electronic reprint

Journal of
Applied Crystallography
ISSN 0021-8898

Elastic strain and stress determination by Rietveld refinement: generalized treatment for textured polycrystals for all Laue classes

N. C. Popa and D. Balzar

Journal of
Applied Crystallography
ISSN 0021-8898

Received 16 October 2000
Accepted 30 January 2001

Elastic strain and stress determination by Rietveld refinement: generalized treatment for textured polycrystals for all Laue classes

N. C. Popa[a,b] and D. Balzar[a,c]*

[a]Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Boulder, CO 80305, USA, [b]National Institute for Materials Physics, PO Box MG-7, Bucharest, Romania, and [c]Department of Physics, University of Colorado, Boulder, CO 80309, USA. Correspondence e-mail: balzar@boulder.nist.gov

A novel approach to model diffraction line shifts caused by elastic residual or applied stresses in textured polycrystals is proposed. The model yields the complete strain and stress tensors as a function of crystallite orientation, as well as the average values of the macroscopic strain and stress tensors. It is particularly suitable for implementation in Rietveld refinement programs. The requirements on refinable parameters for all crystal Laue classes are given. The effects of sample symmetry are also included and the conditions for strain invariance to both the sample symmetries (texture and stress/strain) are discussed.

1. Introduction

Stress state (where the stress can be both applied and residual, that is, resident in the material after the application of external force is removed) influences many different material properties, which is especially important in engineering and technological applications. X-ray and neutron diffraction are the most accurate and widely used methods for stress determination in crystalline materials. There is a substantial amount of literature on this subject. For more information, the reader should consult recent monographs by Noyan & Cohen (1987) and Hauk (1997).

A common approach to strain and stress determination employs the so-called $\sin^2\Psi$ method (Christenson & Rowland, 1953), where the strain is derived from directional measurements of the interplanar spacing d as a function of the angle between the diffraction vector and an arbitrary direction in the specimen. Recently, it was proposed that the strain/stress orientation distribution function (SODF), which is defined as a strain/stress tensor component as a function of crystallite orientation, can be determined similarly to the crystallite orientation distribution function (CODF), through the expansion in a series of generalized spherical harmonics (Wang *et al.*, 1999, 2000; Behnken, 2000). It was assumed in such work that the crystal symmetry acts on the SODF in the same manner as on the CODF. In this context, it means that all six components of the strain tensor in the sample coordinate system are invariant to the point-group symmetry operations. However, consider, for instance, a polycrystalline assembly of non-spherical crystallites under the applied stress. A crystal symmetry operation on a crystallite could in general produce different physical strain states because of interactions with other crystallites in the aggregate, although two orientations are crystallographically equivalent. Therefore, strain/stress tensor elements are not invariant to the crystal symmetry operations in general. Contrarily, we postulate that the observable quantity measured by diffraction in a given sample direction, that is, the interplanar spacing d, averaged around the diffraction vector, is invariant to the point-group symmetry operations. In this paper, we will use this invariance condition to derive the selection rules in SODF harmonic representation for all Laue classes.

An alternative approach to a traditional $\sin^2\Psi$ method of strain determination has been described by Ferrari & Lutterotti (1994) and Balzar *et al.* (1998). It includes the refinement of strain- and stress-related parameters in a Rietveld (1969) refinement program. An advantage of this approach is that all available Bragg reflections are used simultaneously to obtain the strain tensor. Even if the strain/stress determination is not of interest, diffraction line shifts caused by residual stresses will generally be crystal-direction dependent. These diffraction line shifts should be corrected for, in order to carry out an accurate structure determination and refinement using the Rietveld approach, pole-figure (texture) measurements, and similar tasks. However, for a successful application in the Rietveld refinement, the challenge lies in the accurate modeling of strain and stress dependence on the crystallographic direction and the ability to handle arbitrary crystal symmetry. In a recent paper, Popa (2000) presented a method for modeling diffraction line shifts for all Laue classes within the frame of the Voigt (1928) and Reuss (1929) approximations. The aim here is to propose an alternative method to model diffraction line shifts accurately in a Rietveld refinement program for all Laue symmetries without making Voigt or Reuss approximations. This is accomplished by expanding the strain and stress tensor

components in a series of spherical harmonics, similar to the texture modeling as described by Popa (1992) and implemented in the Rietveld refinement program *GSAS* by Von Dreele (1997). Thus, strain and stress are determined by the refinement of the respective coefficients in the least-squares refinement procedure, simultaneously with other refinable parameters.

The general intent in Rietveld refinement is to minimize the number of refinable parameters. Hence, we also describe an alternative approach, where expansion of strain/stress tensor elements into direction cosines replaces the usual description in terms of harmonic components, which significantly lowers the number of refinable parameters. Here we present only the methodology, with the emphasis on introduction of this model into a Rietveld refinement program. An application of the method and a comparison with a traditional $\sin^2\Psi$ analysis will be described elsewhere (Balzar & Popa, 2001).

2. The measured strain, the average strain and stress tensors

The diffraction method directly measures the interplanar spacing d along the direction of the diffraction vector, which must be parallel to a reciprocal-lattice vector **H** for an (*hkl*) diffracting plane. Measured strain is then defined as an average change in the interplanar spacing from a reference value d_0:

$$\langle d\rangle/d_0 - 1 = \langle \Delta d\rangle/d_0 = -\langle \Delta H\rangle/H = \langle \varepsilon_{\mathbf{h}}(\mathbf{y})\rangle, \qquad (1)$$

where the averaging is performed by the rotation for ω around $\mathbf{h} = \mathbf{H}/H$, which is parallel to **y**, the direction of the diffraction vector in the sample. If ε_i are the strain tensor elements in the crystallite coordinate system (in the condensed Voigt notation), (1) can be written as (Popa, 2000)

$$\langle \varepsilon_{\mathbf{h}}(\mathbf{y})\rangle = \sum_{i=1}^{6} E_i \rho_i \frac{\int_0^{2\pi} \mathrm{d}\omega f(\varphi_1', \Phi_0', \varphi_2')\varepsilon_i(\varphi_1', \Phi_0', \varphi_2')}{\int_0^{2\pi} \mathrm{d}\omega f(\varphi_1', \Phi_0', \varphi_2')}. \qquad (2)$$

Averaging is weighted by the CODF $f(\varphi_1, \Phi_0, \varphi_2)$. Here, $(\varphi_1, \Phi_0, \varphi_2)$ are the Euler angles transforming the sample orthogonal coordinate system $(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3)$ into the crystallite orthogonal coordinate system $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, as defined by Bunge (1982). The integration in (2) is evaluated over only values of the Euler angles $(\varphi_1', \Phi_0', \varphi_2')$ that fulfill the condition $\mathbf{h}\|\mathbf{y}$. They depend on the values of the polar and azimuthal angles of **h** in $(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$, denoted as (Φ, β), of **y** in $(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3)$, denoted as (Ψ, γ), and on the rotation angle ω. The pairs of angles (Φ, β) and (Ψ, γ) give the direction cosines of **h** and **y**, respectively, in their coordinate systems:

$$(A_1, A_2, A_3) = (\cos\beta\sin\Phi, \sin\beta\sin\Phi, \cos\Phi), \qquad (3a)$$

$$(B_1, B_2, B_3) = (\cos\gamma\sin\Psi, \sin\gamma\sin\Psi, \cos\Psi). \qquad (3b)$$

