

The Influence of Anisotropic Thermal Vibrations on Absorptive Form Factors for High-Energy Electron Diffraction

A. L. WEICKENMEIER^{a*} AND H. KOHL^b

^aMax-Planck-Institut für Metallforschung, Seestrass 92, D-70174 Stuttgart, Germany, and ^bPhysikalisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany.

E-mail: weickenmeier@vaxww1.mpi-stuttgart.mpg.de

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Abstract

Thermal diffuse scattering is the dominant contribution to the absorptive form factors in high-energy electron diffraction. So far, calculations have been limited to isotropic thermal vibrations. In this paper, a general formula is given for the absorptive form factors that fully accounts for anisotropic temperature factors. The resulting formula is based on the Einstein model and well suited for numerical evaluation. A case study shows that even slight deviations from isotropy lead to a strong directional dependence of the absorptive form factors.

1. Introduction

For the quantitative simulation of energy-filtered elastic electron diffraction patterns, inelastic scattering has to be taken into account properly (Spence & Zuo, 1992). Electrons that are scattered inelastically are either removed from the beam by the energy filtering unit (energy loss more than 5 eV) or scattered into angles different from Bragg angles (thermal diffuse scattering, TDS) and are thus not measured by the observer. From a simple point of view, these electrons have been absorbed. Also, from a theoretical point of view, the influence of inelastic scattering can be incorporated into dynamical theory by means of an absorption potential. It has been shown by Yoshioka (1957) that this is correct in the framework of a first-order perturbation theory.

An equation to calculate the contribution of TDS to the absorption has been given by Hall & Hirsch (1965) on the basis of a phenomenological discussion. Later it was shown by Radi (1970) that TDS is the dominant term in the absorption potential. Subroutines for convenient and accurate computation of this term have been provided for example by Weickenmeier & Kohl (1991).

In the treatment of TDS, two major approximations have been used so far: the Einstein model (each atom is an independent harmonic oscillator) and the isotropy of the atomic vibrations. The first approximation is motivated by the fact that only the Einstein model allows

the computation of absorption potentials without detailed knowledge of phonon dispersion relations. Therefore, we will also use this model as the basis of our calculations. Isotropic vibrations are strictly found only for atoms with cubic site symmetry. Here we generalize the treatment of TDS to cope also with anisotropic vibrations which lead to an anisotropic absorption potential.

In §2, we will give a brief summary of the Yoshioka theory. §3 deals with the evaluation of the TDS contribution for both cases, isotropic and anisotropic vibrations. A numerical example is given in §4.

2. Basic equations

A very detailed study of the perturbative treatment of inelastic scattering has been given by Yoshioka (1957). In this section, we recall the major steps of his calculations that led to an absorption potential.

The time-independent Schrödinger equation for the fast electron and the crystal is given by

$$H\Phi = E\Phi. \quad (1)$$

Here, E is the total energy of the system. The Hamiltonian

$$H = H_e + H_k + H' \quad (2)$$

is composed of the kinetic energy of the fast electron

$$H_e = (\hbar^2/2m)\Delta, \quad (3)$$

the crystal Hamiltonian H_k and the interaction

$$H' = (e^2/4\pi\epsilon_0) \left(\sum_{j=1}^l 1/|\mathbf{r} - \mathbf{r}_j| - \sum_{k=1}^L Z_k/|\mathbf{r} - \mathbf{R}_k| \right). \quad (4)$$

These two terms denote the Coulomb potential between the fast electron and the crystal electrons (coordinates \mathbf{r}_j) and between the fast electron and the nuclei (coordinates \mathbf{R}_k), respectively, e is the electron charge and ϵ_0 the dielectric constant. Here, we neglect exchange and correlation interaction. For further treatment, we assume $H' \ll H_e$.

We consider the complete orthonormal system of eigenfunctions a_n of H_k ,

$$H_k a_n = \varepsilon_n a_n, \quad (5)$$

$$\langle a_n | a_m \rangle = \delta_{nm}, \quad (6)$$

to be known. We expand the wave function Φ using the eigenfunctions of H_k :

$$\Phi = \sum_n \varphi_n(\mathbf{r}) a_n(\mathbf{r}_1, \dots, \mathbf{r}_l, \mathbf{R}_1, \dots, \mathbf{R}_L). \quad (7)$$

We are only interested in the 'elastic' solution $\varphi_0(\mathbf{r})$, which means the crystal remains in the initial state a_0 . Making the Bloch wave *ansatz*

$$\varphi_0 = \exp[i\mathbf{k}\mathbf{r}] \sum_h c_h \exp[i\mathbf{h}\mathbf{r}], \quad (8)$$

we eventually obtain after some steps (*cf.* Yoshioka, 1957) the well known dispersion equation of the dynamical theory:

$$[k_0^2 - (\mathbf{k} + \mathbf{g})^2] c_g + \sum_h U_{g-h} c_h = - \sum_h V_{gh} c_h. \quad (9)$$

