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Anisotropic Thermal Vibrations and Dynamical Electron Diffraction by Crystals

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Abstract

The effect of anisotropy in thermal vibrations on dynamical electron diffraction by a crystal is investigated. Expressions are first derived for both the elastic and thermal diffuse scattering (TDS) absorptive atomic scattering amplitudes for the general case of anisotropic thermal vibrations. These expressions are then used to calculate the complex structure factors for an $SrTiO_3$ single crystal at 293K. It is shown that the errors introduced by using an averaged Debye–Waller factor are typically of the order 1–5% for low- and medium-order reflections.

1. Introduction

In the usual dynamical theory of electron diffraction, the interaction between the incident fast electrons and the crystal is described by a simple periodic potential $V(\mathbf{r})$ (Bethe, 1928; Hirsch, Howie, Nicholson, Pashley & Whelan, 1977; Cowley, 1990; Reimer, 1989; Spence & Zuo, 1992). The wave function involved in the wave equation is assumed to be a single-electron wave function that depends only on the coordinate $\mathbf{r}$ of the incident fast electron. This is, however, a very simplified version of the complicated scattering processes of the electron by a crystal. A crystal is a very complex system of electrons and nuclei that can be excited by the incident and scattered electrons (Ohtsuki, 1983; Reimer, 1989; Wang, 1995; Egerton, 1986). The scattering processes are therefore complicated many-body processes and in general the problem cannot be solved exactly. Instead, an effective potential called optical potential or pseudopotential is introduced to include the complication of many-body interactions (Yoshioka, 1957; Dederichs, 1972; Dudarev, Peng & Whelan, 1992).

For dynamical electron diffraction by a crystal, the optical potential may be divided into two parts, of which the first part is the *averaged potential* and the second part is the *deviation* from the averaged potential. Since the averaged potential is time independent, scattering events involving this part suffer no energy losses and the term is usually referred to as the *elastic potential*. For a real crystal, the deviation from the averaged periodic potential is aperiodic and time dependent. Scattering events involving this deviation potential are therefore associated with *diffuse and inelastic scattering*. It has now been firmly established that among the major inelastic mechanisms, *i.e.* thermal diffuse scattering (TDS), plasmon and inner-shell electronic excitations, TDS contribution dominates over the other two by an order of magnitude for $\mathbf{g} \neq 0$ (Whelan, 1965; Hall & Hirsch, 1965; Humphreys & Hirsch, 1968; Radi, 1970; Rez, 1976). In this paper, we are concerned only with the TDS contribution to the optical potential.

The subject of TDS in electron diffraction has been discussed extensively by many researches, see for example Hall & Hirsch (1965), Rossouw & Bursill (1985), Bird & King (1990), Allen & Rossouw (1989), Dudarev, Peng & Ryazanov (1991), Dudarev, Peng & Whelan (1993*b*, 1995) and Peng, Ren, Dudarev & Whelan (1996). All these studies assumed, however, that the thermal vibrations are isotropic. It is the aim of this paper to investigate the effect of anisotropy in thermal vibrations on dynamical electron diffraction and to shown that for a typical material the anisotropy in thermal vibrations is not negligible. In §2, we will first present a formal derivation of the optical potential for high-energy electron diffraction by a crystal. The general formula will then be used in §§3 and 4 to give general expressions for the elastic and absorptive atomic scattering amplitudes for the general case of anisotropic thermal vibrations. Numerical results are given in §5 for a single crystal of $SrTiO_3$. It is shown that the errors introduced by using an averaged Debye–Waller factor are typically of the order of a few percent for low- and medium-order reflections.

2. Optical potential

In this section, we present a formal derivation of the optical potential for high-energy electron diffraction by a crystal. Following Dederichs (1972), we write the total Hamiltonian of the system as

$$H = h_0 + H_0 + V, \tag{1}$$

in which $h_0 = -(h^2/8\pi^2 m)\nabla^2$ is the free Hamiltonian of the incident electron, H_0 is the Hamiltonian for all the electrons and nuclei of the crystal, and V represents the interaction of the incident electron with the crystal. In general, V depends on all the coordinates of the electrons and nuclei of the crystal, *i.e.*

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$V = V(\mathbf{r}, \ldots, \mathbf{r}_n, \ldots, \mathbf{r}_j, \ldots)$, where $\mathbf{r}_n$ and $\mathbf{r}_j$ denote the coordinates of the nth nucleus and ith crystal electron, respectively. If the incident electron and the crystal are well separated, we have the following expression and equation for the incident plane-wave function:

$$\varphi_k = \exp(i\mathbf{k}\cdot\mathbf{r}), \quad h_0\varphi_k = (h^2/8\pi^2 m)k^2\varphi_k = E_k\varphi_k \quad (2)$$

and for the crystal

$$\phi_\alpha = \phi_\alpha(\ldots, \mathbf{r}_n, \ldots, \mathbf{r}_j, \ldots), \quad H_0\phi_\alpha = E_\alpha\phi_\alpha. \quad (3)$$

In the course of dynamical electron diffraction by a crystal, the incident electron wave function is usually not separable from that of the crystal. Let $\Psi_{k,\alpha} = \Psi_{k,\alpha}(\mathbf{r}, \ldots, \mathbf{r}_n, \ldots, \mathbf{r}_j, \ldots)$ be the total wave function, then we have for the whole system

$$(h_0 + H_0 + V)\Psi_{k,\alpha} = (E_k + E_\alpha)\Psi_{k,\alpha}. \quad (4)$$

To obtain a formal solution of (4), we write

$$\Psi_{k,\alpha} = \varphi_k\phi_\alpha + \Phi_{k,\alpha}. \quad (5)$$

Substitution of (5) into (4) leads to a differential equation

$$(E_k + E_\alpha - H_0 - h_0)\Phi_{k,\alpha} = V\Psi_{k,\alpha}. \quad (6)$$

Symbolically, this equation may be solved with the help of a free-particle Green function G_0, defined as

$$G_0 = 1/(E_k + E_\alpha + i\varepsilon - H_0 - h_0), \quad (7)$$

to give

$$\Phi_{k,\alpha} = G_0 V\Psi_{k,\alpha}, \quad (8)$$

in equation (7), ε is a small quantity.