In (2), we used the following abbreviations:

$$\begin{aligned}(E_1, \ldots, E_6) &= (A_1^2, A_2^2, A_3^2, A_2A_3, A_1A_3, A_1A_2),\\ (\rho_1, \ldots, \rho_6) &= (1, 1, 1, 2, 2, 2).\end{aligned} \qquad (4)$$

The average strain and stress tensors in the sample coordinate system, $\bar{e}_i$ and $\bar{s}_i$ $(i = 1, 6)$, respectively, are defined as (Popa, 2000)

$$\bar{e}_i = (1/8\pi^2)\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \mathrm{d}\varphi_1 \mathrm{d}\Phi_0 \,\mathrm{d}\varphi_2 \sin\Phi_0 f(\varphi_1, \Phi_0, \varphi_2) \times e_i(\varphi_1, \Phi_0, \varphi_2) \qquad (5)$$

and

$$\bar{s}_i = (1/8\pi^2)\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \mathrm{d}\varphi_1 \,\mathrm{d}\Phi_0 \,\mathrm{d}\varphi_2 \sin\Phi_0 f(\varphi_1, \Phi_0, \varphi_2) \times s_i(\varphi_1, \Phi_0, \varphi_2). \qquad (6)$$

If we denote by σ_i the stress tensor elements in the crystallite coordinate system, Hooke's law holds for the elastic part:

$$\sigma_i = \sum_{i=1}^{6} C_{ij}\rho_j\varepsilon_j, \qquad (7)$$

where C_{ij} are the monocrystal elastic stiffness moduli.

The following linear relations link the strain and stress tensor components in the two coordinate systems:

$$s_i = \sum_{j=1}^{6} P_{ij}\sigma_j, \qquad (8a)$$

$$e_i = \sum_{j=1}^{6} P_{ij}\varepsilon_j, \qquad (8b)$$

where the elements of the matrix **P** are sums of the products of two Euler matrix elements. Both the Euler matrix and the matrix **P** have been given explicitly by Popa (2000).

3. The strain expansion in generalized spherical harmonics

We now follow an approach similar to that of Wang (1999, 2000) and Behnken (2000), but with an important distinction that makes the problem of determination of components of the strain tensor equivalent to the texture problem and significantly simplifies the mathematical formalism. This is accomplished by replacing the product of the SODF and CODF by the SODF weighted by texture (WSODF):

$$\varepsilon_i'(\varphi_1, \Phi_0, \varphi_2) = \varepsilon_i(\varphi_1, \Phi_0, \varphi_2) f(\varphi_1, \Phi_0, \varphi_2). \qquad (9)$$

The product (9) explicitly appears in (2) and implicitly in (5) and (6) through (7) and (8). This is an additional advantage in directly determining WSODF instead of SODF, because the texture-weighted strain is actually measured in the diffraction experiment and is required in order to calculate other properties of interest, in particular average strain and stress tensors.

With (9), the integral in the numerator of (2) becomes similar to the expression for calculating the pole distribution function $P_{\mathbf{h}}(\mathbf{y})$:

$$P_{\mathbf{h}}(\mathbf{y}) = (1/2\pi)\int_0^{2\pi} f(\varphi_1', \Phi_0', \varphi_2')\,\mathrm{d}\omega. \qquad (10)$$

Table 1
The relations between the coefficients α_l^{mn}, β_l^{mn}, γ_l^{mn}, δ_l^{mn} and $c_{il}^{mn} = a_{il}^{mn} + ib_{il}^{mn}$.

$\alpha_{il}^{00} = a_{il}^{00}/2$	$\alpha_{il}^{0n} = a_{il}^{0n}$	$\beta_{il}^{0n} = -b_{il}^{0n}$
$\alpha_{il}^{m0} = a_{il}^{m0}$	$\alpha_{il}^{mn} = a_{il}^{mn} + (-1)^n a_{il}^{m,-n}$	$\beta_{il}^{mn} = -b_{il}^{mn} + (-1)^n b_{il}^{m,-n}$
$\gamma_{il}^{m0} = b_{il}^{m0}$	$\gamma_{il}^{mn} = b_{il}^{mn} + (-1)^n b_{il}^{m,-n}$	$\delta_{il}^{mn} = a_{il}^{mn} - (-1)^n a_{il}^{m,-n}$

Hence, the problem of strain becomes equivalent to the problem of texture. The measurable strain $\langle\varepsilon_{\mathbf{h}}(\mathbf{y})\rangle$ is for WSODF what the pole distribution $P_{\mathbf{h}}(\mathbf{y})$ is for CODF. This is useful for implementation in Rietveld refinement programs, because the texture and strain implementations become equivalent, only the selection rules being different.

Now we follow the procedure used by Bunge (1982) for texture, by developing ε_i' in generalized spherical harmonics:

$$\varepsilon_i'(\varphi_1, \Phi_0, \varphi_2) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{n=-l}^{l} c_{il}^{mn}\exp(im\varphi_2)P_l^{mn}(\Phi_0) \times \exp(in\varphi_1). \quad (11)$$

Then, for the integral over ω in the numerator of (2), we have (*cf.* equation 14.160 of Bunge, 1982)

$$\int_0^{2\pi} \mathrm{d}\omega\, \varepsilon_i'(\varphi_1', \Phi_0', \varphi_2') = \sum_{l=0}^{\infty}[4\pi/(2l+1)]\sum_{m=-l}^{l}\sum_{n=-l}^{l} c_{il}^{mn}\exp(-im\beta) \times P_l^m(\Phi)\exp(in\gamma)P_l^n(\Psi). \quad (12)$$

As ε_i' is a real quantity, the coefficients $c_{il}^{mn} = a_{il}^{mn} + ib_{il}^{mn}$ are complex numbers fulfilling the condition

$$c_{il}^{-m,-n} = (-1)^{m+n}c_{il}^{mn*}. \quad (13)$$

With $x = \cos\Phi$, the functions P_l^{mn} and P_l^m are defined as follows:

$$P_l^{mn}(x) = \frac{(-1)^{l-m}i^{n-m}}{2^l(l-m)!}\left[\frac{(l-m)!(l+n)!}{(l+m)!(l-n)!}\right]^{1/2} \times (1-x)^{-(n-m)/2}(1+x)^{-(n+m)/2} \times \frac{\mathrm{d}^{l-n}}{\mathrm{d}x^{l-n}}[(1-x)^{l-m}(1+x)^{l+m}]$$

and

$$P_l^m(x) = \left[\frac{(l+m)!}{(l-m)!}\right]^{1/2}\left(\frac{2l+1}{2}\right)^{1/2}\frac{(-1)^{l-m}}{2^l l!}(1-x^2)^{-m/2} \times \frac{\mathrm{d}^{l-m}}{\mathrm{d}x^{l-m}}(1-x^2)^l.$$

