and also as a consequence of the strong fall-off of the form factor f with $(\sin\theta)/\lambda$. The higher background near the absorption edge, which is also clearly visible in Fig. 4, probably arises from the wavelength spread of the monochromator and harmonics (although 222 is weak) which result in some Yb L fluorescence.

Results and concluding remarks

The experimental values of the real part of the anomalous correction term f' for Yb determined from powder data analyses are 3·3 to 5·1 electron units higher than the theoretical values calculated from the Cromer & Liberman (1970, 1981) theoretical method for K and L edges. These differences are similar to those obtained for Sm and Gd using single crystal methods (Templeton *et al.*, 1980, 1982). We have made some efforts to diminish these differences and Dr Liberman tried some modifications in his program. However, at present, no agreement can be reached for the L edge and the correction terms f' have to be determined experimentally.

We have shown that synchrotron powder data can be used for anomalous scattering studies. Because single crystals with the required elements and well determined structures are not always available, simple compounds with light elements such as oxygen in polycrystalline form can be used to obtain directly the f' value at the wavelength needed for single crystal and powder structure determination.

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Transmission of Non-centrosymmetric Crystals by Fast Electrons in the General Laue Case

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Abstract

On treating electron transmission of non-centrosymmetric crystals by the common many-beam dynamical theory, it is shown that the influence of inclined external or internal crystal boundaries as well as the influence of reflections from non-zero-order Laue zones can be treated as a convenient correction or a perturbation of the fundamental (eigenvalue) equation by means of appropriate small correction terms ε_g. Further corrections, arising from anomalous absorption, are written in a comparable form so that the two corrections can be easily compared for various conditions, mainly in kinematical or dynamical

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situations. It is also shown that at symmetric excitation $s_{-g} = s_g$ on neglecting absorption, and the complex eigenvectors of non-centrosymmetric crystals become either 'complex symmetric' or 'complex antisymmetric'. Similar properties known for centrosymmetry are thus generalized.

1. Introduction

The extended capabilities of electron-microscopic imaging and electron diffraction methods available today require a re-thinking of some of the methods of theoretical interpretation. Particular attention has to be paid to usually adopted approximations and to the limits of their validity.

One of the very common approximations neglects the usually small difference between the symmetrical and the general Laue cases. This means that one neglects the fact that the inclination of an external or internal crystal boundary affects the boundary conditions of the electron waves [conditions more recently discussed by Colella (1970)]. Hence it affects the excitation errors which enter the fundametal (eigenvalue) equation and modifies its solutions, *i.e.* the eigenvalues and eigenvectors (amplitude ratios) of the individual Bloch waves, and the correlated extinction lengths. The consequences of inclining a surface to the fine structure of diffracted beams were treated in early papers, *e.g.* von Laue (1948), McGillavry (1940), Kato (1952), Molière & Niehrs (1954). As argued more recently the sensitivity to boundary inclination increases if diffraction arises from regions of stronger local curvature or of larger inclination of the dispersion surface (Sheinin & Jap, 1979). Related situations occur, for example, on working with weak beams or with many beams (high-resolution electron-microscopic imaging, convergent-beam electron diffraction). In such cases, modifications due to reflections from non-zero-order Laue zones have to be taken into account by suitable approximations, too.

Various attempts have been made to treat the eigenvalue equation of the Bloch waves in these respects. Niehrs & Wagner (1955) first showed that in the general Laue case, also, the fundamental equation can be formulated as an eigenvalue equation and that it can be transformed to a Hermitian form of the dynamical matrix. This work and further studies (Whelan & Hirsch, 1957; Spencer & Humphreys, 1971; Metherell, 1975; Saldin, Whelan & Rossouw, 1978; Gjønnes & Gjønnes, 1985) confirm that the influence of an inclined boundary is usually very small. However, owing to unsuitable choices of angles or of coordinate systems, conveniently small terms to account for such influences have not been obtained.

The present paper shows how the influence of boundary inclination as well as the influence of reflections from non-zero-order Laue zones can be described by convenient small correction terms. They will be treated as perturbations, which method is more clearly justified than in the work of Gjønnes & Gjønnes (1985). Non-centrosymmetry is included.

2. The fundamental equation in the general Laue case

2.1. *Usual approximations*

We refer to the wave-mechanical dynamical theory of high-energy electron transmission of crystals. From the work of Fujiwara (1962), the electron mass m_r and wavelength λ are treated relativistically. The known fundamental equation (*e.g.* Kambe & Molière, 1970) will be written in column-matrix notation

$$(\mathbf{U}+\mathbf{D}^{(l)})\mathbf{C}^{(l)}=\mathbf{0}, \tag{2.1}$$

where $\mathbf{C}^{(l)}$ = column matrix of the amplitude ratios C_g^l of the Bloch wave l to be determined, $\mathbf{U}$ = square matrix of elements,

$$U_{gg'} = U_{g-g'} = V_{g-g'} 2m_r/\hbar^2, \tag{2.2}$$

$V_{g-g'}$ = Fourier amplitude of the periodic potential where non-centrosymmetry and anomalous absorption is included (normal absorption is omitted), $\mathbf{D}^{(l)}$ = diagonal matrix of elements,

$$D_{gg}^{(l)} = \mathbf{k}^2 - (\mathbf{k}^{(l)}+\mathbf{g})^2. \tag{2.3}$$

All vectors of the reciprocal space include 2π, hence $|\mathbf{g}| = 2\pi/d_{hkl}$. All wave propagation vectors refer to the interior of the crystal, *i.e.* they are corrected for refraction by the inner potential term $U_0 = V_0 2m_r/\hbar^2$:

$$\mathbf{k}^2 \equiv K^2 = K_0^2 + U_0, \tag{2.4}$$

where $K_0 \equiv 2\pi/\lambda$.

