character of value	Influence of point group sym.	Dependency on	
					T ($T > \Theta_D$)	$\lvert \boldsymbol{q} \rvert$
1	2	3	4	5	6	7
M_a^μ		0	$M_a^\mu = \mathrm{Re}\{M_a^\mu\}$		T	$\lvert \boldsymbol{q} \rvert^2$
M_b^μ	 $\mathbf{q}_\alpha=0$	1	$M_b^\mu = i \cdot \mathrm{Im}\{M_b^\mu\}$	*	T	$\lvert \boldsymbol{q} \rvert$
M_c^μ	 $\mathbf{q}_\alpha+\mathbf{q}_\beta+\mathbf{q}_\gamma=\mathbf{h}_1$	1	$M_c^\mu = i \cdot \mathrm{Im}\{M_c^\mu\}$	*	T^2	$\lvert \boldsymbol{q} \rvert^3$
M_d^μ	 $\mathbf{q}_\beta=\mathbf{q}_\alpha$	2	$M_d^\mu = \mathrm{Re}\{M_d^\mu\}$		T^2	$\lvert \boldsymbol{q} \rvert^2$
M_e^μ	 $\mathbf{q}_\alpha+\mathbf{q}_\beta+\mathbf{q}_\gamma=\mathbf{h}_1$	2	$M_e^\mu = \mathrm{Re}\{M_e^\mu\}$		T^2	$\lvert \boldsymbol{q} \rvert^2$
M_f^μ	 $\mathbf{q}_\gamma=0 \quad \mathbf{q}_\beta=\mathbf{q}_\alpha$	2	$M_f^\mu = \mathrm{Re}\{M_f^\mu\}$	**	T^2	$\lvert \boldsymbol{q} \rvert^2$
M_g^μ	 $\mathbf{q}_\alpha+\mathbf{q}_\beta+\mathbf{q}_\gamma+\mathbf{q}_\delta=\mathbf{h}_2$	2	$M_g^\mu = \mathrm{Re}\{M_g^\mu\}$		T^3	$\lvert \boldsymbol{q} \rvert^4$
M_h^μ	 $\mathbf{q}_\alpha+\mathbf{q}_\beta+\mathbf{q}_\gamma=\mathbf{h}_1$ $-\mathbf{q}_\alpha+\mathbf{q}_{\beta'}+\mathbf{q}_{\gamma'}=\mathbf{h}_1'$	2	$M_h^\mu = \mathrm{Re}\{M_h^\mu\}$		T^3	$\lvert \boldsymbol{q} \rvert^4$

* The term is not equal to zero only for atoms at noncentrosymmetric sites.

** The term is not equal to zero only for atoms of a polyatomic lattice.

of structure amplitudes and used for deriving atomic thermal parameters of fourth order in $|\boldsymbol{q}|$, X-ray diffraction data should be previously corrected for the anharmonic cross-term. The value of the cross-term may be determined with a model calculation. Otherwise, fourth-order anharmonic parameters, derived by the least-squares method, will be biased by the value of the ignored cross-term.

The following remarks may be made when comparing the expression obtained for the anharmonic TF by Kashiwase's approach [8] in the general case and presented here in the high-temperature limit (see (A.1)), with corresponding expressions obtained with the Green-function method [10, 11]. The results of [11] and the expression (4) are identical when all δ-functions are set equal to zero and minor errors in the TF formula in [11] are eliminated (see M_c^μ, M_g^μ, M_h^μ in (4) and the corresponding terms in [11]). Cowley [10] has derived an incomplete TF expression where the terms M_b^μ and M_f^μ of (4) have not been evaluated, where expressions for the "self-energy" terms M_d^μ and M_e^μ have not been presented, and where the one for the term analogous to M_h^μ of (4) contains minor errors. After elimination of these errors in (8.8) of [10], the results of [8] and [10] become identical. Thus, some discrepancies between the results of [10] and [11] (as was noted in [11]) has simple explanation.

4. Conclusions

Within the framework of Kashiwase's approach [6] the complete expression for the anharmonic TF was derived in the high-temperature limit for atoms in general positions. The terms not higher than second-order ones in λ are taken into account. Anharmonic terms in the TF exponent, which have different dependencies on the temperature and on the scattering vector $\boldsymbol{q}$, are caused by different interactions of phonons in an anharmonic crystal. This fact allows to identify phonon–phonon interactions by X-ray diffraction data. However, it is essential that atomic thermal parameters of fourth order in $|\boldsymbol{q}|$ obtained from X-ray diffraction data may be biased when ignoring the anharmonic cross-term in the intensity of elastic scattering.