The functions P_l^{mn} are real for $m + n$ even and imaginary for $m + n$ odd. They have the following properties:

$$P_l^{nm}(\Phi) = P_l^{mn}(\Phi) = P_l^{-m,-n}(\Phi), \quad (14a)$$

$$P_l^{mn}(\pi - \Phi) = (-1)^{l+m+n}P_l^{-mn}(\Phi). \quad (14b)$$

There is an obvious relation between the functions P_l^{mn} and P_l^m:

$$P_l^{0m}(\Phi) = P_l^{m0}(\Phi) = i^{-m}[2/(2l+1)]^{1/2}P_l^m(\Phi).$$

By introducing this relation in (14), one obtains the following properties for P_l^m:

$$P_l^m(\Phi) = (-1)^m P_l^{-m}(\Phi), \quad (15a)$$

$$P_l^m(\pi - \Phi) = (-1)^{l+m}P_l^m(\Phi). \quad (15b)$$

With equations (15) and (13), we can rearrange (12) and consequently (2) in a more convenient form for our purpose, with only positive indices m, n. Taking into account (4), (2) becomes

$$\langle\varepsilon_{\mathbf{h}}(\mathbf{y})\rangle P_{\mathbf{h}}(\mathbf{y}) = \sum_{l=0}^{\infty}[2/(2l+1)]I_l(\mathbf{h}, \mathbf{y}), \quad (16)$$

where

$$I_l(\mathbf{h}, \mathbf{y}) = A_1^2 t_{1l}(\mathbf{h}, \mathbf{y}) + A_2^2 t_{2l}(\mathbf{h}, \mathbf{y}) + A_3^2 t_{3l}(\mathbf{h}, \mathbf{y}) + 2A_2A_3t_{4l}(\mathbf{h}, \mathbf{y}) + 2A_1A_3t_{5l}(\mathbf{h}, \mathbf{y}) + 2A_1A_2t_{6l}(\mathbf{h}, \mathbf{y}), \quad (17)$$

with

$$t_{il}(\mathbf{h}, \mathbf{y}) = A_{il}^0(\mathbf{y})P_l^0(\Phi) + \sum_{m=1}^{l}[A_{il}^m(\mathbf{y})\cos m\beta + B_{il}^m(\mathbf{y})\sin m\beta]P_l^m(\Phi), \quad (18)$$

$$A_{il}^m(\mathbf{y}) = \alpha_{il}^{m0}P_l^0(\Psi) + \sum_{n=1}^{l}(\alpha_{il}^{mn}\cos n\gamma + \beta_{il}^{mn}\sin n\gamma)P_l^n(\Psi) \quad (m = 0, l), \quad (19)$$

$$B_{il}^m(\mathbf{y}) = \gamma_{il}^{m0}P_l^0(\Psi) + \sum_{n=1}^{l}(\gamma_{il}^{mn}\cos n\gamma + \delta_{il}^{mn}\sin n\gamma)P_l^n(\Psi) \quad (m = 1, l). \quad (20)$$

The coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn} and δ_{il}^{mn} are obtained from the coefficients c_{il}^{mn} by the linear transformations given in Table 1. They can be directly refined in the Rietveld program to yield the WSODF and the average strain tensor. The average stress tensor can also be determined if monocrystal elastic stiffness moduli C_{ij} are known. The required number of refined coefficients to achieve the desired precision of the WSODF, strain and stress tensors will depend on the crystal and sample symmetries, as well as on the magnitude and the gradient of the strain and the texture.

4. The selection rules for all Laue classes

Equation (16) is a general formula for strain (diffraction line shift) determination, valid for triclinic crystal symmetry. For a given value of l, the total number of the coefficients for every i is $(2l + 1)^2$, where the number l takes only even values because of Friedel's law (see §4.2.1). If the crystal and sample symmetries are higher than triclinic, the number of coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn} and δ_{il}^{mn} in (19) and (20) is reduced, some coefficients being zero and some being correlated. To find the selection rules for all Laue classes, we apply the invariance condition to the measured strain, $\langle\varepsilon_{\mathbf{h}}(\mathbf{y})\rangle$, as outlined in the §1.

We denote two operators for the crystal and sample point group by $\mathbf{X}$ and $\mathbf{Y}$, respectively. Because the terms in the sum (16) are independent, the invariance condition has to apply to every I_l in (16):

Table 2
The selection rules imposed by the sample non-cubic symmetries.

r denotes the r-fold axis in the direction $\Psi = 0$.

$$2/m, \bar{3}, 4/m, 6/m: \quad \begin{cases} \alpha_{il}^{m0}; \gamma_{il}^{m0} \\ \alpha_{il}^{mn}, \beta_{il}^{mn}; \gamma_{il}^{mn}, \delta_{il}^{mn}, n = rk \end{cases}$$

$$2/mmm, \bar{3}m, 4/mmm, 6/mmm: \quad \begin{cases} \alpha_{il}^{m0}; \gamma_{il}^{m0} \\ \alpha_{il}^{mn}; \gamma_{il}^{mn}, n = rk, n - \text{even} \\ \beta_{il}^{mn}; \delta_{il}^{mn}, n = rk, n - \text{odd} \end{cases}$$

Table 3
The selection rules imposed by the cubic sample symmetry for $l \leq 4$.

The following constraints must be added to the selection rules for the orthorhombic $2/mmm$ Laue class and the tetragonal $4/mmm$ Laue class, respectively (Table 2).

$$m\bar{3}: \quad \begin{cases} (\alpha_{i2}^{mn}; \gamma_{i2}^{mn}) = 0, (n = 0, 2) \\ (\alpha_{i4}^{m4}; \gamma_{i4}^{m4}) = (10/7)^{1/2}(\alpha_{i4}^{m0}; \gamma_{i4}^{m0}) \end{cases}$$

$$m\bar{3}m: \quad \begin{cases} (\alpha_{i2}^{m0}; \gamma_{i2}^{m0}) = 0 \\ (\alpha_{i4}^{m4}; \gamma_{i4}^{m4}) = (10/7)^{1/2}(\alpha_{i4}^{m0}; \gamma_{i4}^{m0}) \end{cases}$$

Table 4
The selection rules for the monoclinic $2/m$ Laue class.

k is a natural number.

$$i = 1, 2, 3, 6: \quad \begin{cases} A_{il}^{0} \\ A_{il}^{m}, B_{il}^{m}, m = 2k \end{cases}$$

$$i = 4, 5: \quad A_{il}^{m}, B_{il}^{m}, m = 2k - 1$$

Table 5
The selection rules for the tetragonal $4/m$ Laue class.

k is a natural number.

$$i = 1: \quad \begin{cases} A_{1l}^{0} \\ A_{1l}^{m}, B_{1l}^{m}, m = 2k \end{cases}$$

$$i = 2: \quad \begin{cases} A_{2l}^{0} = A_{1l}^{0} \\ A_{2l}^{m} = (-1)^k A_{1l}^{m}, B_{2l}^{m} = (-1)^k B_{1l}^{m}, m = 2k \end{cases}$$

$$i = 3: \quad \begin{cases} A_{3l}^{0} \\ A_{3l}^{m}, B_{3l}^{m}, m = 4k \end{cases}$$

$$i = 4: \quad A_{4l}^{m}, B_{4l}^{m}, m = 2k - 1$$

$$i = 5: \quad A_{5l}^{m} = (-1)^{k-1} B_{4l}^{m}, B_{5l}^{m} = (-1)^k A_{4l}^{m}, m = 2k - 1$$

$$i = 6: \quad A_{6l}^{m}, B_{6l}^{m}, m = 4k - 2$$

Table 6
The selection rules for the trigonal $\bar{3}$ Laue class.