The wave vector $\mathbf{k}^{(l)}$ specific to the Bloch wave l is decomposed by the dispersion-surface construction

$$\mathbf{k}^{(l)} = \mathbf{k} + \Delta\mathbf{k}_l. \tag{2.5}$$

Similarly, the Ewald-sphere construction will be applied to the refraction-corrected wave vectors (von Laue, 1948)

$$|\mathbf{k}+\mathbf{g}+\mathbf{s}_g| = K. \tag{2.6}$$

The vectors $\mathbf{s}_g$ and $\Delta\mathbf{k}_l$ which represent the excitation errors and the *Anpassung* respectively must be orthogonal to the boundary under consideration as known from the boundary conditions. Substitution of (2.5) and (2.6) into (2.3) yields

$$\begin{aligned} D_{gg}^{(l)} &= (\mathbf{k}+\mathbf{g}+\mathbf{s}_g)^2 - (\mathbf{k}+\mathbf{g}+\Delta\mathbf{k}_l)^2 \\ &= 2(\mathbf{k}+\mathbf{g}, \mathbf{s}_g - \Delta\mathbf{k}_l) + \mathbf{s}_g^2 - \Delta\mathbf{k}_l^2. \end{aligned} \tag{2.7}$$

In the usual case known as the high-energy approximation, one neglects the quadratic terms so that

$$D_{gg}^{(l)} = 2(\mathbf{k}+\mathbf{g}, \mathbf{s}_g - \Delta\mathbf{k}_l). \tag{2.8}$$

In the general Laue case, this restriction has to be

checked in detail as will be shown below after evaluating (2.8) by means of correction terms.

2.2. *Correction terms* ε_g

Let us choose a crystallographically fixed Cartesian *xyz* coordinate system whose axis $\mathbf{e}_z$ is parallel to the zone axis of the most strongly excited Laue zone, and is positive along the beam propagation direction. The normal $\mathbf{n}$ of the inclined boundary will be represented by spherical coordinates η, η' (Fig. 1) as

$$\begin{aligned} n_x &= \sin\eta\cos\eta' \\ n_y &= \sin\eta\sin\eta' \\ n_z &= \cos\eta > 0. \end{aligned} \tag{2.9}$$

As a key formula, we decompose the scalar product

$$(\mathbf{k}+\mathbf{g},\mathbf{n})/K = (\mathbf{e}_z,\mathbf{n})(1-\varepsilon'_g), \tag{2.10}$$

where the ε'_g are small correction terms.

$$\begin{aligned} \varepsilon'_g = -\{&g_z + [(k_x+g_x)\cos\eta' \\ &+ (k_y+g_y)\sin\eta']\tan\eta\}/K \end{aligned} \tag{2.11a}$$

by taking $k_z/K = 1$ and neglecting $(k_x/K)^2$, $(k_y/K)^2$. Apparently, ε'_g is comparable to the size of Bragg angles θ_g as long as $\tan\eta$ is of the order of unity. Since $|\tan\eta| \lesssim 10$ as explained below, the $|\varepsilon'_g|$ can reach the order of 0·1. Large $|\varepsilon'_g|$ are also favoured by large x and y components of $\mathbf{k}+\mathbf{g}$.

Below we are interested in the g-dependent part of (2.11*a*):

$$\varepsilon_g = -[g_z + (g_x\cos\eta' + g_y\sin\eta')\tan\eta]/K \tag{2.11b}$$

$$= -(\mathbf{n},\mathbf{g})/K(\mathbf{n},\mathbf{e}_z). \tag{2.11c}$$

It should be noted that in the symmetrical Laue case, where $\eta = 0 = \eta'$, corrections $\varepsilon'_g = -g_z/K = \varepsilon_g$ arise from non-zero-order Laue-zone reflections.

The corrections will be used now to rewrite $D^{(l)}_{gg}$. Replacing $\mathbf{n}$ of (2.10) by $\mathbf{s}_g - \Delta\mathbf{k}_l$ and substituting into (2.8), one gets

$$D^{(l)}_{gg} = 2K[s(\varepsilon)_g - \gamma(\varepsilon)_l](1-\varepsilon_g). \tag{2.12}$$

At this point, ε'_g has been replaced by ε_g since the g-independent part of ε'_g common to all diagonal elements can be omitted.

At the same time, ε-dependent excitation errors and eigenvalues have been introduced according to

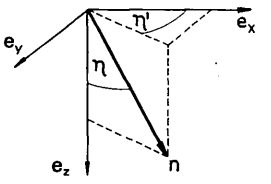

Fig. 1. Spherical coordinates η, η' of the normal $\mathbf{n}$ of the crystal boundary.

usual definitions

$$s(\varepsilon)_g \equiv (\mathbf{s}_g, \mathbf{e}_z) \tag{2.13a}$$

$$\gamma(\varepsilon)_l \equiv (\Delta\mathbf{k}_l, \mathbf{e}_z). \tag{2.13b}$$

The correlation to the known ε-independent 'radial' excitation error $s_g = K - |\mathbf{k}+\mathbf{g}|$ follows (on neglecting s_g^2) from the relationships

$$\begin{aligned} K^2 - (\mathbf{k}+\mathbf{g})^2 &= (K + |\mathbf{k}+\mathbf{g}|)(K - |\mathbf{k}+\mathbf{g}|) = 2Ks_g \\ &= -2(\mathbf{k},\mathbf{g}) - \mathbf{g}^2 \\ &= 2Ks(\varepsilon)_g(1-\varepsilon_g), \end{aligned}$$

where the latter expression is given by comparing (2.3) and (2.12) at $\Delta\mathbf{k}_l = 0$. The radial excitation error is therefore

$$\begin{aligned} s_g &= K - |\mathbf{k}+\mathbf{g}| = -[2(\mathbf{k},\mathbf{g}) + \mathbf{g}^2]/2K \\ &= s(\varepsilon_g)(1-\varepsilon_g). \end{aligned} \tag{2.14}$$

Let us return now to the neglect of the quadratic terms of (2.7). They have to be compared with the small terms $2K\varepsilon_g[s(\varepsilon)_g - \gamma(\varepsilon)_l]$ of (2.12) which arise from the ε_g correction. Hence this correction becomes reasonable if its terms well exceed $|s_g^2 - \Delta\mathbf{k}_l^2|$ or, more simply, if $|K\varepsilon_g| \gg |\mathbf{s}_g|$ or $|\Delta\mathbf{k}_l|$. This condition yields a minimum meaningful angle $|\eta|$ of inclination if we put $|K\varepsilon_g| \simeq |\mathbf{g}\tan\eta|$ because of (2.11). Then we have $|\mathbf{g}\tan\eta| \gg |\mathbf{s}_g|$ or roughly $|\eta| \gg |\theta_g| =$ Bragg angle. This means that the ε_g corrections become meaningful if the inclination of the boundary exceeds the Bragg angle by an order of magnitude.