Substitution of (8) into (5) gives the famous Lippmann–Schwinger equation (Schiff, 1968)

$$\Psi_{k,\alpha} = \varphi_k\phi_\alpha + G_0 V\Psi_{k,\alpha}. \quad (9)$$

The concept of the *optical potential* is introduced to take into account the effect of many-body interactions on the elastic component of the total wave function. By elastic scattering, we mean those processes for which the initial and final states of the crystal are identical. For the total state $\Psi_{k,\alpha}$, the elastic component is defined as

$$\begin{aligned}\psi_{k,\alpha}(\mathbf{r}) &= \langle\phi_\alpha|\Psi_{k,\alpha}(\mathbf{r})\rangle \\ &= \int \ldots \mathrm{d}\mathbf{r}_n \ldots \mathrm{d}\mathbf{r}_j \ldots\ \phi_\alpha^*(\ldots, \mathbf{r}_n, \ldots, \mathbf{r}_j, \ldots) \\ &\quad \times \Psi_{k,\alpha}(\mathbf{r}, \ldots, \mathbf{r}_n, \ldots, \mathbf{r}_j, \ldots). \quad (10)\end{aligned}$$

By averaging (10) over the thermal distribution of the initial crystal states ϕ_α, we obtain for the elastic wave function

$$\begin{aligned}\psi_k(\mathbf{r}) &= \langle\psi_{k,\alpha}\rangle \\ &= (1/\mathcal{Z})\sum_\alpha \exp(-E_\alpha/k_BT)\langle\phi_\alpha|\Psi_{k,\alpha}(\mathbf{r})\rangle, \quad (11)\end{aligned}$$

in which

$$\mathcal{Z} = \sum_\alpha \exp(-E_\alpha/k_BT). \quad (12)$$

Having defined the elastic wave function (11), we now seek to find an equation for this elastic wave function. The optical potential V^{op} is introduced for this purpose. The definition equation for the optical potential is similar to the Lippmann–Schwinger equation (9)

$$\psi_k = \varphi_k + G_0 V^{\mathrm{op}}\psi_k, \quad (13)$$

but now only the elastic wave function is involved. By writing $V = V^{\mathrm{op}} + (V - V^{\mathrm{op}})$ and using equation (9), we obtain

$$\Psi_{k,\alpha} = [1/(1 - G_0 V^{\mathrm{op}})]\varphi_k\phi_\alpha + G_V(V - V^{\mathrm{op}})\Psi_{k,\alpha}, \quad (14)$$

where

$$\begin{aligned}G_V &= [1/(1 - G_0 V^{\mathrm{op}})]G_0 \\ &= 1/(E_k + E_\alpha + i\varepsilon - H_0 - h_0 - V^{\mathrm{op}}). \quad (15)\end{aligned}$$

To manipulate (14) even further, we multiply (13) from the right-hand side by ϕ_α and, after some algebra, we obtain

$$\psi_k\phi_\alpha = [1/(1 - G_0 V^{\mathrm{op}})]\varphi_k\phi_\alpha. \quad (16)$$

Substitution of (16) into (14) gives

$$\begin{aligned}\Psi_{k,\alpha} &= \psi_k\phi_\alpha + G_V(V - V^{\mathrm{op}})\Psi_{k,\alpha} \\ &= \{1/[1 - G_V(V - V^{\mathrm{op}})]\}\psi_k\phi_\alpha \\ &= \Big(1 + G_V(V - V^{\mathrm{op}})\{1/[1 - G_V(V - V^{\mathrm{op}})]\}\Big)\psi_k\phi_\alpha. \quad (17)\end{aligned}$$

Multiplying (17) from the left by ϕ_α and performing the average, *i.e.* $\langle\cdots\rangle$, of the equation obtained over the initial states using equation (11), we obtain

$$\begin{aligned}\langle\psi_{k,\alpha}\rangle &= \psi_k \\ &= \psi_k + [1/(E_k + i\varepsilon - h_0 - V^{\mathrm{op}})] \\ &\quad \times \Big\langle(V - V^{\mathrm{op}})\{1/[1 - G_V(V - V^{\mathrm{op}})]\}\Big\rangle\psi_k, \quad (18)\end{aligned}$$

which gives

$$0 = \Big\langle (V - V^{\rm op})\{1/[1 - G_V(V - V^{\rm op})]\}\Big\rangle$$
$$= \Big\langle (V - V^{\rm op})\Big[1 + \{1/[1 - G_V(V - V^{\rm op})]\} \times G_V(V - V^{\rm op})\Big]\Big\rangle \qquad (19)$$

and finally

$$V^{\rm op} = \langle V\rangle + \Big\langle (V - V^{\rm op})\{1/[1 - G_V(V - V^{\rm op})]\} \times G_V(V - V^{\rm op})\Big\rangle$$
$$= \langle V\rangle + \Big\langle (V - V^{\rm op}) \times [1/(E_k + E_\alpha + i\varepsilon - h_0 - H_0 - V)](V - V^{\rm op})\Big\rangle, \qquad (20)$$

and this is the equation for the optical potential. For high-energy electron diffraction, the interaction between the incident electrons and the crystal is relatively weak, *i.e.* $V << E_k$, we may neglect V in the denominator and iterate equation (20) up to second order to obtain

$$V^{\rm op} \simeq V^{(0)} + V^{(1)} \qquad (21)$$

with

$$V^{(0)} = \langle V\rangle, \qquad (22)$$

being the averaged potential and

$$V^{(1)} = \Big\langle (V - \langle V\rangle)[1/(E_k + E_\alpha + i\varepsilon - h_0 - H_0)] \times (V - \langle V\rangle)\Big\rangle \qquad (23)$$

being the first-order correction due to diffuse scattering. Recent quantitative electron diffraction work shown that this approximation works with high precision (Zuo, Spence & O'Keeffe, 1988; Zuo & Spence, 1991; Spence & Zuo, 1992; Saunders *et al.*, 1995; Ren, Zuo & Peng, 1997).

3. The averaged potential

In the preceding section, we have derived a general expression (21) for the optical potential in which the first term on the right-hand side is simply the averaged crystal potential. Since this term is time independent, scattering by this averaged potential does not involve energy losses and is therefore called elastic scattering.

For TDS and to a good approximation, we may assume that the atomic electrons follow adiabatically the motion of nucleus and that all atomic electrons are in their ground states (Ashcroft & Mermin, 1976). The interacting potential is then given by

$$V(\mathbf{r}, \ldots, \mathbf{r}_n, \ldots) = \sum_n \Big\{ - Z_n e^2/|\mathbf{r} - \mathbf{r}_n| + \textstyle\int (e^2/|\mathbf{r} - \mathbf{R}' - \mathbf{r}_n|)\rho_n^0(\mathbf{R}')\,\mathrm{d}\mathbf{R}'\Big\}$$
$$= \sum_n \int \mathrm{d}\mathbf{R}\,\varphi_n(\mathbf{r} - \mathbf{R})\delta(\mathbf{R} - \mathbf{r}_n), \qquad (24)$$

in which Z_n is the atomic number and $\rho_n^0(\mathbf{R}')$ is the electron density of the nth atom in its ground state, the summation on n is over all atoms in the crystal and $\varphi_n(\mathbf{r})$ is given by

$$\varphi_n(\mathbf{r}) = -Z_n e^2/r + \textstyle\int (e^2/|\mathbf{r} - \mathbf{R}'|)\rho_n^0(\mathbf{R}')\,\mathrm{d}\mathbf{R}'. \qquad (25)$$

Let $\mathbf{r}_n = \mathbf{R}_n + \mathbf{u}_n$, where $\mathbf{R}_n$ denotes the equilibrium position of the nth atom and $\mathbf{u}_n$ represents the thermal displacement of the atom from its thermal equilibrium position, we have for the averaged potential

$$\langle V(\mathbf{r})\rangle = \sum_n \int \mathrm{d}\mathbf{R}\,\varphi_n(\mathbf{r} - \mathbf{R})\langle \delta(\mathbf{R} - \mathbf{R}_n - \mathbf{u}_n)\rangle. \qquad (26)$$