The term on the right-hand side is given by

$$V_{gh} = U''_{gh} + iU'_{gh}. \quad (10)$$

Both terms are of second order in H' . However, U''_{gh} can be understood as a small correction to U_{g-h} and is therefore neglected. The remaining term iU'_{gh} is anti-hermitic and introduces an imaginary part of the wave vector \mathbf{k} , leading to a decay of the elastic wave function φ_0 as a function of penetration depth. According to Yoshioka (1957), U'_{gh} is given by the surface integral

$$U'_{gh} = -(m^2/2\pi^2\hbar^4 V) \sum_{n \neq 0} \int_{K=k_n} d^2\mathbf{K} \times E_{0n}(\mathbf{k} + \mathbf{g} - \mathbf{K}) E_{n0}(\mathbf{K} - \mathbf{k} - \mathbf{h}) / 2k_n, \quad (11)$$

where

$$k_n^2 = (2m/\hbar^2)(E - \varepsilon_n), \quad (12)$$

$$E_{0n}(\mathbf{q}) = \int d^3\mathbf{r} H'_{0n} \exp[-i\mathbf{q}\mathbf{r}] \quad (13)$$

and

$$H'_{mn} = \langle a_m | H' | a_n \rangle. \quad (14)$$

Furthermore, the electron rest mass is denoted by m and V is the volume of the unit cell. The structure factors U_g in (9) are defined as

$$U_g = (2m/V\hbar^2) \int d^3\mathbf{r} \exp[-i\mathbf{g}\mathbf{r}] H'_{00}(\mathbf{r}). \quad (15)$$

3. Treatment of TDS

For the exact treatment of TDS, we need to know the crystal wave functions a_n . But even then the computa-

tion of the U'_{gh} would still be very tedious. Therefore, we limit our investigation to simple approximations.

First we want to simplify (11). The U'_{gh} are defined as a surface integral, where the integration variable \mathbf{K} lies on a sphere with radius k_n . Since we only treat TDS we have $K_n \simeq k_0$ and accordingly $K \simeq k_0$. This means that the sphere is to very good approximation the Ewald sphere. Furthermore, for practical applications, we consider only reflections \mathbf{g} in the Bloch-wave function (8) with $\mathbf{k} + \mathbf{g}$ close to the Ewald sphere. Therefore, replacing U'_{gh} by U'_{g-h} and k_n by k_0 introduces a negligible error. We thus have

$$U'_g = -(m^2/2\pi^2\hbar^4 V) \sum_{n \neq 0} \int_{K=k_0} d^2\mathbf{K} \times E_{0n}(\mathbf{k} - \mathbf{K}) E_{n0}(\mathbf{K} - \mathbf{k} - \mathbf{g}) / 2k_0. \quad (16)$$

In the next step, we have to approximate the Fourier-transformed matrix elements $E_{0n}(\mathbf{q})$ to allow for a general evaluation. First we apply the Born-Oppenheimer approximation, which allows the separation of the wave function n of the nuclei from the electronic part Ψ_n . In the next step, we neglect all bonding effects on the electron wave functions, *i.e.* we choose free-atom wave functions for the electrons. This is an excellent approximation for the deeply bound core electrons and introduces only a very small error for the atomic potentials. Accordingly, each electron can be attributed to a fixed atom and the crystal wave function can be written as

$$a_n = n(\mathbf{R}_1, \dots, \mathbf{R}_L) \Psi_n(\mathbf{r}_{11} - \mathbf{R}_1, \dots, \mathbf{r}_{z_1} - \mathbf{R}_1, \mathbf{r}_{12} - \mathbf{R}_2, \dots), \quad (17)$$

where \mathbf{r}_{ij} denotes the coordinate of electron i of atom j . Now we insert (17) into (13) and obtain

$$E_{n'n}(\mathbf{q}) = (e^2/4\pi\varepsilon_0) \int d^3\mathbf{r} d\tau_e d\tau_K \exp[-i\mathbf{q}\mathbf{r}] n'^* n \Psi_n^* \Psi_n \times \left(\sum_{j=1}^L \sum_{i=1}^{Z_j} 1/|\mathbf{r} - \mathbf{r}_{ij}| - \sum_{j=1}^L Z_j/|\mathbf{r} - \mathbf{R}_j| \right) \quad (18)$$

with

$$d\tau_K = \prod_{j=1}^L d^3\mathbf{R}_j, \quad (19)$$

$$d\tau_e = \prod_{j=1}^L \prod_{i=1}^{Z_j} d^3\mathbf{r}_{ij}, \quad (20)$$

and an additional summation over the spin coordinates. Neglecting electron-phonon interaction, we may set $\Psi_{n'} = \Psi_n$. Since the second term does not depend on the electron coordinates, we may perform the $d\tau_e$ integration. With the normalization $\int d\tau_e |\Psi_n|^2 = 1$, we simply obtain the potential of the nuclei,