Similar considerations yield an upper limit of $|\eta|$. Neglect of the quadratic terms in (2.7) is reasonable if they are small compared with $|(\mathbf{g}, \mathbf{s}_g - \Delta\mathbf{k}_l)|$. The latter quantity becomes extremely large $\simeq |g||\mathbf{s}_g|$ if $\mathbf{s}_g$ (or $\Delta\mathbf{k}_l$) is nearly parallel to $\mathbf{g}$ as it can occur at large inclinations $|\eta|$. Then one neglects, on principle, $\mathbf{s}_g^2 \ll |\mathbf{g}||\mathbf{s}_g|$, *i.e.* $|\mathbf{s}_g| \ll |\mathbf{g}|$. Substitution of $|\mathbf{s}_g| = |s_g/\cos\eta| \simeq |s_g\tan\eta|$, where s_g is the excitation error at $\eta = 0$, yields the condition $|\tan\eta| \ll |\mathbf{g}/s_g|$ as an upper limit for the inclination. As to transmission electron microscopy, standard methods of 'dynamical' imaging work at $|\mathbf{g}/s_g| \simeq 1/\theta_g \simeq 100$ while 'kinematical' weak-beam imaging requires $|\mathbf{g}/s_g| \simeq 5\,\mathrm{nm}^{-1}/0{\cdot}2\,\mathrm{nm}^{-1} = 25$. Therefore, the corresponding boundary inclination in the former and latter cases should not exceed 85 and 70° respectively in order to allow for neglect of the quadratic terms.

2.3. *Matrix notation of the corrected fundamental equation*

The following quantities will be arranged as diagonal matrices:

$$\{s_g\} \equiv \mathbf{s}, \quad \{\varepsilon_g\} \equiv \boldsymbol{\varepsilon}, \quad \{\gamma_l\} \equiv \boldsymbol{\gamma}, \tag{2.15}$$

where the labelling sequence of g corresponds to the fundamental equation. Thus, (2.12) reads $\mathbf{D}^{(l)}/2K =$

$\mathbf{s}-\gamma(\varepsilon)_l(\mathbf{I}-\varepsilon)$ on substituting from (2.14) [where $\mathbf{I}$ = unit matrix and $\mathbf{s}(\varepsilon)(\mathbf{I}-\boldsymbol{\varepsilon})=\mathbf{s}$ due to (2.14)]. The fundamental equation (2.1) thus becomes

$$(\mathbf{U}/2K+\mathbf{s})\mathbf{C}^{(l)}=\gamma(\varepsilon)_l(\mathbf{I}-\boldsymbol{\varepsilon})\mathbf{C}^{(l)}, \qquad (2.16)$$

where $\mathbf{U}/2K\equiv\mathbf{W}$ is the off-diagonal of the dynamical matrix

$$\mathbf{A}\equiv\mathbf{U}/2K+\mathbf{s}\equiv\mathbf{W}+\mathbf{s}. \qquad (2.17)$$

The columns of (2.16) can be combined according to a suitable labelling sequence of l to form a square-matrix equation $\mathbf{AC}(\varepsilon)=(\mathbf{I}-\boldsymbol{\varepsilon})\mathbf{C}(\varepsilon)\boldsymbol{\gamma}(\varepsilon)$, where $\mathbf{C}(\varepsilon)$ is the ε-dependent square matrix composed of the eigenvectors. On neglecting $\boldsymbol{\varepsilon}^2$ this rearranges to

$$\mathbf{C}(\varepsilon)^{-1}(\mathbf{I}+\boldsymbol{\varepsilon})\mathbf{AC}(\varepsilon)=\boldsymbol{\gamma}(\varepsilon). \qquad (2.18)$$

This is an eigenvalue equation where the dynamical matrix $(\mathbf{I}+\boldsymbol{\varepsilon})\mathbf{A}$ is a linear correction of the ε-independent $\mathbf{A}$ of (2.17).

Neglect of $\boldsymbol{\varepsilon}^2$ in (2.18) limits again the angle η of boundary inclination. For an estimation, (2.11) will be simplified as $|\varepsilon_g|\simeq|(\mathbf{g}/K)\tan\eta|\simeq|10^{-2}\tan\eta|$. To obtain $\varepsilon_g^2\ll|\boldsymbol{\varepsilon}_g|$, *i.e.* $|\varepsilon_g|\ll 1$ needs $|\tan\eta|\lesssim 10$, $|\eta|\lesssim 85°$. A similar limit has been set by neglecting $\mathbf{s}_g^2$ as explained above.

2.4. *Properties of the matrices*

As discussed by Spencer & Humphreys (1971), a weak 'asymmetry' of the dynamical matrix results in the general Laue case. In our notation, the matrix $(\mathbf{I}+\boldsymbol{\varepsilon})\mathbf{A}$ of (2.18) is never Hermitian (as a consequence of pre-multiplication by $\mathbf{I}+\boldsymbol{\varepsilon}$). However, suitable transformations allow a Hermitian dynamical matrix to be obtained even in the general Laue case as already shown by Niehrs & Wagner (1955). In our treatment, $\mathbf{A}$ and $\mathbf{C}$ can be transformed to

$$\bar{\mathbf{A}}\equiv(\mathbf{I}+\boldsymbol{\varepsilon}/2)\mathbf{A}(\mathbf{I}+\boldsymbol{\varepsilon}/2)\equiv\bar{\mathbf{W}}+\mathbf{s}(\mathbf{I}+\boldsymbol{\varepsilon})$$
$$=\mathbf{W}+(\boldsymbol{\varepsilon}\mathbf{W}+\mathbf{W}\boldsymbol{\varepsilon})/2+(\mathbf{I}+\boldsymbol{\varepsilon})\mathbf{s} \qquad (2.19a)$$

$$\bar{\mathbf{C}}\equiv(\mathbf{I}-\boldsymbol{\varepsilon}/2)\mathbf{C}(\varepsilon)$$
$$\bar{\mathbf{C}}^{-1}=\mathbf{C}(\varepsilon)^{-1}(\mathbf{I}+\boldsymbol{\varepsilon}/2) \qquad (2.19b)$$

on neglecting $\boldsymbol{\varepsilon}^2$. Thus (2.18) transforms to

$$\boldsymbol{\gamma}(\varepsilon)=\bar{\mathbf{C}}^{-1}\bar{\mathbf{A}}\bar{\mathbf{C}}. \qquad (2.20)$$

The symmetry properties of this equation can be compared with the symmetrical Laue case. This is seen by specifying the following conditions [on abbreviating $\mathbf{s}(\mathbf{I}+\boldsymbol{\varepsilon})\equiv\bar{\mathbf{s}}$ and on writing $\tilde{\mathbf{M}}$ as the transpose of a matrix $\mathbf{M}$].