The Fourier coefficients of the averaged potential is given by

$$V_g = (1/V)\textstyle\int \langle V(\mathbf{r})\rangle \exp(-i\mathbf{g}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r}$$
$$= -(h^2/8\pi^2 m_0)(4\pi/\Omega) \times \sum_i f_i^B(s) T_i(\mathbf{g}) \exp(-i\mathbf{g}\cdot\mathbf{R}_i), \qquad (27)$$

in which m_0 is the rest mass of the electron, V and Ω are the volume of the crystal and a unit cell, respectively, $f_i^B(s)$ is the *Born atomic scattering amplitude* (Cowley, 1992) with $\mathbf{s} = \mathbf{g}/4\pi$, $T_i(\mathbf{g})$ is the *temperature factor* (Willis & Pryor, 1975) of the ith atom, and the summation on i is over a unit cell. In (27), the Born atomic scattering amplitude is related to $\varphi_i(\mathbf{r})$ *via* the following relation:

$$f_i^B(\mathbf{g}) = -(2\pi m_0/h^2)\textstyle\int \varphi_i(\mathbf{r}) \exp(-i\mathbf{g}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad (28)$$

and for a harmonic crystal the temperature factor is given by

$$T_i(\mathbf{g}) = \langle \exp(-\mathbf{g}\cdot\mathbf{u}_i)\rangle = \exp[-\tfrac{1}{2}\langle(\mathbf{g}\cdot\mathbf{u}_i)^2\rangle]. \qquad (29)$$

Let $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ be the real-space lattice vectors and $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ be the reciprocal-space lattice vectors such that

$$\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}.$$

In terms of these vectors, a real-space displacement vector $\mathbf{u}$ can be expressed as

$$\mathbf{u} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3, \tag{30}$$

and a reciprocal-space vector $\mathbf{g}$ as

$$\mathbf{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, \tag{31}$$

we then have

$$\begin{aligned}\langle(\mathbf{g}\cdot\mathbf{u})^2\rangle &= h^2\langle u_1^2\rangle + k^2\langle u_2^2\rangle + l^2\langle u_3^2\rangle \\ &\quad + 2hk\langle u_1u_2\rangle + 2hl\langle u_1u_3\rangle + 2kl\langle u_2u_3\rangle.\end{aligned} \tag{32}$$

In matrix notation the above expression can be written as

$$(\mathbf{g}\cdot\mathbf{u})^2 = (h\,k\,l)\begin{pmatrix}u_1\\u_2\\u_3\end{pmatrix}(u_1\,u_2\,u_3)\begin{pmatrix}h\\k\\l\end{pmatrix} = \mathbf{G}^T(\mathbf{X}\mathbf{X}^T)\mathbf{G},$$

where $\mathbf{G}$ and $\mathbf{X}$ are 3×1 column vectors and their transpose are given by

$$\mathbf{G}^T = (h\,k\,l),$$

and

$$\mathbf{X}^T = (u_1\,u_2\,u_3).$$

The temperature factor (29) then becomes

$$\mathcal{T}_i(\mathbf{g}) = \exp(-\mathbf{G}^T\beta_i\mathbf{G}), \tag{33}$$

in which the matrix $\beta = \frac{1}{2}\langle\mathbf{X}\mathbf{X}^T\rangle$ is a symmetric matrix,

$$\beta = \tfrac{1}{2}\langle\mathbf{X}\mathbf{X}^T\rangle = \tfrac{1}{2}\begin{pmatrix}\langle u_1^2\rangle & \langle u_1u_2\rangle & \langle u_1u_3\rangle\\ \langle u_2u_1\rangle & \langle u_2^2\rangle & \langle u_2u_3\rangle\\ \langle u_3u_1\rangle & \langle u_3u_2\rangle & \langle u_3^2\rangle\end{pmatrix}, \tag{34}$$

and is usually referred to as the *mean-square displacement matrix*. In X-ray crystallography, the general anisotropic vibration parameters are usually given as the elements of a $\mathbf{U}$ matrix that are related to that of the β matrix by the relation

$$\beta_{ij} = 2\pi^2U_{ij}b_ib_j. \tag{35}$$

Explicitly, the anisotropic temperature factor is given by

$$\begin{aligned}\mathcal{T}(\mathbf{g}) = \exp\{-2\pi^2[&U_{11}(hb_1)^2 + U_{22}(kb_2)^2 + U_{33}(lb_3)^2 \\ &+ 2U_{12}(hb_1)(kb_2) + 2U_{13}(hb_1)(lb_3) \\ &+ 2U_{23}(kb_2)(lb_3)]\}.\end{aligned} \tag{36}$$

Experimentally, U_{ij} may be obtained by fitting quantitatively the calculated X-ray beam intensities with the experimentally measured X-ray intensities using the general anisotropic temperature factor (Giacovazzo, 1992).

4. The absorptive potential

In this section, we consider the first-order correction to the average potential. This correction is represented by the second term of (21). In real-space representation, substituting equations (24) and (26) into (23) gives

$$\begin{aligned}V^{(1)}(\mathbf{r},\mathbf{r}') = \sum_{i,j}\Big\langle &\iint \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{R}'\varphi_i(\mathbf{r}-\mathbf{R}) \\ &\times [\delta(\mathbf{R}-\mathbf{r}_i) - \langle\delta(\mathbf{R}-\mathbf{r}_i)\rangle] \\ &\times \Big\langle\mathbf{r}\Big|[1/(E_k + E_\alpha + i\varepsilon - h_0 - H_0)]\Big|\mathbf{r}'\Big\rangle \\ &\times \varphi_j(\mathbf{r}'-\mathbf{R}')[\delta(\mathbf{R}'-\mathbf{r}_j) - \langle\delta(\mathbf{R}'-\mathbf{r}_j)\rangle]\Big\rangle.\end{aligned} \tag{37}$$

For thermal diffuse scattering, since the energies of phonons are much smaller than the energy of the incident electrons, we may neglect E_α and H_0 in (37) to obtain

$$\begin{aligned}V^{(1)}(\mathbf{r},\mathbf{r}') = (8\pi^2m/h^2)&\sum_{i,j}\iint \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{R}'\varphi_i(\mathbf{r}-\mathbf{R}) \\ &\times G_0(\mathbf{r},\mathbf{r}')\varphi_j(\mathbf{r}'-\mathbf{R}') \\ &\times \Big\langle\delta(\mathbf{R}-\mathbf{r}_i)\delta(\mathbf{R}'-\mathbf{r}_j) \\ &- \langle\delta(\mathbf{R}-\mathbf{r}_i)\rangle\langle\delta(\mathbf{R}'-\mathbf{r}_j)\rangle\Big\rangle,\end{aligned} \tag{38}$$

where

$$\begin{aligned}&G_0(\mathbf{r},\mathbf{r}') \\ &\quad = (h^2/8\pi^2m)\langle\mathbf{r}|[1/(E_k + i\varepsilon - h_0)]|\mathbf{r}'\rangle \\ &\quad = -(1/4\pi)[\exp(ik_0|\mathbf{r}-\mathbf{r}'|)]/|\mathbf{r}-\mathbf{r}'| \\ &\quad = [1/(2\pi)^3]\int\{\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]\}/(\mathbf{k}_0^2-\mathbf{k}^2)\,\mathrm{d}\mathbf{k}\end{aligned} \tag{39}$$