k is a natural number.

$$i = 1: \quad \begin{cases} A_{1l}^{0} \\ A_{1l}^{m}, B_{1l}^{m}, m = 3k - 2, 3k - 1, 3k \end{cases}$$

$$i = 2: \quad \begin{cases} A_{2l}^{0} = A_{1l}^{0} \\ A_{2l}^{m} = A_{1l}^{m}, B_{2l}^{m} = B_{1l}^{m}, m = 3k \\ A_{2l}^{m} = -A_{1l}^{m}, B_{2l}^{m} = -B_{1l}^{m}, m = 3k - 2, 3k - 1 \end{cases}$$

$$i = 3: \quad \begin{cases} A_{3l}^{0} \\ A_{3l}^{m}, B_{3l}^{m}, m = 3k \end{cases}$$

$$i = 4: \quad A_{4l}^{m}, B_{4l}^{m}, m = 3k - 2, 3k - 1$$

$$i = 5: \quad \begin{cases} A_{5l}^{m} = B_{4l}^{m}, B_{5l}^{m} = -A_{4l}^{m}, m = 3k - 2 \\ A_{5l}^{m} = -B_{4l}^{m}, B_{5l}^{m} = A_{4l}^{m}, m = 3k - 1 \end{cases}$$

$$i = 6: \quad \begin{cases} A_{6l}^{m} = B_{1l}^{m}, B_{6l}^{m} = -A_{1l}^{m}, m = 3k - 2 \\ A_{6l}^{m} = -B_{1l}^{m}, B_{6l}^{m} = A_{1l}^{m}, m = 3k - 1 \end{cases}$$

$$I_l(\mathbf{X} \cdot \mathbf{h}, \mathbf{Y} \cdot \mathbf{y}) = I_l(\mathbf{h}, \mathbf{y}). \tag{21}$$

4.1. Selection rules imposed by the sample symmetry

For textured samples under stress, two sample symmetries must be distinguished: texture and stress/strain sample symmetry. Sometimes they are identical, but generally the strain sample symmetry can be lower than the texture sample symmetry. Furthermore, according to (16), the texture sample symmetry operations must form a supergroup of the strain sample symmetry point group because $P_{\mathbf{h}}(\mathbf{y})$ must be invariant to both symmetry operations. An example is the dependence of the observed strain on the direction in a sample with randomly orientated crystallites, derived in the Reuss (1929) approximation by Popa (2000). Here the texture has a spherical symmetry but the dependence of $\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle$ on $\mathbf{y}$, in general, shows triclinic symmetry and only for hydrostatic stress does it become independent of $\mathbf{y}$ (isotropic). Moreover, consider the uniaxial stress acting on the sample with a cubic sample texture. The symmetry for strain is tetragonal if the stress axis is along the cube axis, trigonal if the stress axis is along the body diagonal, but triclinic if this axis is oriented in an arbitrary direction.

For strain sample symmetry higher than triclinic, the invariance relation (21) for any $\mathbf{h}$, with $\mathbf{X} = \mathbf{E}$ (where $\mathbf{E}$ is the identity operator), requires the invariance of the functions $A_{il}^{m}(\mathbf{y})$ and $B_{il}^{m}(\mathbf{y})$ in (18) independently for every m. In other words, the coefficients of different strain tensor components are independent. This implies that the selection rules that apply to the coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn} and δ_{il}^{mn} are identical to those for the texture of the same sample symmetry. These rules were previously given by Popa (1992) and are summarized in Tables 2 and 3. Therefore, although strain and texture sample symmetries may be different, the selection rules for the same symmetry are identical, which greatly simplifies implementation in the Rietveld refinement programs.

4.2. Selection rules imposed by the crystal symmetry

With $\mathbf{Y} = \mathbf{E}$ in (21), the selection rules are obtained by solving the system of equations for crystal symmetry operators

Table 7
The selection rules for the hexagonal 6/*m* Laue class.

k is a natural number.

$$
\begin{aligned}
i=1:&\ \begin{cases} A^0_{1l} \\ A^m_{1l},\ B^m_{1l},\ m=6k-4,6k-2,6k \end{cases}\\
i=2:&\ \begin{cases} A^0_{2l}=A^0_{1l} \\ A^m_{2l}=A^m_{1l},\ B^m_{2l}=B^m_{1l},\ m=6k \\ A^m_{2l}=-A^m_{1l},\ B^m_{2l}=-B^m_{1l},\ m=6k-4,6k-2 \end{cases}\\
i=3:&\ \begin{cases} A^0_{3l} \\ A^m_{3l},\ B^m_{3l},\ m=6k \end{cases}\\
i=4:&\ A^m_{4l},\ B^m_{4l},\ m=6k-5,6k-1\\
i=5:&\ \begin{cases} A^m_{5l}=B^m_{4l},\ B^m_{5l}=-A^m_{4l},\ m=6k-5 \\ A^m_{5l}=-B^m_{4l},\ B^m_{5l}=A^m_{4l},\ m=6k-1 \end{cases}\\
i=6:&\ \begin{cases} A^m_{6l}=-B^m_{1l},\ B^m_{6l}=A^m_{1l},\ m=6k-4 \\ A^m_{6l}=B^m_{1l},\ B^m_{6l}=-A^m_{1l},\ m=6k-2 \end{cases}
\end{aligned}
$$

Table 8
The selection rules for a twofold axis in the direction $\Phi=\pi/2$, $\beta=0$.

k is a natural number.

$$
\begin{aligned}
i=1,2,3,4:&\ \begin{cases} A^0_{il} \\ A^m_{il},\ m=2k \\ B^m_{il},\ m=2k-1 \end{cases}\\
i=5,6:&\ \begin{cases} B^m_{il},\ m=2k \\ A^m_{il},\ m=2k-1 \end{cases}
\end{aligned}
$$

Table 9
The selection rules for the orthorhombic 2/*mmm* Laue class.

k is a natural number.

$$
\begin{aligned}
i=1,2,3:&\ \begin{cases} A^0_{il} \\ A^m_{il},\ m=2k \end{cases}\\
i=4:&\ B^m_{4l},\ m=2k-1\\
i=5:&\ A^m_{5l},\ m=2k-1\\
i=6:&\ B^m_{6l},\ m=2k
\end{aligned}
$$

Table 10
The selection rules for the tetragonal 4/*mmm* Laue class.

k is a natural number.

$$
\begin{aligned}
i=1:&\ \begin{cases} A^0_{1l} \\ A^m_{1l},\ m=2k \end{cases}\\
i=2:&\ \begin{cases} A^0_{2l}=A^0_{1l} \\ A^m_{2l}=(-1)^k A^m_{1l},\ m=2k \end{cases}\\
i=3:&\ \begin{cases} A^0_{3l} \\ A^m_{3l},\ m=4k \end{cases}\\
i=4:&\ B^m_{4l},\ m=2k-1\\
i=5:&\ A^m_{5l}=(-1)^{k-1}B^m_{4l},\ m=2k-1\\
i=6:&\ B^m_{6l},\ m=4k-2
\end{aligned}
$$

Table 11
The selection rules for the trigonal $\bar{3}m$ Laue class.