(1) No anomalous absorption: $\tilde{\bar{\mathbf{A}}}^*=\bar{\mathbf{A}}$ is Hermitian. Hence, as known,

$$\bar{\mathbf{C}}^{-1}\bar{\mathbf{A}}\bar{\mathbf{C}}=\boldsymbol{\gamma}(\varepsilon)=\tilde{\bar{\mathbf{C}}}^*\bar{\mathbf{A}}\widetilde{\bar{\mathbf{C}}^{-1}}^*=\widetilde{\boldsymbol{\gamma}(\varepsilon)}^*,$$

therefore

$$\boldsymbol{\gamma}(\varepsilon)\text{ real}, \qquad \bar{\mathbf{C}}\text{ unitary: }\bar{\mathbf{C}}^{-1}=\tilde{\bar{\mathbf{C}}}^*. \qquad (2.21)$$

(2) Centrosymmetry: $\tilde{\bar{\mathbf{A}}}=\bar{\mathbf{A}}$, inclusion of absorption yields

$$\bar{\mathbf{C}}^{-1}\bar{\mathbf{A}}\bar{\mathbf{C}}=\boldsymbol{\gamma}(\varepsilon)=\widetilde{\boldsymbol{\gamma}(\varepsilon)}=\tilde{\bar{\mathbf{C}}}\bar{\mathbf{A}}\widetilde{\bar{\mathbf{C}}^{-1}},$$

therefore

$$\boldsymbol{\gamma}(\varepsilon)\text{ complex}, \qquad \bar{\mathbf{C}}\text{ 'orthogonal': }\tilde{\bar{\mathbf{C}}}=\bar{\mathbf{C}}^{-1}, \quad \tilde{\bar{\mathbf{C}}}\bar{\mathbf{C}}=\mathbf{I}. \qquad (2.22)$$

3. Perturbation treatment of the general Laue case

For solving the eigenvalue equation numerically, either (2.20) or (2.18) may be used. It is, however, more illustrative to solve it for $\boldsymbol{\varepsilon}=\mathbf{0}$ and to treat the small correction $\boldsymbol{\varepsilon}$ as perturbation. The corresponding procedure outlined in Appendix 1 requires the case of degeneracy $\gamma_{l'}=\gamma_l$ to be excluded (critical voltage effect). Absorption will be neglected; it is treated in § 4 by perturbation also.

The eigenvalue equation (2.18) is represented by (*A*1.4) on identifying $\boldsymbol{\Delta}\mathbf{A}\equiv\boldsymbol{\varepsilon}\mathbf{A}$, on putting $\mathbf{X}=\mathbf{0}$, and

$$\mathbf{C}(\varepsilon)\equiv\mathbf{C}(\mathbf{I}+\mathbf{Y})$$
$$\mathbf{C}(\varepsilon)^{-1}\equiv(\mathbf{I}-\mathbf{Y})\tilde{\mathbf{C}}^*. \qquad (3.1a)$$

3.1. *Correction of the eigenvalues*.

Equation (*A*1.6) yields (by use of $\mathbf{AC}=\mathbf{C}\boldsymbol{\gamma}$, $\tilde{\mathbf{C}}^*\mathbf{A}=\boldsymbol{\gamma}\tilde{\mathbf{C}}^*$)

$$\Delta\gamma_l=(\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{AC})_{ll}=\gamma_l(\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C})_{ll}=(\tilde{\mathbf{C}}^*\mathbf{A}\boldsymbol{\varepsilon}\mathbf{C})_{ll}$$

so that

$$\Delta\gamma_l/\gamma_l=\sum_g|C_{gl}|^2\varepsilon_g \qquad (3.2)$$

are real corrections, the signs of which depend on the sign of the inclination η if $g_z=0$.

These corrections disappear although $\eta\neq 0$ in the case of 'symmetric excitation' (see Appendix 2) since then $|C_{-gl}|=|C_{gl}|$ in addition to $\varepsilon_{-g}=-\varepsilon_g$, $\varepsilon_0=0$, *cf.* (2.11*c*).

If, on the other hand, the orientation is far from any Bragg position, the kinematical approximation $\mathbf{C}\simeq\mathbf{I}$, $\gamma_l=s_g$ specifies (3.2) as

$$\gamma(\varepsilon)_l=s(\varepsilon)_g=s_g(1+\varepsilon_g) \qquad (3.3)$$

in agreement with (2.14).

3.2. *Correction of the eigenvectors*

Equation (*A*1.7) yields the elements of $\mathbf{Y}$ in (3.1*a*) as

$$Y_{ll'}=(\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{AC})_{ll'}/(\gamma_{l'}-\gamma_l)=(\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C})_{ll'}\gamma_{l'}/(\gamma_{l'}-\gamma_l)$$
$$=\left(\sum_g C_{gl}^*C_{gl'}\varepsilon_g\right)\Big/(1-\gamma_l/\gamma_{l'}) \qquad (3.1b)$$

(by use of $\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{AC}=\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C}\tilde{\mathbf{C}}^*\mathbf{AC}=\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C}\boldsymbol{\gamma}$). The same results can be obtained if the transformed equation

(2.20) is identified with (*A*1.4) on taking $\mathbf{\Delta A} \equiv (\boldsymbol{\varepsilon}\mathbf{A}+\mathbf{A}\boldsymbol{\varepsilon})/2$ and $\mathbf{X} \equiv -\boldsymbol{\varepsilon}/2$.

In the extreme kinematical case the approximation $\mathbf{C}=\mathbf{I}$, $\mathbf{A}=\mathbf{s}$ makes $\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{A}\mathbf{C}$ of (3.1*b*) diagonal, hence the correction of the eigenvectors disappears.