is the free-space Green function (see for example Dudarev, Peng & Whelan, 1993*a*). When the equation acts on the dynamical electron wave function, we have

$$\begin{aligned}V^{(1)}\psi_k &= \int V^{(1)}(\mathbf{r},\mathbf{r}')\psi_k(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \\ &= -(2\pi m/h^2)\sum_{i,j}\int \mathrm{d}\mathbf{r}'\psi_k(\mathbf{r}') \\ &\quad \times \{[\exp(ik_0|\mathbf{r}-\mathbf{r}'|)]/|\mathbf{r}-\mathbf{r}'|\}\iint \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{R}' \\ &\quad \times \varphi_i(\mathbf{r}-\mathbf{R})\varphi_j(\mathbf{r}'-\mathbf{R}')\Big\langle\delta(\mathbf{R}-\mathbf{r}_i)\delta(\mathbf{R}'-\mathbf{r}_j) \\ &\quad - \langle\delta(\mathbf{R}-\mathbf{r}_i)\rangle\langle\delta(\mathbf{R}'-\mathbf{r}_j)\rangle\Big\rangle.\end{aligned} \tag{40}$$

In equation (40), we note that the integrand depends on the phase difference between wave scattered at $\mathbf{r}$ and $\mathbf{r}'$ *via* a rapidly oscillating function $\exp(ik_0|\mathbf{r}-\mathbf{r}'|)$. Contributions from different atoms with $i \neq j$ will be cancelled out with each other after the integration. We may therefore retain in the summation only those terms with $i = j$. This simplification is equivalent to the use of an Einstein model for TDS (Hall & Hirsch, 1965).

Equation (40) then becomes

$$\begin{aligned} V^{(1)}\psi_k = &- (2\pi m/h^2) \sum_i \int \mathrm{d}\mathbf{r}' \psi_k(\mathbf{r}') \\ &\times [\exp(ik_0|\mathbf{r} - \mathbf{r}'|)/|\mathbf{r} - \mathbf{r}'|] \iint \mathrm{d}\mathbf{R}\, \mathrm{d}\mathbf{R}' \\ &\times \varphi_i(\mathbf{r} - \mathbf{R})\varphi_i(\mathbf{r}' - \mathbf{R}')\Big\langle \delta(\mathbf{R} - \mathbf{r}_i)\delta(\mathbf{R}' - \mathbf{r}_i) \\ &- \langle \delta(\mathbf{R} - \mathbf{r}_i)\rangle\langle \delta(\mathbf{R}' - \mathbf{r}_i)\rangle \Big\rangle. \end{aligned} \tag{41}$$

Fourier transforming equation (41) leads to

$$\begin{aligned} \mathcal{F}V^{(1)}\psi_k = &[1/(2\pi)^3](2\gamma h^2/m_0\Omega) \int [\mathrm{d}\mathbf{k}/(k_0^2 - k^2 + i\varepsilon)] \\ &\times \sum_i \int \mathrm{d}\mathbf{h} f_i^B(\mathbf{g} - \mathbf{k}) f_i^B(\mathbf{k} - \mathbf{h})\psi(\mathbf{h}) \\ &\times \Big(\langle \exp[-i(\mathbf{g} - \mathbf{h}) \cdot \mathbf{r}_i]\rangle \\ &- \langle \exp[-i(\mathbf{g} - \mathbf{k}) \cdot \mathbf{r}_i]\rangle \\ &\times \langle \exp[-i(\mathbf{k} - \mathbf{h}) \cdot \mathbf{r}_i]\rangle\Big) \\ = &\int V^{\mathrm{TDS}}(\mathbf{g}, \mathbf{h})\psi(\mathbf{h})\, \mathrm{d}\mathbf{h}, \end{aligned} \tag{42}$$

in which $\psi(\mathbf{h})$ is the Fourier transform of the elastic wave function

$$\psi(\mathbf{h}) = [1/(2\pi)^3] \int \psi_k(\mathbf{r}) \exp(-i\mathbf{g} \cdot \mathbf{r})\mathrm{d}\mathbf{r} \tag{43}$$

and

$$\begin{aligned} V^{\mathrm{TDS}}(\mathbf{g}, \mathbf{h}) = &[1/(2\pi)^3](2\gamma h^2/m_0\Omega) \int [\mathrm{d}\mathbf{k}/(k_0^2 - k^2 + i\varepsilon)] \\ &\times \sum_i f_i^B(\mathbf{g} - \mathbf{k}) f_i^B(\mathbf{k} - \mathbf{h}) \\ &\times \exp[-i(\mathbf{g} - \mathbf{h}) \cdot \mathbf{R}_i] \\ &\times \{\langle \exp[-i(\mathbf{g} - \mathbf{h}) \cdot \mathbf{u}_i]\rangle \\ &- \langle \exp[-i(\mathbf{g} - \mathbf{k}) \cdot \mathbf{u}_i]\rangle \\ &\times \langle \exp[-i(\mathbf{k} - \mathbf{h}) \cdot \mathbf{u}_i]\rangle\}, \end{aligned} \tag{44}$$

where $\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i$ and the summation over i is over a unit cell.

Using Dirac's formula

$$1/(k_0^2 - k^2 + i\varepsilon) = \mathcal{P}[1/(k_0^2 - k^2)] - i(\pi/2k_0)\delta(k_0 - k) \tag{45}$$

and substituting (45) into (44) shows that $V^{(1)}\psi_k$ is in general a complex quantity. The real part of this complex quantity is due to *virtual diffuse scattering* and the imaginary part is due to *real diffuse scattering*. It has been shown that the contribution resulting from virtual diffuse scattering is of an order of magnitude less than that resulting from real diffuse scattering (Rez, 1976). In what follows, we shall therefore consider only the imaginary part. If the real part is neglected, equation (44) becomes

$$\begin{aligned} V^{\mathrm{TDS}}(\mathbf{g}, \mathbf{h}) = &[1/(2\pi)^3](2\gamma h^2/m_0\Omega)(-i\pi/2k_0) \\ &\times \sum_i \int \mathrm{d}\mathbf{k}\, \delta(k - k_0) f_i^B(\mathbf{g} - \mathbf{k}) f_i^B(\mathbf{k} - \mathbf{h}) \\ &\times \exp[-i(\mathbf{g} - \mathbf{h}) \cdot \mathbf{R}_i]\{\mathcal{T}_i(\mathbf{g} - \mathbf{h}) \\ &- \mathcal{T}_i(\mathbf{g} - \mathbf{k})\mathcal{T}_i(\mathbf{k} - \mathbf{h})\}. \end{aligned} \tag{46}$$

To simplify the above expression, we introduce two new parameters, $4\pi\mathbf{s} = \mathbf{g} - \mathbf{h}$ and $\mathbf{s}'$, such that

$$\mathbf{k} - \mathbf{h} = (\mathbf{s}/2 + \mathbf{s}')4\pi, \quad \mathbf{g} - \mathbf{k} = (\mathbf{s}/2 - \mathbf{s}')4\pi.$$