There are two distinct situations: for *m* even, at the left side of the vertical bar, and for *m* odd, at the right side of the bar. *k* is a natural number.

$$
\begin{aligned}
i=1:&\ \begin{cases} A^0_{1l}| \\ A^m_{1l}|B^m_{1l},\ m=3k-2,3k-1,3k \end{cases}\\
i=2:&\ \begin{cases} A^0_{2l}=A^0_{1l}| \\ A^m_{2l}=A^m_{1l}|B^m_{2l}=B^m_{1l},\ m=3k \\ A^m_{2l}=-A^m_{1l}|B^m_{2l}=-B^m_{1l},\ m=3k-2,3k-1 \end{cases}\\
i=3:&\ \begin{cases} A^0_{3l}| \\ A^m_{3l}|B^m_{3l},\ m=3k \end{cases}\\
i=4:&\ A^m_{4l}|B^m_{4l},\ m=3k-2,3k-1\\
i=5:&\ \begin{cases} B^m_{5l}=-A^m_{4l}|A^m_{5l}=B^m_{4l},\ m=3k-2 \\ B^m_{5l}=A^m_{4l}|A^m_{5l}=-B^m_{4l},\ m=3k-1 \end{cases}\\
i=6:&\ \begin{cases} B^m_{6l}=-A^m_{1l}|A^m_{6l}=B^m_{1l},\ m=3k-2 \\ B^m_{6l}=A^m_{1l}|A^m_{6l}=-B^m_{1l},\ m=3k-1 \end{cases}
\end{aligned}
$$

Table 12
The selection rules for the hexagonal 6/*mmm* Laue class.

k is a natural number.

$$
\begin{aligned}
i=1:&\ \begin{cases} A^0_{1l} \\ A^m_{1l},\ m=6k-4,6k-2,6k \end{cases}\\
i=2:&\ \begin{cases} A^0_{2l}=A^0_{1l} \\ A^m_{2l}=A^m_{1l},\ m=6k \\ A^m_{2l}=-A^m_{1l},\ m=6k-4,6k-2 \end{cases}\\
i=3:&\ \begin{cases} A^0_{3l} \\ A^m_{3l},\ m=6k \end{cases}\\
i=4:&\ B^m_{4l},\ m=6k-5,6k-1\\
i=5:&\ \begin{cases} A^m_{5l}=B^m_{4l},\ m=6k-5 \\ A^m_{5l}=-B^m_{4l},\ m=6k-1 \end{cases}\\
i=6:&\ \begin{cases} B^m_{6l}=A^m_{1l},\ m=6k-4 \\ B^m_{6l}=-A^m_{1l},\ m=6k-2 \end{cases}
\end{aligned}
$$

X in an arbitrary sample direction **y**. A crystal symmetry operator **X** acts on both the functions $t_{il}(\mathbf{h},\mathbf{y})$ and the coefficients A_iA_j in (17). As a result, selection rules for the harmonic representation of the WSODF are more complex than selection rules for the harmonic representation of the CODF.

4.2.1. The inversion center. The inversion center is imposed by Friedel's law. It transforms (Φ,β) into $(\pi-\Phi,\pi-\beta)$ and A_i into $-A_i$. From the condition (21), one obtains the following equations: $t_{il}(\pi-\Phi,\pi-\beta,\mathbf{y})=t_{il}(\Phi,\beta,\mathbf{y})$. By using (18) and (15*b*), these equations become: $(-1)^l t_{il}(\Phi,\beta,\mathbf{y})=t_{il}(\Phi,\beta,\mathbf{y})$. Therefore, we must take $l=2l'$ as an even number.

4.2.2. The *r*-fold axis in the direction Φ = 0, *r* = 2, 3, 4, 6. An *r*-fold axis in the direction $\Phi=0$ transforms β into $\beta+2\pi/r$ and (A_1, A_2) into $[A_1\cos(2\pi/r)-A_2\sin(2\pi/r),\ A_1\sin(2\pi/r)+A_2\cos(2\pi/r)]$. After applying (21), one obtains a system of six

Table 13
The selection rules for the cubic $m\bar{3}$ Laue class.

The following constraints must be added to the selection rules for the orthorhombic 2/*mmm* Laue class (Table 9). k is a natural number.

$$
\begin{aligned}
l = 0: \quad & A_{30}^0 = A_{20}^0 = A_{10}^0 \\
l = 2: \quad & A_{12}^2 = (2/3)^{1/2}(A_{12}^0 + 2A_{32}^0) \\
& A_{22}^2 = -(2/3)^{1/2}(A_{22}^0 + 2A_{32}^0) \\
& A_{32}^2 = -(2/3)^{1/2}(A_{12}^0 - A_{22}^0) + 2(B_{42}^1 - A_{52}^1) \\
& B_{62}^2 = (3/2)^{1/2}(A_{12}^0 + A_{22}^0 + A_{32}^0)/2 + (B_{42}^1 + A_{52}^1)/2 \\
l = 4: \quad & A_{14}^4 = -3(2/35)^{1/2}A_{14}^0 + 8(2/35)^{1/2}A_{34}^0 + 2A_{14}^2/7^{1/2} \\
& A_{24}^4 = -3(2/35)^{1/2}A_{24}^0 + 8(2/35)^{1/2}A_{34}^0 - 2A_{24}^2/7^{1/2} \\
& B_{44}^3 = -2(A_{14}^0 + 3A_{24}^0)/35^{1/2} + (27/4)A_{34}^0/35^{1/2} \\
& \qquad - (1/2)(6A_{24}^2 + 5A_{34}^2)/14^{1/2} - (3B_{44}^1 + 4A_{54}^1)/7^{1/2} + (1/4)A_{34}^4/2^{1/2} \\
& A_{54}^3 = 2(3A_{14}^0 + A_{24}^0)/35^{1/2} - (27/4)A_{34}^0/35^{1/2} \\
& \qquad - (1/2)(6A_{14}^2 + 5A_{34}^2)/14^{1/2} + (4B_{44}^1 + 3A_{54}^1)/7^{1/2} - (1/4)A_{34}^4/2^{1/2} \\
& B_{64}^2 = (2/5)^{1/2}(A_{14}^0 + A_{24}^0 - 2A_{34}^0) - (A_{14}^2 - A_{24}^2)/2 - 2^{1/2}(B_{44}^1 + A_{54}^1) \\
& B_{64}^4 = -(2/35)^{1/2}(A_{14}^0 - A_{24}^0) + (A_{14}^2 + A_{24}^2 + 3A_{34}^2/2)/7^{1/2} \\
& \qquad - (2/7)^{1/2}(B_{44}^1 - A_{54}^1)
\end{aligned}
$$

Table 14
The selection rules for the cubic $m\bar{3}m$ Laue class.