$$V_j^K(\mathbf{r} - \mathbf{R}_j) = -(e^2/4\pi\varepsilon_0) Z_j/|\mathbf{r} - \mathbf{R}_j|, \quad (21)$$

of the individual atoms. The first term results in the

electron potentials

$$(e^2/4\pi\epsilon_0) \sum_{j=1}^L \sum_{i=1}^{Z_j} \int d\tau_e |\Psi_n|^2 / |\mathbf{r} - \mathbf{r}_{ij}|, \quad (22)$$

which can be interpreted as the sum of atomic electron potentials

$$\sum_{j=1}^L V_j^e(\mathbf{r} - \mathbf{R}_j). \quad (23)$$

Accordingly, we obtain for $E_{n'n}$:

$$\begin{aligned} E_{n'n}(\mathbf{q}) &= (4\pi\hbar^2/2m) \sum_j f_j(\mathbf{q}) \int d\tau_k n'^* n \exp[-i\mathbf{q}\mathbf{R}_j] \\ &= (4\pi\hbar^2/2m) \sum_j f_j(\mathbf{q}) \langle n' | \exp[-i\mathbf{q}\mathbf{R}_j] | n \rangle, \end{aligned} \quad (24)$$

where $f_j(\mathbf{q})$ denotes the atomic scattering amplitude of atom j to first-order Born approximation, which is proportional to the Fourier transform of the potential of atom j . We insert this result in (16). Then, the Fourier coefficient of the absorption potential is given by

$$\begin{aligned} U'_g &= -(1/k_0 V) \sum_{j'j} \sum_{n \neq 0} \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k} - \mathbf{K}) f_{j'}(\mathbf{K} - \mathbf{k} - \mathbf{g}) \\ &\times \langle 0 | \exp[-i(\mathbf{k} - \mathbf{K})\mathbf{R}_j] | n \rangle \\ &\times \langle n | \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_{j'}] | 0 \rangle. \end{aligned} \quad (25)$$

We add and subtract the term $n = 0$. Making use of the completeness $1 = \sum_n |n\rangle \langle n|$ of the basis $|n\rangle$, we have

$$\sum_{n \neq 0} |n\rangle \langle n| = 1 - |0\rangle \langle 0| \quad (26)$$

and thus

$$\begin{aligned} U'_g &= -(1/k_0 V) \sum_{j'j} \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k} - \mathbf{K}) f_{j'}(\mathbf{K} - \mathbf{k} - \mathbf{g}) \\ &\times \{ \langle 0 | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{R}_j] \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_{j'}] | 0 \rangle \\ &- \langle 0 | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{R}_j] | 0 \rangle \\ &\times \langle 0 | \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_{j'}] | 0 \rangle \}. \end{aligned} \quad (27)$$

We see that the absorption coefficients (also the structure factors) depend on the initial state of the crystal. As a consequence, for a strict treatment, the dispersion, equation (9), has to be solved for each possible initial state of the solid, followed by an appropriate averaging procedure. To avoid this tedious and time-consuming task, the absorption potential as well as the real potential are replaced by averages. For the structure factors, this leads to the well known temperature factors. The absorption coefficients are written as the thermal average over all phonon states:

$$\begin{aligned} \sum_n P_n \{ &\langle n | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{R}_j] \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_{j'}] | n \rangle \\ &- \langle n | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{R}_j] | n \rangle \\ &\times \langle n | \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_{j'}] | n \rangle \}. \end{aligned} \quad (28)$$

Here, p_n denotes the probability for the crystal being in the phonon state $|n\rangle$.

It is quite clear that the result of (28) does depend on the phonon spectrum of the specimen. Since we do not intend to resolve particular phonon modes or analyze the direction dependence of the phonon scattered electrons but integrate over all directions \mathbf{K} and average over all states $|n\rangle$, we will introduce only a small error by applying the Einstein approximation. This allows (28) to be evaluated without prior study of phonon states.

In the Einstein model, the thermal motion of the atoms is uncorrelated and the wave functions and probability distributions can be factorized into single atom terms

$$n(\mathbf{R}_1, \dots, \mathbf{R}_L) = n_1(\mathbf{R}_1) \dots n_L(\mathbf{R}_L) \quad (29)$$

$$p_n = p^{(1)}(n_1) p^{(2)}(n_2) \dots p^{(L)}(n_L) \quad (30)$$

$$\sum_{n_j} p^{(j)}(n_j) = 1. \quad (31)$$

Here, $p^{(j)}(n_j)$ denotes the probability that atom j is in the state $|n_j\rangle$. Then, the terms with $j \neq j'$ in (28) vanish and we have

$$\begin{aligned} \sum_{n_j} p^{(j)}(n_j) \{ &\langle n_j | \exp[i\mathbf{g}\mathbf{R}_j] | n_j \rangle \\ &- \langle n_j | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{R}_j] | n_j \rangle \\ &\times \langle n_j | \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{R}_j] | n_j \rangle \}. \end{aligned} \quad (32)$$