To a good approximation, we may neglect the curvature of the Ewald sphere in evaluating (46) and this approximation is called the *high-energy approximation* (Cowley, 1990). Under this approximation, we have

$$\begin{aligned} V^{\mathrm{TDS}}(\mathbf{g}, \mathbf{h}) &= - (h^2/8\pi^2 m_0)(4\pi/\Omega) \\ &\quad \times \sum_i f_i^{\mathrm{TDS}}(\mathbf{s}) \exp[-i(\mathbf{g} - \mathbf{h}) \cdot \mathbf{R}_i] \\ &= V^{\mathrm{TDS}}(\mathbf{g} - \mathbf{h}), \end{aligned} \tag{47}$$

where

$$\begin{aligned} f_i^{\mathrm{TDS}}(\mathbf{s}) = &(2h/m_0 v) \int \mathrm{d}\mathbf{s}' f_i(|\mathbf{s}/2 + \mathbf{s}'|) f_i(|\mathbf{s}/2 - \mathbf{s}'|) \\ &\times \{\mathcal{T}_i(\mathbf{s}) - \mathcal{T}_i(\mathbf{s}/2 + \mathbf{s}')\mathcal{T}_i(\mathbf{s}/2 - \mathbf{s}')\} \end{aligned} \tag{48}$$

and this expression is identical to the conventional formula (Hall & Hirsch, 1965) in form. The only difference between the present expression and that of Hall & Hirsch is that their isotropic temperature factor is now replaced by the general anisotropic temperature factor.

Substitution of (47) into (42) gives

$$\begin{aligned} \mathcal{F}\{V^{(1)}\psi_k\} &= \int V^{\mathrm{TDS}}(\mathbf{g} - \mathbf{h})\Psi(\mathbf{h})\, \mathrm{d}\mathbf{h} \\ &= V^{\mathrm{TDS}}(\mathbf{g}) \star \Psi(\mathbf{g}). \end{aligned} \tag{49}$$

Inverse Fourier transformation of (49) gives an expression for $V^{(1)}\psi_k$:

$$\begin{aligned} V^{(1)}\psi_k &= \mathcal{F}^{-1}\{V^{\mathrm{TDS}}(\mathbf{g}) \star \Psi(\mathbf{g})\} \\ &= V^{(1)}(\mathbf{r})\Psi_k(\mathbf{r}), \end{aligned} \tag{50}$$

in which

$$V^{(1)}(\mathbf{r}) = \int V^{\mathrm{TDS}}(\mathbf{g}) \exp(i\mathbf{g} \cdot \mathbf{r})\, \mathrm{d}\mathbf{g}, \tag{51}$$

and this expression clearly shows that $V^{(1)}$ is a *local potential*, *i.e.* it depends only on one site coordinate $\mathbf{r}$.

5. Calculations

In this section, we are concerned with applications of equations (27), (36) and (48) for calculating the general complex anisotropic structure factors. Combining (27) and (48), we obtain a general expression for the complex anisotropic structure factors

$$F_g = \sum_i \{f_i^B(s)\mathcal{T}_i(\mathbf{g}) + f_i^{\mathrm{TDS}}(s)\} \exp(-i\mathbf{g}\cdot\mathbf{R}_i), \quad (52)$$

in which $f_i^B(s)$ is the Born atomic scattering amplitude (28) of the ith atom, $f_i^{\mathrm{TDS}}(s)$ is the TDS atomic scattering amplitude (48), $\mathcal{T}_i(\mathbf{g})$ is the temperature factor (36) and the summation is over all atoms within a unit cell. Suppose that within the unit cell there exist a total of t symmetry-independent atoms and that all atoms are related by a total of m symmetry operators (m being the order of the space group), then the expression for the structure factor may be rewritten as

$$F_g = \sum_{j=1}^{t} n_j \sum_{s=1}^{m} \{f_j^B(s)\mathcal{T}_{js}(\mathbf{g}) + f_{js}^{\mathrm{TDS}}(s)\} \exp(-i\mathbf{g}\cdot\mathbf{R}_{js}), \quad (53)$$

in which n_j is the occupation number of the jth atom, which is defined as m_j/m, m_j being the number of different atomic positions that are symmetry equivalent to the jth atom. For the jth group of symmetry-equivalent atoms, the sth symmetry operator $\mathcal{R}\mathcal{W}_s = (\mathcal{R}_s, \mathcal{T}_s)$, in which $\mathcal{R}_s$ denotes a 3×3 rotation matrix and $\mathcal{T}_s$ a 3×1 translation vector. Using these operators, we have for the sth atom within the jth group

$$\mathbf{R}_{js} = \mathcal{R}_s\mathbf{R}_j + \mathcal{T}_s \quad (54)$$

and

$$\mathcal{T}_{js}(\mathbf{g}) = \exp(-\mathbf{G}^T\beta_{js}\mathbf{G}) = \exp[-\mathbf{G}^T(\mathcal{R}_s\beta_j\mathcal{R}_s^T)\mathbf{G}]. \quad (55)$$

For an atom lying on a special site, there exist n symmetry operations that leave the site invariant. We then have the invariant of the temperature matrices,

$$\beta_s = \mathcal{R}_s\beta\mathcal{R}_s^T = \beta, \quad s = 1, \ldots, n. \quad (56)$$

From these conditions, the β restrictions may be derived (Willis & Pryor, 1975).

To demonstrate the effect of anisotropy in thermal vibrations on the structure factors, we first define an isotropic temperature or Debye–Waller factor. This quantity may be obtained by defining a **B** matrix with respect to Cartesian axes. Let

$$\mathbf{u} = u_x\mathbf{i} + u_y\mathbf{j} + u_z\mathbf{k},$$

and

$$\mathbf{g} = g_x\mathbf{i} + g_y\mathbf{j} + g_z\mathbf{k},$$

we then have

$$\langle(\mathbf{u}\cdot\mathbf{g})^2\rangle = 4\pi^2\mathbf{H}^T\mathbf{B}\mathbf{H}, \quad (57)$$

in which $2\pi\mathbf{H}^T = (g_x, g_y, g_z)$ and

$$\mathbf{B} = \begin{pmatrix} \langle u_x^2\rangle & \langle u_xu_y\rangle & \langle u_xu_z\rangle \\ \langle u_yu_x\rangle & \langle u_y^2\rangle & \langle u_yu_z\rangle \\ \langle u_zu_x\rangle & \langle u_zu_y\rangle & \langle u_z^2\rangle \end{pmatrix} \quad (58)$$

The general anisotropic temperature factor is given by

$$\mathcal{T}(\mathbf{g}) = \exp(-2\pi^2\mathbf{H}^T\cdot\mathbf{B}\cdot\mathbf{H}). \quad (59)$$

The relation between the **B** matrix and the β matrix introduced in §3 may be obtained by comparing (33) and (59), giving

$$2\pi^2\mathbf{H}^T\cdot\mathbf{B}\cdot\mathbf{H} = \mathbf{G}^T\cdot\beta\cdot\mathbf{G}. \quad (60)$$