The following constraints must be added to the selection rules for the tetragonal 4/*mmm* Laue class (Table 10). k is a natural number.

$$
\begin{aligned}
l = 0: \quad & A_{30}^0 = A_{10}^0 \\
l = 2: \quad & A_{12}^2 = (2/3)^{1/2}(A_{12}^0 + 2A_{32}^0) \\
& B_{62}^2 = (3/2)^{1/2}(A_{12}^0 + A_{32}^0/2) + B_{42}^1 \\
l = 4: \quad & A_{14}^4 = -3(2/35)^{1/2}A_{14}^0 + 8(2/35)^{1/2}A_{34}^0 + 2A_{14}^2/7^{1/2} \\
& B_{44}^3 = -8A_{14}^0/35^{1/2} + (27/4)A_{34}^0/35^{1/2} + 3A_{14}^2/14^{1/2} \\
& \qquad - 7^{1/2}B_{44}^1 + (1/4)A_{34}^4/2^{1/2} \\
& B_{64}^2 = 2(2/5)^{1/2}(A_{14}^0 - A_{34}^0) - A_{14}^2 - 8^{1/2}B_{44}^1
\end{aligned}
$$

linear equations of the following form: $t_{il}(\Phi,\ \beta + 2\pi/r,\ \mathbf{y}) = \sum_{k=1}^{6} f_{ik}t_{kl}(\Phi,\ \beta,\ \mathbf{y})$, where f_{ik} is the matrix with its elements determined by r. Furthermore, with (18), one obtains a system of homogenous equations for the functions A_{il}^m and B_{il}^m. This system has a non-trivial solution only for certain values of m. This non-trivial solution is valid for any $\mathbf{y}$; therefore, these are the selection rules for the corresponding coefficients α_{il}^{mn}, β_{il}^{mn} and γ_{il}^{mn}, δ_{il}^{mn}. For the Laue classes 2/m, 4/m, $\bar{3}$ and 6/m, the selection rules are given in Tables 4 to 7. For brevity, we write selection rules for the functions A_{il}^m, B_{il}^m rather than for the corresponding coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn}, δ_{il}^{mn}.

4.2.3. Twofold axis in the direction $\Phi = \pi/2$, $\beta = 0$. This axis transforms Φ into $\pi - \Phi$, β into $-\beta$, and (A_2, A_3) into $(-A_2, -A_3)$. Then we proceed similarly as in §4.2.2 and obtain the selection rules given in Table 8. Combining this table with Tables 4 to 7, one obtains the selection rules for the Laue classes 2/*mmm*, 4/*mmm*, $\bar{3}m$ and 6/*mmm*. These are given in Tables 9 to 12.

4.2.4. The cubic groups. To obtain selection rules for the cubic groups $m\bar{3}$ and $m\bar{3}m$, we need to add a threefold axis on the body diagonal of the orthorhombic 2/*mmm* and tetragonal 4/*mmm* unit cells, respectively. This axis transforms $(A_1,\ A_2,\ A_3)$ into (A_2, A_3, A_1). However, the angles $(\Phi,\ \beta)$ are no longer linearly transformed, which makes the use of the same procedure as in §§4.2.2 and 4.2.3 practically impossible. We proceed here in a different way, by evaluating the expression (18) in terms of direction cosines A_1, A_2, A_3 for $m\bar{3}$ from orthorhombic 2/*mmm*, and for $m\bar{3}m$ from tetragonal 4/*mmm* symmetry. The resulting expression for $t_{il}(\mathbf{h}, \mathbf{y})$ contains polynomials of degree l in A_1, A_2, A_3. The invariant I_l is a polynomial of degree $l + 2$ in these variables, the coefficients being linear combinations of A_{il}^m and B_{il}^m. Furthermore, by using the invariance condition for I_l for the threefold axis, one finds a homogenous system of equations for A_{il}^m and B_{il}^m. The matrix rank of this system is always smaller than the number of coefficients A_{il}^m and B_{il}^m, and we find linear

Table 15
Functions $R_k(\varphi_1,\ \Phi_0,\ \varphi_2)$.

$x = \cos\Phi_0$ in the listed functions.

$$
\begin{aligned}
& R_0(\varphi_1, x, \varphi_2) = 2Q_0^{00}(x) \\
& R_1(\varphi_1, x, \varphi_2) = 2Q_2^{00}(x) \\
& R_2(\varphi_1, x, \varphi_2) = \sin\varphi_1 Q_2^{10}(x) \\
& R_3(\varphi_1, x, \varphi_2) = -\cos\varphi_1 Q_2^{10}(x) \\
& R_4(\varphi_1, x, \varphi_2) = \cos 2\varphi_1 Q_2^{20}(x) \\
& R_5(\varphi_1, x, \varphi_2) = \sin 2\varphi_1 Q_2^{20}(x) \\
& R_6(\varphi_1, x, \varphi_2) = \sin\varphi_2 Q_2^{10}(x) \\
& R_7(\varphi_1, x, \varphi_2) = \big[\cos(\varphi_2 + \varphi_1)Q_2^{11}(x) - \cos(\varphi_2 - \varphi_1)Q_2^{11}(-x)\big]/2 \\
& R_8(\varphi_1, x, \varphi_2) = \big[\sin(\varphi_2 + \varphi_1)Q_2^{11}(x) + \sin(\varphi_2 - \varphi_1)Q_2^{11}(-x)\big]/2 \\
& R_9(\varphi_1, x, \varphi_2) = \big[\sin(\varphi_2 + 2\varphi_1)Q_2^{21}(x) - \sin(\varphi_2 - 2\varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{10}(\varphi_1, x, \varphi_2) = \big[-\cos(\varphi_2 + 2\varphi_1)Q_2^{21}(x) - \cos(\varphi_2 - 2\varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{11}(\varphi_1, x, \varphi_2) = \cos\varphi_2 Q_2^{10}(x) \\
& R_{12}(\varphi_1, x, \varphi_2) = \big[-\sin(\varphi_2 + \varphi_1)Q_2^{11}(x) + \sin(\varphi_2 - \varphi_1)Q_2^{11}(-x)\big]/2 \\
& R_{13}(\varphi_1, x, \varphi_2) = \big[\cos(\varphi_2 + \varphi_1)Q_2^{11}(x) + \cos(\varphi_2 - \varphi_1)Q_2^{11}(-x)\big]/2 \\
& R_{14}(\varphi_1, x, \varphi_2) = \big[\cos(\varphi_2 + 2\varphi_1)Q_2^{21}(x) - \cos(\varphi_2 - 2\varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{15}(\varphi_1, x, \varphi_2) = \big[\sin(\varphi_2 + 2\varphi_1)Q_2^{21}(x) + \sin(\varphi_2 - 2\varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{16}(\varphi_1, x, \varphi_2) = \cos 2\varphi_2 Q_2^{20}(x) \\
& R_{17}(\varphi_1, x, \varphi_2) = \big[\sin(2\varphi_2 + \varphi_1)Q_2^{21}(x) + \sin(2\varphi_2 - \varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{18}(\varphi_1, x, \varphi_2) = \big[-\cos(2\varphi_2 + \varphi_1)Q_2^{21}(x) + \cos(2\varphi_2 - \varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{19}(\varphi_1, x, \varphi_2) = \big[\cos(2\varphi_2 + 2\varphi_1)Q_2^{22}(x) + \cos(2\varphi_2 - 2\varphi_1)Q_2^{22}(-x)\big]/2 \\
& R_{20}(\varphi_1, x, \varphi_2) = \big[\sin(2\varphi_2 + 2\varphi_1)Q_2^{22}(x) - \sin(2\varphi_2 - 2\varphi_1)Q_2^{22}(-x)\big]/2 \\
& R_{21}(\varphi_1, x, \varphi_2) = -\sin 2\varphi_2 Q_2^{20}(x) \\
& R_{22}(\varphi_1, x, \varphi_2) = \big[\cos(2\varphi_2 + \varphi_1)Q_2^{21}(x) + \cos(2\varphi_2 - \varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{23}(\varphi_1, x, \varphi_2) = \big[\sin(2\varphi_2 + \varphi_1)Q_2^{21}(x) - \sin(2\varphi_2 - \varphi_1)Q_2^{21}(-x)\big]/2 \\
& R_{24}(\varphi_1, x, \varphi_2) = \big[-\sin(2\varphi_2 + 2\varphi_1)Q_2^{22}(x) - \sin(2\varphi_2 - 2\varphi_1)Q_2^{22}(-x)\big]/2 \\
& R_{25}(\varphi_1, x, \varphi_2) = \big[\cos(2\varphi_2 + 2\varphi_1)Q_2^{22}(x) - \cos(2\varphi_2 - 2\varphi_1)Q_2^{22}(-x)\big]/2
\end{aligned}
$$