We now decompose the vector \mathbf{R}_j pointing to the atom j into a static vector to the ideal lattice position $\mathbf{R}_j^{(0)}$ and a thermal displacement \mathbf{u}_j . The phases depending on $\mathbf{R}_j^{(0)}$ can be extracted and we keep the notation \mathbf{R}_j for the static positions. Then we obtain

$$U'_g = (1/V) \sum_j \exp[i\mathbf{g}\mathbf{R}_j] f'_j(\mathbf{g}) \quad (33)$$

with the definition

$$\begin{aligned} f'_j(\mathbf{g}) &= -(1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k} - \mathbf{K}) f_j(\mathbf{K} - \mathbf{k} - \mathbf{g}) \\ &\times \sum_{n_j} p^{(j)}(n_j) \{ \langle n_j | \exp[i\mathbf{g}\mathbf{u}_j] | n_j \rangle \\ &- \langle n_j | \exp[i(\mathbf{K} - \mathbf{k})\mathbf{u}_j] | n_j \rangle \\ &\times \langle n_j | \exp[-i(\mathbf{K} - \mathbf{k} - \mathbf{g})\mathbf{u}_j] | n_j \rangle \} \end{aligned} \quad (34)$$

of the absorptive form factor for atom j . In Appendix A, we compute the thermal averages

$$I(\mathbf{K}) = \sum_n p(n) \langle n | \exp[i\mathbf{K}\mathbf{r}] | n \rangle \quad (35)$$

$$J(\mathbf{K}, \mathbf{K}') = \sum_n p(n) \langle n | \exp[i\mathbf{K}\mathbf{r}] | n \rangle \langle n | \exp[-i\mathbf{K}'\mathbf{r}] | n \rangle \quad (36)$$

in the harmonic approximation.

3.1. The isotropic case

Atoms in cubic site symmetry vibrate isotropically. In this case, the thermal vibrations of each atom j are characterized by one number, the thermal mean square displacement $\langle u_j^2 \rangle$ and we obtain for the absorptive form factor

$$f_j'(\mathbf{g}) = -(1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k}-\mathbf{K})f_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \\ \times \{ \exp[-\frac{1}{2}\langle u_j^2 \rangle g^2] - \exp[-\frac{1}{2}\langle u_j^2 \rangle (\mathbf{K}-\mathbf{k})^2] \\ \times \exp[-\frac{1}{2}\langle u_j^2 \rangle (\mathbf{K}-\mathbf{k}-\mathbf{g})^2] \\ \times I_0[(\mathbf{K}-\mathbf{k})(\mathbf{K}-\mathbf{k}-\mathbf{g})(\langle u_j^2 \rangle^2 - \langle u_{0j}^2 \rangle^2)^{1/2}] \}. \quad (37)$$

For temperatures well below the Einstein temperature, the mean square displacement $\langle u_j^2 \rangle$ is close to the zero temperature value $\langle u_{0j}^2 \rangle$. Then the argument of the modified Bessel function I_0 is close to zero and the Bessel function may be replaced by unity. We then obtain the expression

$$f_j'(\mathbf{g}) \approx -(1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k}-\mathbf{K})f_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \\ \times \{ \exp[-\frac{1}{2}\langle u_j^2 \rangle g^2] - \exp[-\frac{1}{2}\langle u_j^2 \rangle (\mathbf{K}-\mathbf{k})^2] \\ \times \exp[-\frac{1}{2}\langle u_j^2 \rangle (\mathbf{K}-\mathbf{k}-\mathbf{g})^2] \}. \quad (38)$$

This equation has also been derived by Hall & Hirsch (1965) using more phenomenological arguments. They implicitly assumed that the crystal is in the ground state, which is only true for zero temperature. It can be shown that ignoring the Bessel function leads to slightly smaller values of $f_j'(\mathbf{g})$. Using an appropriate parameterization for the elastic scattering amplitudes $f_j(\mathbf{g})$, (38) can be integrated analytically (Weickenmeier & Kohl, 1991)

3.2. The anisotropic case

We can evaluate (34) also in the case of anisotropic vibrations. We assume that the thermal vibration matrix is diagonal and the principal axes coincide with the xyz coordinate system. Then, the absorptive form factor is given by (see Appendix A)

$$f_j'(\mathbf{g}) = -(1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k}-\mathbf{K})f_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \\ \times \left(\exp[-\frac{1}{2}(\langle u_{jx}^2 \rangle g_x^2 + \langle u_{jy}^2 \rangle g_y^2 + \langle u_{jz}^2 \rangle g_z^2)] \right. \\ \left. - \exp[-\frac{1}{2}\langle u_{jx}^2 \rangle [(k_x - K_x)^2 + (K_x - k_x - g_x)^2]] \right) \\ \times I_0[(k_x - K_x)(K_x - k_x - g_x)(\langle u_{jx}^2 \rangle^2 - \langle u_{j0x}^2 \rangle^2)^{1/2}] \\ \times \exp[-\frac{1}{2}\langle u_{jy}^2 \rangle [(k_y - K_y)^2 + (K_y - k_y - g_y)^2]] \\ \times I_0[(k_y - K_y)(K_y - k_y - g_y)(\langle u_{jy}^2 \rangle^2 - \langle u_{j0y}^2 \rangle^2)^{1/2}] \\ \times \exp[-\frac{1}{2}\langle u_{jz}^2 \rangle [(k_z - K_z)^2 + (K_z - k_z - g_z)^2]] \\ \times I_0[(k_z - K_z)(K_z - k_z - g_z) \\ \times (\langle u_{jz}^2 \rangle^2 - \langle u_{j0z}^2 \rangle^2)^{1/2}]. \quad (39)$$