Appendix A

The expressions for different contributions to the exponent of $T_\mu(\boldsymbol{q})$ in the high-temperature limit ($T > \Theta_{\mathrm{D}}$) are represented below:

$$M_{\mathrm{a}}^{\mu} = \frac{k_{\mathrm{B}} T}{2 s N} \cdot \sum_{\alpha} \frac{|\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu}|^2}{m_\mu\, \omega_\alpha^2} ;$$

$$M_{\mathrm{b}}^{\mu} = i\, \frac{k_{\mathrm{B}} T}{2 s N} \cdot \sum_{\alpha \beta} \frac{\Phi_{-\alpha, \beta, -\beta}}{\omega_\alpha^2\, \omega_\beta^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu})}{m_\mu^{1/2}} ;$$

$$M_{\mathrm{c}}^{\mu} = i\, \frac{(k_{\mathrm{B}} T)^2}{6 (s N)^2} \cdot \sum_{\alpha, \beta, \gamma} \frac{\Phi_{\alpha \beta \gamma}}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma)^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu *})\, (\boldsymbol{q}\, \boldsymbol{e}_{\beta}^{\mu *})\, (\boldsymbol{q}\, \boldsymbol{e}_{\gamma}^{\mu *})}{m_\mu^{3/2}} \cdot \exp(i\, \boldsymbol{h}_1\, \boldsymbol{r}_\mu);$$

$$M_{\mathrm{d}}^{\mu} = -\frac{(k_{\mathrm{B}} T)^2}{4 (s N)^2} \cdot \sum_{\alpha, \beta, \gamma} \frac{\Phi_{-\alpha, \beta, \gamma, -\gamma}}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma)^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu})\, (\boldsymbol{q}\, \boldsymbol{e}_{\beta}^{\mu *})}{m_\mu} ;$$

$$M_{\mathrm{e}}^{\mu} = \frac{(k_{\mathrm{B}} T)^2}{4 (s N)^2} \cdot \sum_{\alpha, \beta, \gamma} \frac{|\Phi_{\alpha \beta \gamma}|^2}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma^2)^2} \cdot \frac{|\boldsymbol{q}\, \boldsymbol{e}_{\gamma}^{\mu *}|^2}{m_\mu} ;$$

$$M_{\mathrm{f}}^{\mu} = \frac{(k_{\mathrm{B}} T)^2}{4 (s N)^2} \cdot \sum_{\alpha, \beta, \gamma, \delta} \frac{\Phi_{-\alpha, \beta, \gamma}\, \Phi_{-\gamma, \delta, -\delta}}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma\, \omega_\delta)^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu})\, (\boldsymbol{q}\, \boldsymbol{e}_{\beta}^{\mu *})}{m_\mu} ;$$

$$M_{\mathrm{g}}^{\mu} = \frac{(k_{\mathrm{B}} T)^3}{24 (s N)^3} \cdot \sum_{\alpha, \beta, \gamma, \delta} \frac{\Phi_{\alpha \beta \gamma \delta}}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma\, \omega_\delta)^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\alpha}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\beta}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\gamma}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\delta}^{\mu *})}{m_\mu^2} \cdot \exp\{i\, \boldsymbol{h}_2\, \boldsymbol{r}_\mu) ;$$

$$M_{\mathrm{h}}^{\mu} = -\frac{(k_{\mathrm{B}} T)^3}{8 (s N)^3} \cdot \sum_{\alpha, \beta, \gamma, \beta', \gamma'} \frac{\Phi_{\alpha \beta \gamma}\, \Phi_{-\alpha, \beta', \gamma'}}{(\omega_\alpha\, \omega_\beta\, \omega_\gamma\, \omega_{\beta'}\, \omega_{\gamma'})^2} \cdot \frac{(\boldsymbol{q}\, \boldsymbol{e}_{\beta}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\gamma}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\beta'}^{\mu *}) (\boldsymbol{q}\, \boldsymbol{e}_{\gamma'}^{\mu *})}{m_\mu^2} \exp(i\, \boldsymbol{h}_3\, \boldsymbol{r}_\mu) . \tag{A.1}$$

Here k_{B} is the Boltzmann constant; s is the number of atoms in the unit cell; N is the number of unit cells in the crystal; m_μ is the mass of the μth atom; $\boldsymbol{e}_\alpha^\mu$ and ω_α are, respectively, the unit polarisation vector of the μth atom and the frequency of the αth phonon that belongs to the λ_αth branch and has the wave vector $\boldsymbol{q}_\alpha$ ($\alpha \equiv (\boldsymbol{q}_\alpha \lambda_\alpha)$). The anharmonic parameters $\Phi_{\alpha\beta\gamma}$ and $\Phi_{\alpha\beta\gamma\delta}$ represent the Fourier transforms of the coupling parameters of third and of fourth order, respectively. $\boldsymbol{h}_1$, $\boldsymbol{h}_2$, and $\boldsymbol{h}_3$ are reciprocal lattice vectors that satisfy the relations

$$\boldsymbol{h}_1 = \boldsymbol{q}_\alpha + \boldsymbol{q}_\beta + \boldsymbol{q}_\gamma; \quad \boldsymbol{h}_2 = \boldsymbol{q}_\alpha + \boldsymbol{q}_\beta + \boldsymbol{q}_\gamma + \boldsymbol{q}_\delta;$$
$$\boldsymbol{h}_3 = \boldsymbol{q}_\beta + \boldsymbol{q}_\gamma + \boldsymbol{q}_{\beta'} + \boldsymbol{q}_{\gamma'} . \tag{A.2}$$

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