Following Willis & Pryor (1975), we choose the following Cartesian axes to define the **B** matrix. Let the x axis lie along $\mathbf{b}_1$, the y axis lie in the plane containing $\mathbf{b}_1$ and $\mathbf{b}_2$, and the z axis complete a right-handed set. The vector **G** is then given in terms of **H** *via* a transformation matrix

$$\mathbf{G} = \mathbf{F}\cdot\mathbf{H}, \quad (61)$$

where

$$\mathbf{F} = 2\pi\begin{pmatrix} 1/b_1 & -\cot\beta_3/b_1 & a_1\cos\alpha_2 \\ 0 & 1/(b_2\sin\beta_3) & a_2\cos\alpha_1 \\ 0 & 0 & a_3 \end{pmatrix} \quad (62)$$

and the α_is and β_is are the angles of the direct and reciprocal cells. Substitution of (61) into (60) gives

$$\mathbf{B} = (1/2\pi^2)\mathbf{F}^T\cdot\beta\cdot\mathbf{F}. \quad (63)$$

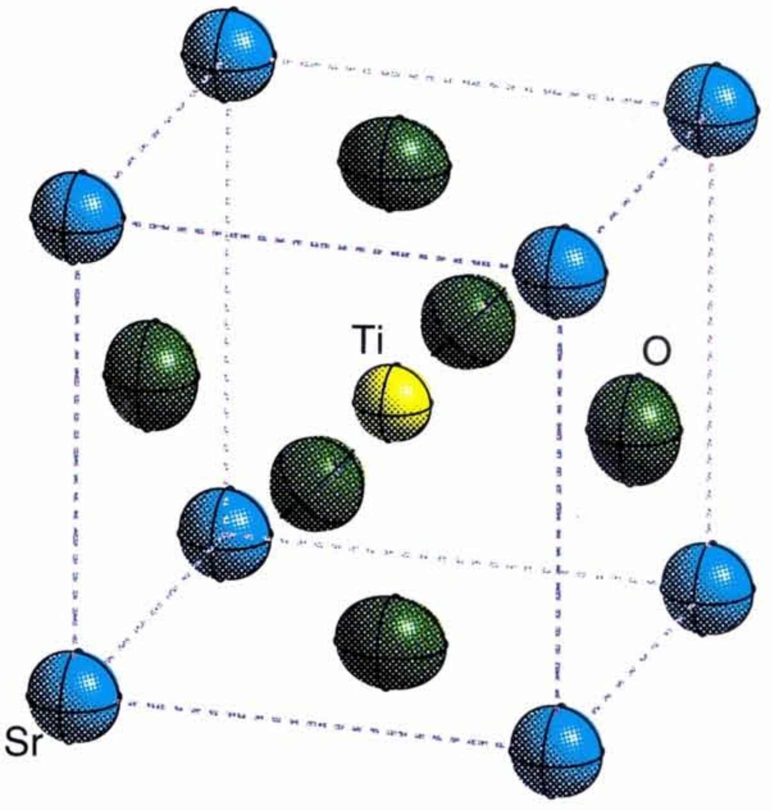

Fig. 1. Graphic representation of the thermal ellipsoids for an $SrTiO_3$ single crystal at 296 K.

Table 1. *Structural and anisotropic vibration parameters* (Å^{-2}) *for strontium titanate (Abramov, Tsirelson, Zavodnik, Ivanov & Brown, 1995)*

a (Å)	U(Sr)	B(Sr)	U(Ti)	B(Ti)	U_{11}(O)	U_{22}(O)	B(O)
3.901	0.00787	0.6214	0.00557	0.4398	0.004675	0.011575	0.7323

In terms of the elements of the **B** matrix, the *averaged mean-square displacement* is given by

$$\langle u^2\rangle = \tfrac{1}{3}\mathrm{trace}(\mathbf{B}) = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}). \quad (64)$$

The usual Debye–Waller factor is related to the mean-square displacement *via* the *temperature B factors*, which are defined as

$$B = 8\pi^2\langle u^2\rangle, \quad (65)$$

and the *Debye–Waller factor* M_g is given by

$$M_g = (g^2/4\pi^2)B. \quad (66)$$

We now consider the calculations of complex structure factors for strontium titanate, *i.e.* $SrTiO_3$. This structure belongs to the important perovskite ABX_3 series and was recently studied by high-precision single-crystal X-ray analysis (Abramov, Tsirelson, Zavodnik, Ivanov & Brown, 1995). At room temperature, it shows a cubic structure and the space group is $Pm\bar{3}m$. Table 1 gives a summary of the relevant structural and anisotropic thermal vibration parameters. Shown in Fig. 1 is a graphic representation of the thermal ellipsoids, which is generated using the Cerius^2 software.

In an $SrTiO_3$ single crystal, the Sr atom is at the special site (a), *i.e.* at (0, 0, 0) and the Ti atom is at the special site (b), *i.e.* at (0.5, 0.5, 0.5), for space group 221 (Hahn, 1983). The β_{ij} restrictions for both sites are case 17, requiring $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$ (Willis & Pryor, 1975). The **U** matrices [which are related to β *via* (35)] for the two atoms are therefore of the isotropic form

$$\mathbf{U} = \begin{pmatrix} U & 0 & 0 \\ 0 & U & 0 \\ 0 & 0 & U \end{pmatrix}. \quad (67)$$

The three O atoms in $SrTiO_3$ are at the special site (c), and their atomic coordinates are (0, 0.5, 0.5), (0.5, 0, 0.5), (0.5, 0.5, 0). For the first O atom at (0, 0.5, 0.5), the β_{ij} restrictions are $\beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$. The **U** matrix for this O atom is of the form

$$\mathbf{U}(\mathrm{O}_1) = \begin{pmatrix} U_{11} & 0 & 0 \\ 0 & U_{22} & 0 \\ 0 & 0 & U_{22} \end{pmatrix}. \quad (68)$$

The second O atom at (0.5, 0, 0.5) is related to the first O atom by a rotation $3^+[111]$. The corresponding rotation matrix and temperature matrix $\mathbf{U}(\mathrm{O}_2)$ for this atom are given by

$$\mathcal{R}_2 = 3^+[111] = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix},$$

$$\mathbf{U}(\mathrm{O}_2) = \mathcal{R}_2\mathbf{U}(\mathrm{O}_1)\mathcal{R}_2^T = \begin{pmatrix} U_{22} & 0 & 0 \\ 0 & U_{11} & 0 \\ 0 & 0 & U_{22} \end{pmatrix}. \quad (69)$$

The third O atom at (0.5, 0.5, 0) is related to the first O atom by the symmetry operation $3^-[111]$. The corresponding rotation matrix and temperature matrix $\mathbf{U}(\mathrm{O}_3)$ are given by

$$\mathcal{R}_3 = 3^-[111] = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix},$$

$$\mathbf{U}(\mathrm{O}_3) = \mathcal{R}_3\mathbf{U}(\mathrm{O}_1)\mathcal{R}_3^T = \begin{pmatrix} U_{22} & 0 & 0 \\ 0 & U_{22} & 0 \\ 0 & 0 & U_{11} \end{pmatrix}. \quad (70)$$

The mean-square displacement and the B factor are obtained using equations (64) and (65). For strontium, we have $\langle u^2\rangle = 0.007\,87$ Å^2 and $B = 0.6214$ Å^2. For titanium, $\langle u^2\rangle = 0.00557$ Å^2 and $B = 0.4398$ Å^2. For oxygen, we have $\langle u^2\rangle = 0.009\,275$ Å^2 and $B = 0.7323$ Å^2.