In the limit of low temperatures, we may again approximate the modified Bessel function by unity and obtain the simpler expression

$$f_j'(\mathbf{g}) \approx (1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k}-\mathbf{K})f_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \\ \times \left(\exp[-\frac{1}{2}(\langle u_{jx}^2 \rangle g_x^2 + \langle u_{jy}^2 \rangle g_y^2 + \langle u_{jz}^2 \rangle g_z^2)] \right. \\ \left. - \exp[-\frac{1}{2}\langle u_{jx}^2 \rangle [(k_x - K_x)^2 + (K_x - k_x - g_x)^2]] \right) \\ \times \exp[-\frac{1}{2}\langle u_{jy}^2 \rangle [(k_y - K_y)^2 + (K_y - k_y - g_y)^2]] \\ \times \exp[-\frac{1}{2}\langle u_{jz}^2 \rangle [(k_z - K_z)^2 + (K_z - k_z - g_z)^2]]. \quad (40)$$

In the general case, no coordinate system exists in which the displacement matrices are diagonal for all atoms in the unit. Accordingly, we define the temperature factor as (see *e.g.* Willis & Pryor, 1975)

$$T_j(\mathbf{k}) = \exp[-\frac{1}{2}\mathbf{k}^T \mathbf{M}_j \mathbf{k}] \quad (41)$$

with the atomic displacement matrix \mathbf{M} being no longer diagonal. Then, the anisotropic absorptive form factor is given by the general form

$$f_j'(\mathbf{g}) \approx -(1/k_0) \int_{K=k_0} d^2\mathbf{K} f_j(\mathbf{k}-\mathbf{K})f_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \\ \times \{ T_j(\mathbf{g}) - T_j(\mathbf{k}-\mathbf{K})T_j(\mathbf{K}-\mathbf{k}-\mathbf{g}) \}. \quad (42)$$

It should be kept in mind, however, that (40) can be derived from (42) *via* a coordinate transformation.

4. A case study

As an example, we study the anisotropy of the absorptive form factor for an aluminium atom located at a position that allows anisotropic vibrations. We keep the average mean square displacement

$$\langle u^2 \rangle = \frac{1}{3}(\langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle) \quad (43)$$

constant at 0.0025 \AA^2 with $\langle u_x^2 \rangle = \langle u_y^2 \rangle$ and $\langle u_z^2 \rangle / \langle u_x^2 \rangle = \alpha^2$. Equation (40) is evaluated by numerical integration. The values for the elastic scattering amplitudes are calculated using the *FSCATT* subroutine (Weickenmeier & Kohl, 1991). The computed absorptive form factors are depicted in Figs. 1 and 2 for $\alpha = 1.1$ and $\alpha = 2^{1/2}$, respectively, as a function of the modulus $s = g/(4\pi)$ of the scattering vector. Relativistic effects due to the acceleration voltage of 120 kV are included in the atomic scattering amplitudes. The wave vector \mathbf{k} of the incident beam is along the y axis and we give the absorptive form factors for \mathbf{g} along the x and z axes, respectively. For comparison, the result for the isotropic case with the average mean square displacement is also plotted.

From Figs. 1 and 2, we see that for $s = 0$ there is no directional dependency and we thus obtain the same result for the isotropic and anisotropic cases. For

increasing s , the anisotropy becomes increasingly important. As can be seen from Fig. 1(a), even for a very small deviation from isotropy ($\alpha = 1.1$) the ratio of the absorptive form factors for the two different directions is significant. For better visibility, the form factors multiplied with $(1 + s^2/s_0^2)$ are plotted in Fig. 1(b). In the range of s values between 0.5 and 3 \AA^{-1} , which is most important for electron diffraction, the ratio exceeds a factor of two. Figs. 2(a) and (b) show the corresponding curves for $\alpha = 2^{1/2}$. As expected, the direction dependency increases with increasing anisotropy of the temperature factor. Figs. 1 and 2 also indicate that using the isotropic formula with an averaged mean square displacement is only a good approximation for very small deviations ($\alpha < 0.1$) from isotropy.