Table 16
The non-zero elements of the matrix **w**.

$k = 0$: $\bar{w}_{ij0} = 2/3$ for $i, j = 1, 3$.
$k = 1$: $\bar{w}_{ij1} = 1/15$ for $i, j = 1, 2$; $\bar{w}_{ij1} = 4/15$ for $(3, 3)$;
$\bar{w}_{ij1} = -2/15$ for $(1, 3), (2, 3), (3, 1), (3, 2)$.
$k = 2$: $\bar{w}_{ij2} = -(1/30)(3/2)^{1/2}$ for $(5, 1), (5, 2)$; $\bar{w}_{ij2} = (1/15)(3/2)^{1/2}$ for $(5, 3)$.
$k = 3$: $\bar{w}_{ij3} = -(1/30)(3/2)^{1/2}$ for $(4, 1), (4, 2)$; $\bar{w}_{ij3} = (1/15)(3/2)^{1/2}$ for $(4, 3)$.
$k = 4$: $\bar{w}_{ij4} = -(1/30)(3/2)^{1/2}$ for $(1, 1), (1, 2)$; $\bar{w}_{ij4} = (1/15)(3/2)^{1/2}$ for $(1, 3)$;
$\bar{w}_{ij4} = (1/30)(3/2)^{1/2}$ for $(2, 1), (2, 2)$; $\bar{w}_{ij4} = -(1/15)(3/2)^{1/2}$ for $(2, 3)$.
$k = 5, 6$: $\bar{w}_{ijk} = -(1/30)(3/2)^{1/2}$ for $(6, 1), (6, 2)$; $\bar{w}_{ijk} = (1/15)(3/2)^{1/2}$ for $(6, 3)$.
$k = 7$: $\bar{w}_{ij7} = 1/60$ for $(5, 5)$.
$k = 8$: $\bar{w}_{ij8} = 1/60$ for $(4, 5)$.
$k = 9$: $\bar{w}_{ij9} = 1/10$ for $(1, 5)$; $\bar{w}_{ij9} = -1/10$ for $(2, 5)$.
$k = 10$: $\bar{w}_{ij,10} = 1/10$ for $(6, 5)$.
$k = 11$: $\bar{w}_{ij,11} = -(1/15)(3/2)^{1/2}$ for $(1, 4), (2, 4)$; $\bar{w}_{ij,11} = (2/15)(3/2)^{1/2}$ for $(3, 4)$.
$k = 12$: $\bar{w}_{ij,12} = 1/60$ for $(5, 4)$.
$k = 13$: $\bar{w}_{ij,13} = 1/60$ for $(4, 4)$.
$k = 14$: $\bar{w}_{ij,14} = 1/10$ for $(1, 4)$; $\bar{w}_{ij,14} = -1/10$ for $(2, 4)$.
$k = 15$: $\bar{w}_{ij,15} = 1/10$ for $(6, 4)$.
$k = 16$: $\bar{w}_{ij,16} = -(1/30)(3/2)^{1/2}$ for $(1, 1), (2, 1)$;
$\bar{w}_{ij,16} = (1/30)(3/2)^{1/2}$ for $(1, 2), (2, 2)$;
$\bar{w}_{ij,16} = (1/15)(3/2)^{1/2}$ for $(3, 1)$; $\bar{w}_{ij,16} = -(1/15)(3/2)^{1/2}$ for $(3, 2)$.
$k = 17$: $\bar{w}_{ij,17} = 1/20$ for $(5, 1)$; $\bar{w}_{ij,17} = -1/20$ for $(5, 2)$.
$k = 18$: $\bar{w}_{ij,18} = 1/20$ for $(4, 1)$; $\bar{w}_{ij,18} = -1/20$ for $(4, 2)$.
$k = 19$: $\bar{w}_{ij,19} = 1/20$ for $(1, 1), (2, 2)$; $\bar{w}_{ij,19} = -1/20$ for $(1, 2), (2, 1)$.
$k = 20$: $\bar{w}_{ij,20} = 1/20$ for $(6, 1)$; $\bar{w}_{ij,20} = -1/20$ for $(6, 2)$.
$k = 21$: $\bar{w}_{ij,21} = -(1/15)(3/2)^{1/2}$ for $(1, 6), (2, 6)$; $\bar{w}_{ij,21} = (2/15)(3/2)^{1/2}$ for $(3, 6)$.
$k = 22$: $\bar{w}_{ij,22} = 1/10$ for $(5, 6)$.
$k = 23$: $\bar{w}_{ij,23} = 1/10$ for $(4, 6)$.
$k = 24$: $\bar{w}_{ij,24} = 1/10$ for $(1, 6)$; $\bar{w}_{ij,24} = -1/10$ for $(2, 6)$.
$k = 25$: $\bar{w}_{ij,25} = 1/10$ for $(6, 6)$.

Table 17
The invariant polynomials $J_{k,l+2}$ for the orthorhombic Laue classes.

Additional terms that should be added for the monoclinic Laue classes are enclosed in square brackets.

$l = 0$: $A_1^2, A_2^2, A_3^2, [A_1A_2]$
$l = 2$: $A_1^4, A_2^4, A_3^4, A_2^2A_3^2, A_1^2A_3^2, A_1^2A_2^2, [A_1^3A_2, A_1A_3^3, A_1A_2A_3^2]$
$l = 4$: $A_1^6, A_2^6, A_3^6, A_1^4A_2^2, A_1^2A_2^4, A_1^4A_3^2, A_1^2A_3^4, A_2^4A_3^2, A_2^2A_3^4, A_1^2A_2^2A_3^2,$
$[A_1^5A_2, A_1A_2^5, A_1^3A_2^3, A_1^3A_2A_3^2, A_1A_2^3A_3^2, A_1A_2A_3^4]$

Table 18
The invariant polynomials $J_{k,l+2}$ for the tetragonal 4/*mmm* Laue class.