Shown in Tables 2–4 are some calculated zero-order Laue-zone (ZOLZ) structure factors for three main zone axes of the $SrTiO_3$ single crystal at 296 K, using an isotropic Debye–Waller factor and the general anisotropic vibration parameters listed in Table 1. The error introduced by using the isotropic Debye–Waller factor is evaluated using the expression

$$\mathrm{Error} = ||U_{\mathrm{iso}}| - |U_{\mathrm{aniso}}||/|U_{\mathrm{iso}}|. \quad (71)$$

The calculations listed in the tables were made for 100 keV primary-beam energy. In evaluating the absorptive scattering amplitudes, we have used the multidimensional integrating subroutine *D01FCF* of the NAG library for integration of the integrals. This subroutine uses an adaptive subdivision procedure and the multidimensional integration may be performed to a specified accuracy. The general-purpose two-dimensional integrating subroutine *D01DAF* of the NAG library (used in Bird & King, 1990) has also been used. We found, however, that, although the subroutine is extremely fast, this subroutine lacks control in its relative accuracy and in almost all our calculations we failed to achieve

Table 2. *Some [001] zone axis structure factors of $SrTiO_3$ (in $Å^{-2}$) for isotropic and anisotropic thermal vibrations*

h	k	l	Re(U_{iso})	Im(U_{iso})	Re(U_{aniso})	Im(U_{aniso})	Error (%)
2	0	0	0.6269E−01	0.2733E−02	0.6269E−01	0.2727E−02	0.011
1	1	0	0.4496E−01	0.2335E−02	0.4485E−01	0.2377E−02	0.264
4	0	0	0.2380E−01	0.2014E−02	0.2381E−01	0.2010E−02	0.082
3	1	0	0.1857E−01	0.1908E−02	0.1831E−01	0.1931E−02	1.362
2	2	0	0.4153E−01	0.2451E−02	0.4153E−01	0.2445E−02	0.016
6	0	0	0.1039E−01	0.1313E−02	0.1043E−01	0.1312E−02	0.369
5	1	0	0.8357E−02	0.1361E−02	0.8088E−02	0.1364E−02	3.187
4	2	0	0.1934E−01	0.1839E−02	0.1935E−01	0.1835E−02	0.068
3	3	0	0.1158E−01	0.1601E−02	0.1132E−01	0.1613E−02	2.236
8	0	0	0.4921E−02	0.7628E−03	0.4973E−02	0.7669E−03	1.061
7	1	0	0.4249E−02	0.8657E−03	0.4020E−02	0.8565E−03	5.305
6	2	0	0.9176E−02	0.1212E−02	0.9206E−02	0.1211E−02	0.325
5	3	0	0.6453E−02	0.1165E−02	0.6214E−02	0.1165E−02	3.649
4	4	0	0.1189E−01	0.1424E−02	0.1190E−01	0.1420E−02	0.081
8	2	0	0.4498E−02	0.7074E−03	0.4542E−02	0.7104E−03	0.980
7	3	0	0.3549E−02	0.7488E−03	0.3351E−02	0.7406E−03	5.468
6	4	0	0.6577E−02	0.9587E−03	0.6593E−02	0.9562E−03	0.252
5	5	0	0.4249E−02	0.8657E−03	0.4053E−02	0.8616E−03	4.532
8	4	0	0.3488E−02	0.5648E−03	0.3516E−02	0.5657E−03	0.794
7	5	0	0.2562E−02	0.5622E−03	0.2408E−02	0.5553E−03	5.888
6	6	0	0.4122E−02	0.6562E−03	0.4134E−02	0.6539E−03	0.298

Table 3. *Some [011] zone axis structure factors of $SrTiO_3$ (in $Å^{-2}$) for isotropic and anisotropic thermal vibrations*

h	k	l	Re(U_{iso})	Im(U_{iso})	Re(U_{aniso})	Im(U_{aniso})	Error (%)
2	0	0	0.6269E−01	0.2733E−02	0.6269E−01	0.2729E−02	0.008
4	0	0	0.2380E−01	0.2014E−02	0.2381E−01	0.2012E−02	0.081
0	−1	1	0.4496E−01	0.2335E−02	0.4485E−01	0.2308E−02	0.254
1	−1	1	0.3301E−01	0.1630E−02	0.3301E−01	0.1627E−02	0.011
2	−1	1	0.2646E−01	0.2100E−02	0.2667E−01	0.2090E−02	0.803
3	−1	1	0.1499E−01	0.1297E−02	0.1500E−01	0.1294E−02	0.049
4	−1	1	0.1158E−01	0.1601E−02	0.1202E−01	0.1618E−02	3.794
5	−1	1	0.6332E−02	0.8717E−03	0.6357E−02	0.8708E−03	0.384
0	−2	2	0.4153E−01	0.2451E−02	0.4153E−01	0.2448E−02	0.009
2	−2	2	0.3047E−01	0.2216E−02	0.3047E−01	0.2212E−02	0.010
4	−2	2	0.1615E−01	0.1685E−02	0.1616E−01	0.1682E−02	0.046
0	−3	3	0.1158E−01	0.1601E−02	0.1132E−01	0.1566E−02	2.253
1	−3	3	0.9127E−02	0.1057E−02	0.9131E−02	0.1055E−02	0.048
2	−3	3	0.9725E−02	0.1474E−02	0.9607E−02	0.1450E−02	1.218
3	−3	3	0.6332E−02	0.8717E−03	0.6332E−02	0.8691E−03	0.042
4	−3	3	0.6453E−02	0.1165E−02	0.6551E−02	0.1163E−02	1.489

Table 4. *Some [111] zone axis structure factors of $SrTiO_3$ (in $Å^{-2}$) for isotropic and anisotropic thermal vibrations*

h	k	l	Re(U_{iso})	Im(U_{iso})	Re(U_{aniso})	Im(U_{aniso})	Error (%)
−1	1	0	0.4496E−01	0.2335E−02	0.4485E−01	0.2332E−02	0.248
−1	0	1	0.4496E−01	0.2335E−02	0.4485E−01	0.2332E−02	0.248
−1	−1	2	0.2646E−01	0.2100E−02	0.2667E−01	0.2111E−02	0.803
−2	2	0	0.4153E−01	0.2451E−02	0.4153E−01	0.2449E−02	0.007
−2	1	1	0.2646E−01	0.2100E−02	0.2667E−01	0.2111E−02	0.803
−2	0	2	0.4153E−01	0.2451E−02	0.4153E−01	0.2449E−02	0.007
−2	−1	3	0.1427E−01	0.1743E−02	0.1423E−01	0.1741E−02	0.287
−2	−2	4	0.1615E−01	0.1685E−02	0.1616E−01	0.1684E−02	0.043
−3	3	0	0.1158E−01	0.1601E−02	0.1132E−01	0.1582E−02	2.239
−3	2	1	0.1427E−01	0.1744E−02	0.1423E−01	0.1741E−02	0.287
−3	1	2	0.1427E−01	0.1744E−02	0.1423E−01	0.1741E−02	0.287
−3	0	3	0.1158E−01	0.1601E−02	0.1132E−01	0.1582E−02	2.239
−3	−1	4	0.8357E−02	0.1361E−02	0.8571E−02	0.1380E−02	2.533
−4	4	0	0.1189E−01	0.1424E−02	0.1190E−01	0.1424E−02	0.071
−4	3	1	0.8357E−02	0.1361E−02	0.8571E−02	0.1380E−02	2.533
−4	2	2	0.1615E−01	0.1685E−02	0.1616E−01	0.1684E−02	0.043
−4	1	3	0.8357E−02	0.1361E−02	0.8571E−02	0.1380E−02	2.533
−4	0	4	0.1189E−01	0.1424E−02	0.1190E−01	0.1424E−02	0.071

convergence. It is seen that errors due to the use of an isotropic vibration model vary from less than 1% to more than 5%.