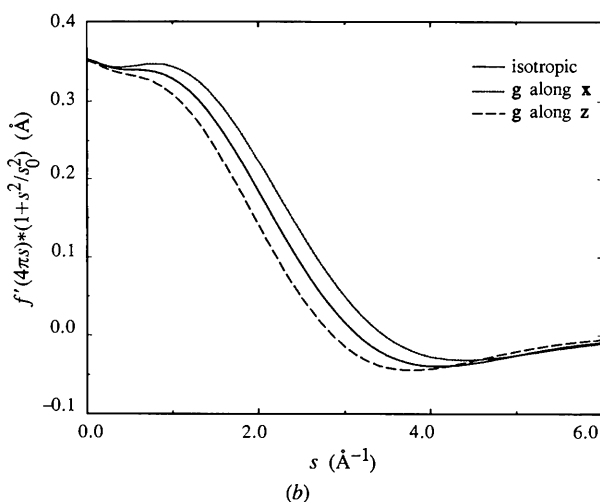
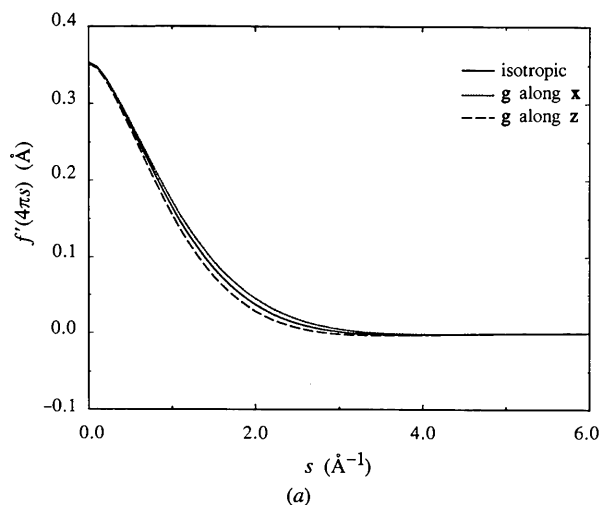


Fig. 1. (a) The anisotropic absorptive form factor for $\alpha = 1.1$ for g along the x direction (dotted line) and along the z direction (dashed line). The solid line gives the isotropic result for the average mean square displacement. (b) Same curves as in (a) but multiplied by $(1 + s^2/s_0^2)$ with $s_0 = 1 \text{ \AA}^{-1}$ to show the large ratio of the form factors for different directions.

5. Discussion

The influence of inelastic scattering processes on the elastic wave function has been incorporated into the dynamical theory of electron diffraction by Yoshioka (1957). He introduced an absorption potential, which is quantum-mechanically correct to first-order Born approximation. Here, we discuss the contribution of thermal diffuse scattering to the absorption potential. In particular, the effect of anisotropic vibrations is studied for the first time. For the special case of isotropic vibrations and low temperatures, the expression given by Hall & Hirsch (1965) is reproduced.

In order to obtain a general formula, we have to use the Einstein approximation, which treats each atom as an independent harmonic oscillator. This appears to be a contradiction in itself: for high temperatures (near the melting point), the vibrations are weakly correlated but also the harmonic approximation breaks down and

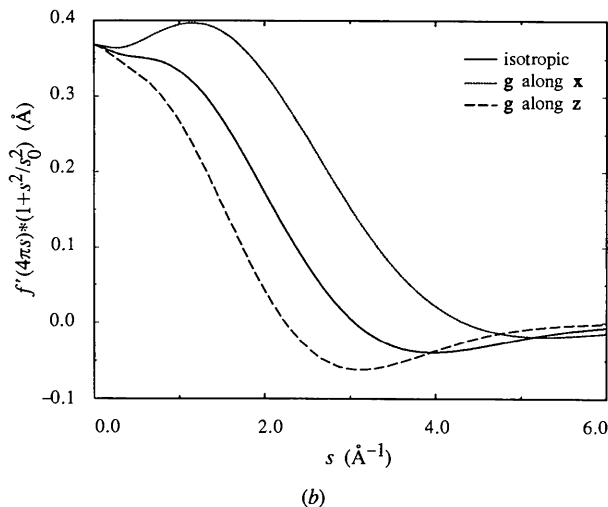
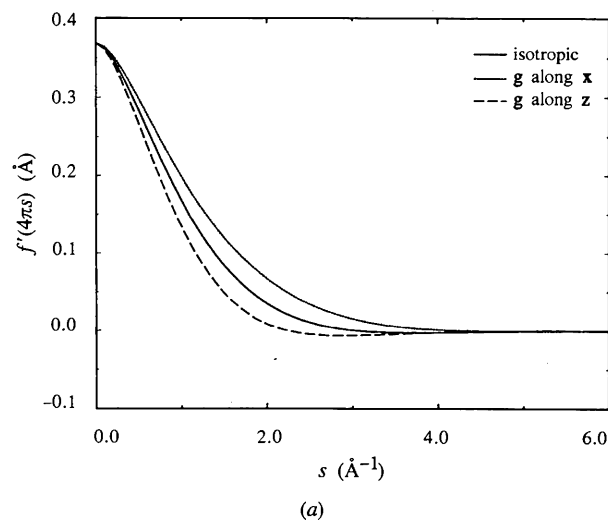