In the dynamical case of 'symmetric excitation' (Appendix 2), the symmetry properties of the eigenvectors in addition to $\varepsilon_{-g}=-\varepsilon_g$ make the $Y_{ll'}$ become if not zero either real or imaginary as follows:

If $\mathbf{C}^{(l)}$ and $\mathbf{C}^{(l')}$ are of the same type of symmetry, $C^*_{-gl}C_{-gl'}=(C^*_{gl}C_{gl'})^*$, imaginary corrections arise:

$$Y_{ll'} = i2\ \mathrm{Im}\left(\sum_g C^*_{gl}C_{gl'}\varepsilon_g\right)\Big/(1-\gamma_l/\gamma_{l'}). \quad (3.4)$$

If $\mathbf{C}^{(l)}$ and $\mathbf{C}^{(l')}$ are of different symmetry, $C^*_{-gl}C_{-gl'}=-(C^*_{gl}C_{gl'})^*$, real corrections arise:

$$Y_{ll'} = 2\ \mathrm{Re}\left(\sum_g C^*_{gl}C_{gl'}\varepsilon_g\right)\Big/(1-\gamma_l/\gamma_{l'}). \quad (3.5)$$

3.3. *Specification to the two-beam case*

As an illustrative example we consider the two-beam approximation. In this case, non-centrosymmetry can be eliminated by a suitable choice of origin for the Fourier expansion of the lattice potential. The absorption-free **A** and **C** become real,

$$\mathbf{A}=\begin{bmatrix} 0 & \sigma_0/2 \\ \sigma_0/2 & s_g \end{bmatrix} \quad (3.6)$$

$$\mathbf{C}=\begin{bmatrix} C_{02} & C_{01} \\ C_{g2} & C_{g1} \end{bmatrix}=\begin{bmatrix} \cos\vartheta & \sin\vartheta \\ -\sin\vartheta & \cos\vartheta \end{bmatrix}$$
$$=2^{-1/2}\begin{bmatrix} (1+w_r)^{1/2} & (1-w_r)^{1/2} \\ -(1-w_r)^{1/2} & (1+w_r)^{1/2} \end{bmatrix}, \quad (3.7)$$

where

$$\sigma_0 \equiv |U_g|/K$$
$$\cot 2\vartheta \equiv w = s_g/\sigma_0 = s_g\xi_g/2\pi$$
$$\cos 2\vartheta = w_r \equiv w/(1+w^2)^{1/2}.$$

Indices 1 and 2 refer to the upper and lower branch, respectively, of the dispersion surface.

The known eigenvalues and anomalous absorption terms can be written as

$$\mathrm{Re}\ \gamma_{1,2} = (s_g \pm \sigma)/2 = (w_r \pm 1)\sigma/2 \quad (3.8)$$

$$\mathrm{Im}\ \gamma_{1,2} = \pm|U'_g|/2K(1+w^2)^{1/2}, \quad (3.9)$$

where

$$\sigma \equiv \sigma_0(1+w^2)^{1/2}.$$

The correction terms (2.11*b*) read (if $\mathbf{e}_x$ is along $\mathbf{g}$)

$$\varepsilon_0 = 0, \qquad \varepsilon_g = -(\cos\eta'\tan\eta)\lambda/d_{hkl}. \quad (3.10)$$

Following the comment to (2.12) we can add the small quantity $-\varepsilon_g/2$ to both ε_0 and ε_g which thus become more symmetrical corrections ε_- and ε_+ respectively:

$$\varepsilon_\mp = \mp\varepsilon_g/2 = \pm(\cos\eta'\tan\eta)\lambda/2d_{hkl}. \quad (3.11)$$

The above expressions yield explicitly

$$\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C} = \begin{bmatrix} w & 1 \\ 1 & -w \end{bmatrix}\frac{\varepsilon_-}{(1+w^2)^{1/2}}. \quad (3.12)$$

The diagonal elements yield the relative corrections of the eigenvalues

$$(\Delta\gamma/\gamma)_{1,2} = \mp w_r\varepsilon_- = \mp w_r(\cos\eta'\tan\eta)\lambda/2d_{hkl}. \quad (3.13)$$

As generally stated above these corrections disappear at the Bragg position ('symmetric excitation') where $w=0=w_r$.

If $w\neq 0$, the difference $\gamma_1-\gamma_2=\sigma$ is corrected to

$$(\gamma_1+\Delta\gamma_1)-(\gamma_2+\Delta\gamma_2) = \gamma_1-\gamma_2-w_r\varepsilon_-(\gamma_1+\gamma_2)$$
$$= \sigma - w_r s_g\varepsilon_-$$
$$= \sigma(1-w_r^2\varepsilon_-).$$

Hence the w-dependent extinction distance $\xi_{\mathrm{eff}}=2\pi/\sigma$ is corrected to

$$\xi_{\mathrm{eff}}(\varepsilon) = \xi_{\mathrm{eff}}(1+w_r^2\varepsilon_-)$$
$$= \xi_{\mathrm{eff}}[1+w_r^2(\cos\eta'\tan\eta)\lambda/2d_{hkl}]. \quad (3.14)$$

It is seen that the extinction distance increases or decreases if $\eta>0$ or $\eta<0$, respectively. This conclusion agrees at least qualitatively with the experiments of Kim, Perez & Sheinin (1982). At a given inclination η', η the correction of ξ_{eff} maximizes for extreme kinematical conditions where $w^2\gg 1$, $w_r^2\simeq 1$. This change may amount to up to $\simeq 10\%$ if $|\tan\eta|\gg 1$.