6. Discussions and conclusions

We have derived the general expressions for calculating both the elastic and absorptive atomic scattering amplitudes for the general case of anisotropic thermal vibrations. These expressions are derived formally *via* the method of optical potential and the usual assumptions for TDS are employed. These assumptions include:

(i) The electrons that are diffusely scattered are regarded to have been lost to the elastic wave field. This is because once electrons are diffusely scattered outside the elastic wave field they can hardly return to the elastic wave field and may therefore be regarded as lost.

(ii) The correlation between thermal displacements occurring at different atomic sites is not important to the total absorptive scattering amplitudes. This is equivalent to the use of the Einstein model of lattice vibrations.

(iii) The strength of the aperiodic potential due to thermal vibration is weak in comparison with both the primary-beam energy and the averaged periodic potential and a first-order-perturbation treatment is used for dealing with the effect of the diffusely scattered electrons on the elastic wave field. Dynamical diffraction of the diffusely scattered electrons hardly affects the total absorptive atomic scattering amplitude and is neglected in the first-order treatment of TDS.

(iv) The virtual diffuse scattering effect is small and is neglected.

Under these approximations, the derived expressions have identical forms to the usual expressions derived for an isotropically vibrating crystal, except that now the temperature factor takes a general anisotropic form. For an isotropically vibrating crystal, the general temperature factor reduces to the usual form $\exp(-M_s)$ in which M_s is the isotropic Debye–Waller factor.

Numerical results are presented for one perovskite ABX_3 compound, *i.e.* $SrTiO_3$. The effect of anisotropy in thermal vibrations is investigated for crystal structure factors. Our results show that the use of an averaged isotropic temperature factor introduces an error of the order of a few percent for low- and medium-order structure factors. It should be noted that these values are comparable with that due to crystal bonding (Spence, 1993). For silicon and 200 keV, the bonding effect may alter the scaled structure factors U_g by about 5% for (111) reflection, but the effect decreases rapidly to be less than 1% for (331) reflection. For $SrTiO_3$, we would expect the bonding effect to be of the order of a few percent for low-order reflections. The effect of anisotropy in TDS should therefore be taken into account should any attempt be made to measure the bonding effect in this material.

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References

Abramov, Y. A., Tsirelson, V. G., Zavodnik, V. E., Ivanov, S. A. & Brown, I. D. (1995). *Acta Cryst.* **B51**, 942–951.

Allen, L. J. & Rossouw, C. J. (1989). *Phys. Rev. B*, **39**, 8313–8321.

Ashcroft, N. W. & Mermin, N. D. (1976). *Solid State Physics*. Philadephia, PA: Saunders College.

Bethe, H. (1928). *Ann. Phys. (Leipzig)*, **87**, 55–129.

Bird, D. M. & King, Q. A. (1990). *Acta Cryst.* **A46**, 202–208.

Cowley, J. M. (1990). *Diffraction Physics*, 2nd ed. Amsterdam: North-Holland.

Cowley, J. M. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 223–244. Dordrecht: Kluwer Academic Publishers.

Dederichs, P. H. (1972). *Solid State Phys.* **27**, 125.

Dudarev, S. L., Peng, L.-M. & Ryazanov, M. I. (1991). *Acta Cryst.* **A47**, 170–176.

Dudarev, S. L., Peng, L.-M. & Whelan, M. J. (1992). *Surf. Sci.* **279**, 380–394.

Dudarev, S. L., Peng, L.-M. & Whelan, M. J. (1993*a*). *Phys. Rev. B*, **48** 13408–13429.

Dudarev, S. L., Peng, L.-M. & Whelan, M. J. (1993*b*). *Proc. R. Soc. London Ser. A*, **440**, 567–588.

Dudarev, S. L., Peng, L.-M. & Whelan, M. J. (1995). *Surf. Sci.* **330**, 86–100.

Egerton, R. F. (1986). *Electron Energy Loss Spectroscopy in the Electron Microscope*. New York: Plenum Press.

Giacovazzo, C. (1992). *Fundamentals of Crystallography*. Oxford University Press.

Hahn, Th. (1983). Editor. *International Tables for Crystallography*, Vol. A. Dordrecht: Kluwer.

Hall, C. R. & Hirsch, P. B. (1965). *Proc. R. Soc. London Ser. A*, **286**, 158–177.

Hirsch, P. B., Howie, A., Nicholson, R. N., Pashley, D. W. & Whelan, M. J. (1977). *Electron Microscopy of Thin Crystals*. Malabar/Florida: Krieger Publishing Company.

Humphreys, C. J. & Hirsch, P. B. (1968). *Philos. Mag.* **18**, 115–122.

Ohtsuki, Y.-H. (1983). *Charged Beam Interaction with Solids*. New York: Taylor and Francis.

Peng, L.-M., Ren, G., Dudarev, S. L. & Whelan, M. J. (1996). *Acta Cryst.* **A52**, 257–276, 456–470.

Radi, G. (1970). *Acta Cryst.* **A26**, 41–56.

Reimer, L. (1989). *Transmission Electron Microscopy – Physics of Image Formation and Microanalysis*, 2nd ed. Berlin: Springer-Verlag.

Ren, G., Zuo, J. M. & Peng, L.-M. (1997). *Micron*. In the press.

Rez, P. (1976). PhD thesis. Oxford University, England.

Rossouw, C. J. & Bursill, L. A. (1985). *Acta Cryst.* **A41**, 320–327.

Saunders, M., Bird, D. M., Zaluzec, N. J., Burgess, W. G., Preston, A. R. & Humphreys, C. J. (1995). *Ultramicroscopy*, **60**, 311–323.

Schiff, L. I. (1968). *Quantum Mechanics*. London: McGraw-Hill.

Spence, J. C. H. (1993). *Acta Cryst.* A**49**, 231–260.

Spence, J. C. H. & Zuo, J. M. (1992). *Electron Microdiffraction*. New York/London: Plenum Press.

Wang, Z. L. (1995). *Elastic and Inelastic Scattering in Electron Diffraction and Imaging*. New York/London: Plenum Press.

Whelan, M. J. (1965). *Appl. Phys.* **36**, 2099–2103, 2103–2110.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.

Yoshioka, H. (1957). *J. Phys. Jpn*, **12**, 618–628.

Zuo, J. M. & Spence, J. C. H. (1991). *Ultramicroscopy*, **35**, 185–196.

Zuo, J. M., Spence, J. C. H. & O'Keeffe, M. (1988). *Phys. Rev. Lett.* **61** 353–356.