Fig. 2. (a) Same curves as in Fig. 1(a) but for $\alpha = 2^{1/2}$. (b) Same curves as in Fig. 1(b) but for $\alpha = 2^{1/2}$.

should not be used. On the other hand, the thermal motion of the atoms is highly correlated at temperatures well below the Debye temperature. However, since its publication, the formula given by Hall & Hirsch (1965) has been successfully used as the basis for the calculation of the absorptive form factor. This is because no attempt is made to calculate the contribution of individual phonon states but an average is taken over all states. Also, electrons scattered out of the Bragg beams by TDS are considered as absorbed without asking in which particular direction they might have been scattered. Again, this leads to an integration over final states and to a smaller sensitivity to a particular state, thereby reducing the errors due to the choice of the Einstein model.

The influence of the anisotropic mean square displacement has been studied using aluminium as the scattering atom. We find that even for a small anisotropy the absorption potential is strongly direction dependent and the ratio of the absorptive form factors for different directions can exceed a value of 2. Therefore, the isotropic formula cannot be used as an approximation to the anisotropic formula derived here. However, numerical evaluation of (40) is straightforward and can be done in acceptable computing time. A computer subroutine programmed in standard Fortran77 is available on request.

APPENDIX A

We have to calculate the expressions

$$I(\mathbf{K}) = \sum_n p(n) \langle n | \exp[i\mathbf{K}\mathbf{r}] | n \rangle \quad (44)$$

and

$$J(\mathbf{K}, \mathbf{K}') = \sum_n p(n) \langle n | \exp[i\mathbf{K}\mathbf{r}] | n \rangle \langle n | \exp[-i\mathbf{K}'\mathbf{r}] | n \rangle. \quad (45)$$

We will limit our calculations to the harmonic approximation. Therefore, the states $|n\rangle$ are the eigenstates of the three-dimensional harmonic oscillator. We chose a Cartesian coordinate system xyz , which coincides with the principal axes of the thermal displacement matrix (*i.e.* in this system the vibration matrix is diagonal) of the specified atom. We want to point out that these axes are not necessarily parallel to the basis vectors of the unit cell and also that for different atoms the principal axes might point in different directions.

Using the Cartesian representation, the states $|n\rangle$ as well as the probabilities $p(n)$ can be factorized in a product of three one-dimensional oscillator states and probabilities

$$|n\rangle = |n_x\rangle |n_y\rangle |n_z\rangle \quad (46)$$

$$p(n) = p_x(n_x) p_y(n_y) p_z(n_z). \quad (47)$$

For each coordinate $i = xyz$, we have

$$p_i(n) = (1 - \xi_i) \xi_i^n, \quad (48)$$

$$\xi_i = \exp[-\hbar\omega_{Ei}/(k_B T)] \quad (49)$$

with the Einstein frequency ω_{Ei} and the Boltzmann constant k_B . Also, the exponential $\exp[i\mathbf{K}\mathbf{r}]$ factorizes, therefore we can study each coordinate direction independently. For the next steps of the calculation, we use the creation and annihilation operators b^+ , b for the one-dimensional harmonic oscillator. We also need the relations

$$\exp[i\kappa(b^+ + b)] = \exp[\frac{1}{2}\kappa^2] \exp[i\kappa b] \exp[i\kappa b^+] \quad (50)$$

$$\langle n | \exp[i\kappa b] \exp[i\kappa b^+] | n \rangle = \sum_m \binom{n+m}{n} \frac{(-\kappa^2)^m}{m!} \quad (51)$$

$$\sum_n p(n) \langle n | \exp[i\kappa b] \exp[i\kappa b^+] | n \rangle = \exp[-\kappa^2(\bar{n} + 1)], \quad (52)$$

which can be found in standard text books (*e.g.* Davydov, 1971). Here, \bar{n} denotes the expectation value

$$\begin{aligned} \bar{n} &= \sum_n p(n) \langle n | b^+ b | n \rangle \\ &= \xi/(1 - \xi). \end{aligned} \quad (53)$$

In the first step, we calculate $I(\mathbf{K})$ for one coordinate direction. We set

$$K_x x = \kappa(b^+ + b) \quad (54)$$

with

$$\kappa = (\hbar/2m\omega_E)^{1/2} K_x \quad (55)$$

and the atom mass m . Using (50) and (52), we obtain

$$\sum_{n_x} p_x(n_x) \langle n_x | \exp[i\kappa(b^+ + b)] | n_x \rangle = \exp[-\frac{1}{2}\langle u_x^2 \rangle K_x^2] \quad (56)$$

with the mean square displacement in the x direction

$$\langle u_x^2 \rangle = (\hbar/m\omega_{Ex})(\bar{n}_x + \frac{1}{2}). \quad (57)$$