The correction (3.1*b*) of the eigenvectors is given by substitution from (3.12) and (3.11),

$$Y_{12,21} = \varepsilon_-(1\pm w_r)/2(1+w^2)^{1/2}$$
$$= (\cos\eta'\tan\eta)(1\pm w_r)\lambda/4d_{hkl}(1+w^2)^{1/2}. \quad (3.15)$$

These real corrections disappear at large $|w|\gg 1$ but not at the Bragg position where **Y** becomes symmetric

$$Y_{21} = Y_{12} = (\cos\eta'\tan\eta)\lambda/4d_{hkl}. \quad (3.16)$$

4. A comparison with anomalous absorption

4.1. *Absorption correction in the symmetrical Laue case*

Phenomenologically, anomalous absorption can be taken into account by introducing imaginary potential terms $iU'_{gg'}$ (Yoshioka, 1957) which can be treated as a perturbation of the eigenvalue equation (which has to be solved for the absorption-free case). In our notation the $U'_{gg'}/2K$ will be represented by a matrix **W'**. Following Appendix 1, we identify in (*A*1.4) $\mathbf{\Delta A} \equiv i\mathbf{W}'$ and $\mathbf{X}\equiv\mathbf{0}$ in order to determine $\mathbf{\Delta\gamma}$ and

$\mathbf{Y} \equiv i\mathbf{Y}'$ from (*A*1.6) and (*A*1.7) respectively:

$$\gamma_l = \text{Re } \gamma_l + i(\tilde{\mathbf{C}}^*\mathbf{W}'\mathbf{C})_{ll} \tag{4.1}$$

$$\mathbf{C} \to \mathbf{C}(\mathbf{I} + i\mathbf{Y}'), \qquad \mathbf{C}^{-1} \to (\mathbf{I} - i\mathbf{Y}')\tilde{\mathbf{C}}^*$$

$$Y'_{ll'} = (\tilde{\mathbf{C}}^*\mathbf{W}'\mathbf{C})_{ll'}/(\gamma_{l'} - \gamma_l) \tag{4.2}$$

in agreement with known solutions (*e.g.* Wilkens, Katerbau & Rühle, 1973) and assuming $\gamma_{l'} \neq \gamma_l$.

A simpler matrix multiplication as well as some physical conclusion can be obtained if we use the rough approximation

$$\mathbf{W}' = a'\mathbf{W}, \tag{4.3}$$

where $0 < a' \ll 1$, as in the case of the two-beam approximation. The matrix product $\tilde{\mathbf{C}}^*\mathbf{W}'\mathbf{C}$ can then be decomposed according to the absorption-free eigenvalue equation $\tilde{\mathbf{C}}^*\mathbf{W}\mathbf{C} = \boldsymbol{\gamma} - \tilde{\mathbf{C}}^*\mathbf{s}\mathbf{C}$. Equations (4.1), (4.2) thus yield

$$\text{Im } \gamma_l = a' \text{ Re } \gamma_l - a'(\tilde{\mathbf{C}}^*\mathbf{s}\mathbf{C})_{ll}$$

$$= a' \text{ Re } \gamma_l - a' \sum_g s_g |C_{gl}|^2 \tag{4.4}$$

$$Y'_{ll'} = a'(\tilde{\mathbf{C}}^*\mathbf{s}\mathbf{C})_{ll'}/(\gamma_l - \gamma_{l'}). \tag{4.5}$$

Some specific cases will be considered. Anomalous absorption is a dynamical phenomenon. It disappears at extreme kinematical conditions where $\mathbf{C} = \mathbf{I}$, $\text{Re } \boldsymbol{\gamma} = \mathbf{s}$ can be used in (4.1)–(4.5) to show that both $\text{Im } \boldsymbol{\gamma}$ and $\mathbf{Y}'$ become zero.

Let us suppose dynamical conditions of 'symmetric excitation' (see Appendix 2). If in that case the Bragg condition is satisfied for the smallest $|\mathbf{g}|$ all further reflections contribute with $s_g < 0$. Hence the second member of (4.4) becomes > 0, which means enhancement of absorption, but the first member can be modified by dynamical interaction in a more complicated way, as known.

The corrections $iY'_{ll'}$ of the eigenvectors become (if not zero) either imaginary or real if the correlated $\mathbf{C}^{(l)}$ and $\mathbf{C}^{(l')}$ are of equal or of different type of symmetry, respectively. [To be shown as in the case of (3.4), (3.5).] In the two-beam case, (4.5) yields

$$Y'_{21,12} = \pm a' s_g / 2\sigma(1 + w^2)^{1/2}$$

$$= \pm a' w / 2(1 + w^2). \tag{4.6}$$

Hence, $\mathbf{Y}'$ becomes zero at $w = 0$ and at $w^2 \gg 1$, while at $|w| = 1$ maxima $|Y_{ll'}| = a'/4$ arise.

4.2. *Comparison of the absorption and* $\boldsymbol{\varepsilon}$ *corrections*

Since the corrections due to anomalous absorption and $\boldsymbol{\varepsilon}$ were made by first-order perturbation, they simply add if applied simultaneously. The eigenvalues are thus corrected by

$$\Delta\gamma_l = (\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C})_{ll} \text{ Re } \gamma_l + i(\tilde{\mathbf{C}}^*\mathbf{W}'\mathbf{C})_{ll} \tag{4.7a}$$

or, on approximating $\mathbf{W}' = a'\mathbf{W}$ and using (4.4),

$$\Delta\gamma_l = (\tilde{\mathbf{C}}^*\boldsymbol{\varepsilon}\mathbf{C})_{ll} \text{ Re } \gamma_l + ia'[\text{Re } \gamma_l - (\tilde{\mathbf{C}}^*\mathbf{s}\mathbf{C})_{ll}]. \tag{4.7b}$$

For dynamical conditions, the first term is usually of lower magnitude than the absorption term. This situation reverses, however, for kinematical conditions where the $\boldsymbol{\varepsilon}$ correction maximizes while the absorption tends to disappear.

The eigenvectors are corrected by combining (3.1*b*) and (4.5) (if $\mathbf{W}' = a'\mathbf{W}$):

$$(\mathbf{Y} + i\mathbf{Y}')_{ll'} = [\tilde{\mathbf{C}}^*(\boldsymbol{\varepsilon} \text{ Re } \gamma_{l'} - ia'\mathbf{s})\mathbf{C}]_{ll'}/(\gamma_{l'} - \gamma_l). \tag{4.8}$$

As in the case of the eigenvalues, both corrections are comparable if ε_g and a' are of comparable magnitude. As stated above both corrections disappear at extreme kinematical conditions. In the dynamical case of 'symmetric excitation' both corrections simultaneously become real or imaginary, depending on the symmetry of the eigenvectors. If the Bragg condition of the two-beam case is satisfied the absorption correction of the eigenvectors disappears but their $\boldsymbol{\varepsilon}$ dependency remains.

5. Concluding remarks

The inclination η of any crystal boundary (general Laue case) and also reflections of non-zero-order Laue zones modify the eigenvalue equation by a weak correction owing to a diagonal matrix of elements ε_g. The inclination-induced part of the correction becomes meaningful if $|\eta|$ well exceeds the Bragg angles θ_g. In this frequent case, factors like $1/\cos\theta_g$ often used for multiplying the off-diagonal elements of the dynamical matrix become meaningless. The $\boldsymbol{\varepsilon}$ corrections fail if $|\eta|$ exceeds about 70 or 85° in the kinematical or dynamical case, respectively, in electron-microscopic imaging.

The corrected eigenvalue equation can be transformed to a Hermitian form of the dynamical matrix (if absorption is neglected).

Independently of this form, solutions can be obtained from the uncorrected equation by means of perturbation. The latter method shows that the corrections of the eigenvalues are real.

On introducing anomalous absorption by corresponding, sometimes simplified, perturbation, close comparisons to the $\boldsymbol{\varepsilon}$ corrections can be made with the following results:

At extreme kinematical diffraction conditions the absorption corrections naturally disappear while the $\boldsymbol{\varepsilon}$ corrections disappear for the eigenvectors but not for the eigenvalues. The corresponding two-beam extinction length may be modified up to about ±10% for extreme $\eta \gtrless 0$.

Dynamical diffraction conditions can be usefully specified to 'symmetric excitation' $s_{-g} = s_g$ where any eigenvector becomes either 'complex symmetric' or 'complex antisymmetric' (at non-centrosymmetry without absorption).

In this case, the $\boldsymbol{\varepsilon}$ correction of the eigenvalues disappears. The remaining corrections to the eigen-

vectors (due to ε and absorption) are made by real and imaginary elements, depending on the symmetry of the related eigenvectors.

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APPENDIX 1
First-order perturbation of an eigenvalue equation

We suppose an eigenvalue equation

$$\mathbf{C}^{-1}\mathbf{A}\mathbf{C}=\boldsymbol{\gamma} \qquad (A1.1)$$

of known solutions C_{gl} and γ_l, where degeneracy $\gamma_{l'}=\gamma_l$ does not occur. If a matrix $\Delta\mathbf{A}$ of small elements $|\Delta A_{gg'}|\ll|A_{gg'}|$ is added to $\mathbf{A}$ the modified solutions will be written as

$$\begin{aligned}\boldsymbol{\gamma}(\Delta)&\equiv\boldsymbol{\gamma}+\Delta\boldsymbol{\gamma}\\ \mathbf{C}(\Delta)&=(\exp\mathbf{X})\mathbf{C}(\exp\mathbf{Y}),\end{aligned} \qquad (A1.2)$$

where $\mathbf{X}$ and $\mathbf{Y}$ are square matrices of small elements $|X_{gg'}|\ll 1$, $|Y_{ll'}|\ll 1$, and $Y_{ll}=0$. The first-order evaluation

$$\begin{aligned}\mathbf{C}(\Delta)&=(\mathbf{I}+\mathbf{X})\mathbf{C}(\mathbf{I}+\mathbf{Y})\\ \mathbf{C}(\Delta)^{-1}&=(\mathbf{I}-\mathbf{Y})\mathbf{C}^{-1}(\mathbf{I}-\mathbf{X})\end{aligned} \qquad (A1.3)$$

violates $\mathbf{C}(\Delta)\mathbf{C}(\Delta)^{-1}=\mathbf{I}$ in quadratic and higher-order terms of $\mathbf{X}$ and $\mathbf{Y}$. Substitution into (A1.1),

$$\boldsymbol{\gamma}+\Delta\boldsymbol{\gamma}=(\mathbf{I}-\mathbf{Y})\mathbf{C}^{-1}(\mathbf{I}-\mathbf{X})(\mathbf{A}+\Delta\mathbf{A})(\mathbf{I}+\mathbf{X})\mathbf{C}(\mathbf{I}+\mathbf{Y}), \qquad (A1.4)$$

yields perturbation to first order of $\Delta\mathbf{A}$, $\mathbf{XC}$, $\mathbf{CY}$ *etc*:

$$\begin{aligned}\Delta\boldsymbol{\gamma}&=-\mathbf{Y}\boldsymbol{\gamma}+\boldsymbol{\gamma}\mathbf{Y}+\mathbf{C}^{-1}(-\mathbf{X}\mathbf{A}+\mathbf{A}\mathbf{X}+\Delta\mathbf{A})\mathbf{C}\\ &=-\mathbf{Y}\boldsymbol{\gamma}+\boldsymbol{\gamma}\mathbf{Y}-\mathbf{C}^{-1}\mathbf{X}\mathbf{C}\boldsymbol{\gamma}+\boldsymbol{\gamma}\mathbf{C}^{-1}\mathbf{X}\mathbf{C}+\mathbf{C}^{-1}\Delta\mathbf{A}\mathbf{C}.\end{aligned} \qquad (A1.5)$$

Since $\Delta\boldsymbol{\gamma}$ is diagonal and $\boldsymbol{\gamma}\mathbf{Y}-\mathbf{Y}\boldsymbol{\gamma}$ as well as $\boldsymbol{\gamma}\mathbf{C}^{-1}\mathbf{X}\mathbf{C}-\mathbf{C}^{-1}\mathbf{X}\mathbf{C}\boldsymbol{\gamma}$ is diagonal-free, (A1.5) decomposes, yielding the unknown

$$\Delta\gamma_l=[\mathbf{C}^{-1}(\Delta\mathbf{A}-\mathbf{X}\mathbf{A}+\mathbf{A}\mathbf{X})\mathbf{C}]_{ll}=(\mathbf{C}^{-1}\Delta\mathbf{A}\mathbf{C})_{ll} \qquad (A1.6)$$

$$Y_{ll'}=[\mathbf{C}^{-1}(\Delta\mathbf{A}-\mathbf{X}\mathbf{A}+\mathbf{A}\mathbf{X})\mathbf{C}]_{ll'}/(\gamma_{l'}-\gamma_l) \qquad (A1.7)$$

provided $|\gamma_{l'}-\gamma_l|$ is large enough to satisfy $|Y_{ll'}|\ll 1$.