After similar calculations for the yz coordinate directions, we finally obtain

$$I(\mathbf{K}) = \exp[-\frac{1}{2}(\langle u_x^2 \rangle K_x^2 + \langle u_y^2 \rangle K_y^2 + \langle u_z^2 \rangle K_z^2)]. \quad (58)$$

In the case of the isotropic oscillator $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle = \langle u^2 \rangle$, this reduces to the well known expression

$$I(\mathbf{K}) = \exp[-\frac{1}{2}\langle u^2 \rangle K^2]. \quad (59)$$

For the calculation of $J(\mathbf{K}, \mathbf{K}')$ we need some additional relations. The Laguerre polynomials are defined as

$$L_n(x) = \frac{\exp[x]}{n!} \left(\frac{d}{dx} \right)^n \{x^n \exp[-x]\} \quad (60)$$

(see Hochstrasser, 1970). The generating function of these orthogonal polynomials is

$$\exp[-xz/(1-z)] = (1-z) \sum_{n=0}^{\infty} z^n L_n(x) \quad (61)$$

(Hochstrasser, 1970). Furthermore, the addition theorem is

$$(1-z) \sum_{n=0}^{\infty} z^n L_n(x)L_n(y) = \exp[-(x+y)/(1-z)] I_0[2(xy)^{1/2}/(1-z)] \quad (62)$$

(Bateman, 1953) with the modified Bessel function of zeroth order I_0 . After some calculations, we find

$$\sum_{m=0}^{\infty} \binom{n+m}{n} \frac{x^m}{m!} = \exp[x] L_n(-x). \quad (63)$$

We can now calculate $J(\mathbf{K}, \mathbf{K}')$, which can also be factorized:

$$J(\mathbf{K}, \mathbf{K}') = F_x(K_x, K'_x) F_y(K_y, K'_y) F_z(K_z, K'_z) \quad (64)$$

with

$$F_x(K_x, K'_x) = \sum_{n_x} p_x(n_x) \langle n_x | \exp[iK_x x] | n_x \rangle \times \langle n_x | \exp[-iK'_x x] | n_x \rangle \quad (65)$$

and the corresponding terms for the yz coordinates. Therefore, it suffices to evaluate one coordinate direction. In the first step, we insert the creation and annihilation operators and obtain

$$F_x = (1-\xi) \sum_n \xi^n \langle n | \exp[i\kappa(b^+ + b)] | n \rangle \times \langle n | \exp[-i\kappa'(b^+ + b)] | n \rangle. \quad (66)$$

Inserting (50) and (51), we get

$$F_x = (1-\xi) \exp[\frac{1}{2}(\kappa^2 + \kappa'^2)] \times \sum_n \xi^n \sum_{m=0}^{\infty} \binom{n+m}{n} \frac{(-\kappa^2)^m}{m!} \times \sum_{m'=0}^{\infty} \binom{n+m'}{n} \frac{(-\kappa'^2)^{m'}}{m'!}. \quad (67)$$

From (63), it follows that

$$F_x = (1-\xi) \exp[-\frac{1}{2}(\kappa^2 + \kappa'^2)] \sum_n \xi^n L_n(\kappa^2) L_n(\kappa'^2). \quad (68)$$

Finally, we make use of (62) and obtain for each coordinate direction

$$F_x = \exp[-\frac{1}{2}(\kappa^2 + \kappa'^2)(1+\xi)/(1-\xi)] \times I_0[2\xi^{1/2}\kappa\kappa'/(1-\xi)]. \quad (69)$$

After back substitution of ξ, κ, κ' , we obtain for the final result

$$J(\mathbf{K}, \mathbf{K}') = \exp[-\frac{1}{2}(\langle u_x^2 \rangle (K_x^2 + K_x'^2))] \times I_0[K_x K_x' (\langle u_x^2 \rangle^2 - \langle u_{0x}^2 \rangle^2)^{1/2}] \times \exp[-\frac{1}{2}(\langle u_y^2 \rangle (K_y^2 + K_y'^2))] \times I_0[K_y K_y' (\langle u_y^2 \rangle^2 - \langle u_{0y}^2 \rangle^2)^{1/2}] \times \exp[-\frac{1}{2}(\langle u_z^2 \rangle (K_z^2 + K_z'^2))] \times I_0[K_z K_z' (\langle u_z^2 \rangle^2 - \langle u_{0z}^2 \rangle^2)^{1/2}]. \quad (70)$$

Here, $\langle u_{0i}^2 \rangle = \hbar/(2m\omega_{Ei})$ is the thermal mean square displacement at zero temperature for the coordinate $i = xyz$.

If the oscillator is isotropic, then we can derive a simpler expression. In this case, we find

$$J(\mathbf{K}, \mathbf{K}') = \exp[-\frac{1}{2}(\langle u^2 \rangle (K^2 + K'^2))] \times I_0[\mathbf{K}\mathbf{K}' (\langle u^2 \rangle^2 - \langle u_0^2 \rangle^2)^{1/2}]. \quad (71)$$

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