The $\Delta\gamma_l$ are independent of $\mathbf{X}$. Hence $\mathbf{X}$ can be arbitrarily used for transforming $\mathbf{C}$ or $\mathbf{A}$ due to (A1.3), (A1.4).

If $\mathbf{A}$ is Hermitian, $\mathbf{C}$ becomes unitary $\mathbf{C}^{-1}=\tilde{\mathbf{C}}^*$. If $\Delta\mathbf{A}$ is also Hermitian and $\mathbf{X}$ skew-Hermitian or zero, $\tilde{\mathbf{C}}^*(\Delta\mathbf{A}-\mathbf{X}\mathbf{A}+\mathbf{A}\mathbf{X})\mathbf{C}$ becomes Hermitian, hence $\Delta\boldsymbol{\gamma}$ is real and $\mathbf{Y}=-\tilde{\mathbf{Y}}^*$ is skew-Hermitian. Then, unitarity $\widetilde{\mathbf{C}(\Delta)}^*=(\mathbf{I}-\mathbf{Y})\tilde{\mathbf{C}}^*(\mathbf{I}-\mathbf{X})=\mathbf{C}(\Delta)^{-1}$ is satisfied in linear terms of $\mathbf{X}$ and $\mathbf{Y}$.

APPENDIX 2
Symmetry of the eigenvectors (symmetrical Laue case)

For centrosymmetric crystals, it is known (*e.g.* Metherell, 1975) that any eigenvector becomes either symmetric or antisymmetric if a Bragg position is satisfied within a row of systematic reflections. Let us generalize this behavior by allowing for non-centrosymmetry for all reflections of the zeroth Laue zone and supposing 'symmetric excitation'. The latter condition means that $s_{-g}=s_g$ exists or can be achieved by suitable indexing of $g(hkl)$. A possibility of symmetric excitation is to satisfy the Bragg condition for any $\mathbf{g}_0$ of this Laue zone while keeping the plane of $\mathbf{k}$, $\mathbf{k}+\mathbf{g}_0$ orthogonal to the zone. The simple case where $\mathbf{k}$ is along the zone axis is included (formally $\mathbf{g}_0=0$). Absorption will be neglected.

Under the condition $s_{-g}=s_g$, a reversal of sign g does not alter the diagonal $\mathbf{s}$ of the dynamical matrix $\mathbf{A}$ but it changes $\mathbf{A}$ into $\mathbf{A}^*$ since $U_{g-g'}$ is changed into $U_{g'-g}=U^*_{g-g'}$. The eigenvalues $\boldsymbol{\gamma}=\tilde{\mathbf{C}}^*\mathbf{A}\mathbf{C}$ are real and then read

$$\begin{aligned}\gamma_l&=\sum_{g,g'}A_{gg'}C^*_{gl}C_{g'l}=\sum_{g,g'}A^*_{gg'}C^*_{-g,l}C_{-g',l}\\ &=\gamma_l^*=\sum_{gg'}A^*_{gg'}C_{gl}C^*_{g'l}.\end{aligned}$$

It follows that $C_{-g,l}=\pm C^*_{gl}$ since an eigenvector is determined except for its sign. Thus there are two possibilities:

'complex symmetric' eigenvectors of

$$C_{-g,l}=C^*_{gl}, \qquad \mathrm{Im}\,C_{0l}=0, \qquad (A2.1a)$$

'complex antisymmetric' eigenvectors of

$$C_{-g,l}=-C^*_{gl}, \qquad \mathrm{Re}\,C_{0l}=0. \qquad (A2.1b)$$

Specification to centrosymmetry ($\mathbf{C}$ real) and to systematic reflections is known (*e.g.* Metherell, 1975).

A number of consequences follow concerning the crystal-defect-induced scattering (transition) of Bloch waves. For example, transitions forbidden at centrosymmetry can be allowed due to non-centrosymmetry (Kästner, 1986).

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Computer Simulation of Bragg and Diffuse Scattering Intensities against Temperature for a Structural Phase Transition

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Abstract

Molecular dynamics has been used to estimate the properties of a two-dimensional crystal exhibiting a second-order soft-mode phase transition. Using a vibrational potential for the crystal which is *temperature independent*, the essential features observed experimentally in the coherent scattering from analogous real systems are reproduced in the computer simulation. The potential consists of an effective one-particle component with multiple minima and a harmonic nearest-neighbour coupling component. It is emphasized that the coupling component is essential to reproduce correctly the qualitative features not only of the diffuse scattering, but also of the mean-square displacements as a function of temperature. The condition for appearance of a cusp at T_C in the mean-square displacement *versus* temperature curve is discussed and the formation of superlattice peaks in the diffuse scattering is demonstrated.

Introduction

Crystallographic studies of structural phase transitions can provide information on the nature of the phase change through measurements of:

(*a*) the structure of the high- and low-temperature phases (with associated measurement of order parameters);

(*b*) the temperature factors as a function of temperature; and

(*c*) the diffuse scattering as a function of temperature.

The crystallographic literature contains many examples of such experimental studies, especially in the case of structural work. As experimental techniques become more efficient and data more reliable, it is apparent that more information could potentially be extracted from detailed measurements than is customary at present. For example, diffuse scattering can provide information on the pair-displacement correlations, and ultimately the pair-correlation function, and the temperature factors can help to establish whether soft modes are present and which atoms are involved.

Recognizing that a need exists for parallel theoretical studies of structural phase transitions, we aim in the present work to calculate crystallographic properties [namely, mean-square displacements (MSD's) and coherent scattering distributions] for a model system possessing a second-order soft-mode structural phase transition. The work follows on from calculations on a one-dimensional system (a chain) of coupled anharmonically vibrating atoms. MSD's, one-particle probability densities, effective one-particle potentials and fourth-order cumulants of the displacements were calculated (Mair, 1983*a*, *b*) as well as pair-displacement correlations (Johnson & Mair, 1985) and disorder diffuse scattering (Mair, 1984*a*). The present model is an extension of the system to two dimensions and so ordering can occur at a finite temperature, T_C. Unlike the one-dimensional case, which could be treated in a semi-analytical way, the two-dimensional calculations are made with the technique of molecular dynamics.

The details of the model and numerical methods have already been reported (Mair, 1986) so only an outline of these will be presented. Mair (1986) also gives results on MSD's, some of which are repeated

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