Additional terms that should be added for the tetragonal 4/*m* Laue class are enclosed in square brackets.

$l = 0$: $A_1^2 + A_2^2, A_3^2$
$l = 2$: $A_1^4 + A_2^4, A_3^4, (A_1^2 + A_2^2)A_3^2, A_1^2A_2^2, [(A_1^2 - A_2^2)A_1A_2]$
$l = 4$: $A_1^6 + A_2^6, A_3^6, (A_1^4 + A_2^4)A_3^2, (A_1^2 + A_2^2)A_3^4, A_1^2A_2^2A_3^2,$
$(A_1^2 + A_2^2)A_1^2A_2^2, [(A_1^2 - A_2^2)A_1A_2A_3^2, (A_1^4 - A_2^4)A_1A_2]$

constraints between these coefficients. Except for $l = 0$, more than two coefficients define the constraints. Unfortunately, the problem cannot be solved in general, but only for every value of l independently. For cubic $m\bar{3}m$ symmetry, additional tetragonal constraints are appended to those for the orthorhombic crystal system with respect to the selection rules for the $m\bar{3}$ Laue class. The constraints obtained in this way for $l =$ 0, 2, 4 are given in Tables 13 and 14.

5. Determination of average strain and stress tensors

For the calculation of both average elastic strain and stress tensors, $\bar{e}_i$ and $\bar{s}_i$, only the coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn} and δ_{il}^{mn} with $l = 0$ and $l = 2$ are needed. This is easy to see by combining (11) and (8*b*) into (5) for strain, and (11), (7) and (8*a*) into (6) for stress. The integrals of the terms with $l = 1$ and $l > 2$ are zero because the elements of the matrix **P** are sums of

products of two Euler matrix elements and the generalized harmonics are orthogonal. So, keeping in (11) only the terms with $l = 0$ and $l = 2$, and rearranging to have only positive indices m, n, in place of ε_i' we have the following:

$$\varepsilon_i''(\varphi_1, \Phi_0, \varphi_2) = \sum_{k=0}^{25} g_{ik} R_k(\varphi_1, \Phi_0, \varphi_2). \tag{22}$$

The functions $R_k(\varphi_1, \Phi_0, \varphi_2)$ are linear combinations of $\cos(m\varphi_2 \pm n\varphi_1) Q_l^{mn}(\pm\cos\Phi_0)$ or $\sin(m\varphi_2 \pm n\varphi_1) \times Q_l^{mn}(\pm\cos\Phi_0)$ terms, where $Q_l^{mn} = P_l^{mn}$ for $m + n$ even and $Q_l^{mn} = iP_l^{mn}$ for $m + n$ odd. They are tabulated in Table 15. The vector $\mathbf{g}_i$ is defined as follows (the index t stands for transposed):

$$\mathbf{g}_i^t = \begin{pmatrix} \alpha_{i0}^{00}; \alpha_{i2}^{00}, \alpha_{i2}^{01}, \beta_{i2}^{01}, \alpha_{i2}^{02}, \beta_{i2}^{02}; \alpha_{i2}^{10}, \alpha_{i2}^{11}, \beta_{i2}^{11}, \alpha_{i2}^{12}, \beta_{i2}^{12}; \\ \gamma_{i2}^{10}, \gamma_{i2}^{11}, \delta_{i2}^{11}, \gamma_{i2}^{12}, \delta_{i2}^{12}; \alpha_{i2}^{20}, \alpha_{i2}^{21}, \beta_{i2}^{21}, \alpha_{i2}^{22}, \beta_{i2}^{22}; \\ \gamma_{i2}^{20}, \gamma_{i2}^{21}, \delta_{i2}^{21}, \gamma_{i2}^{22}, \delta_{i2}^{22} \end{pmatrix}.$$

By introducing (22) in (8*b*) and, consequently, (8*b*) in (5), one obtains

$$\bar{e}_i = \sum_{j=1}^{6} \sum_{k=0}^{25} \bar{w}_{ijk} g_{jk}. \tag{23}$$

Similarly, for stress one obtains after combining (22), (7), (8*a*) and (6), and rearranging the terms, the following:

$$\bar{s}_i = \sum_{j=1}^{6} \sum_{k=0}^{25} \bar{w}_{ijk} g'_{jk}, \tag{24}$$

where $g'_{jk} = \sum_{l=1}^{6} C_{jl} g_{lk}$. In (23) and (24), $\mathbf{w}$ is

$$\bar{w}_{ijk} = (1/8\pi^2) \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \mathrm{d}\varphi_1 \, \mathrm{d}\Phi_0 \, \mathrm{d}\varphi_2 \, \sin\Phi_0 \, P_{ij}(\varphi_1, \Phi_0, \varphi_2) \times R_k(\varphi_1, \Phi_0, \varphi_2).$$

In principle, these integrals could be calculated analytically, but because there are 936 such integrals, we obtained components of $\mathbf{w}$ by numerical integration, with better than 10^{-6} precision, by using Gauss quadrature over Φ_0 and Simpson quadrature over φ_1 and φ_2. Only 73 elements are different from zero and many are interrelated by an integer factor. The exact values of unique elements were calculated analytically and all non-zero elements are given in Table 16.

Table 19
The invariant polynomials $J_{k,l+2}$ for the trigonal $\bar{3}m$ Laue class.

Additional terms that should be added for the trigonal $\bar{3}$ Laue class are enclosed in square brackets.

$l = 0$:	$A_1^2 + A_2^2, A_3^2$
$l = 2$:	$(A_1^2 + A_2^2)^2, A_3^4, (A_1^2 + A_2^2)A_3^2, (3A_1^2 - A_2^2)A_2A_3, [(A_1^2 - 3A_2^2)A_1A_3]$
$l = 4$:	$(A_1^2 + A_2^2)^3, A_3^6, (A_1^2 + A_2^2)^2A_3^2, (A_1^2 + A_2^2)A_3^4, (3A_1^2 - A_2^2)A_2A_3,$ $(3A_1^2 - A_2^2)A_2A_3^3, A_1^6 - 15A_1^4A_2^2 + 15A_1^2A_2^4 - A_2^6,$ $[(A_1^2 + A_2^2)(A_1^2 - 3A_2^2)A_1A_3, (A_1^2 - 3A_2^2)A_1A_3^3, (3A_1^2 - A_2^2)(A_1^2 - 3A_2^2)A_1A_2]$

Table 20
The invariant polynomials $J_{k,l+2}$ for the hexagonal 6/*mmm* Laue class.

Additional terms that should be added for the hexagonal 6/*m* Laue class are enclosed in square brackets.

$l = 0$:	$A_1^2 + A_2^2, A_3^2$
$l = 2$:	$(A_1^2 + A_2^2)^2, A_3^4, (A_1^2 + A_2^2)A_3^2$
$l = 4$:	$(A_1^2 + A_2^2)^3, A_3^6, (A_1^2 + A_2^2)^2A_3^2, (A_1^2 + A_2^2)A_3^4,$ $A_1^6 - 15A_1^4A_2^2 + 15A_1^2A_2^4 - A_2^6, [(3A_1^2 - A_2^2)(A_1^2 - 3A_2^2)A_1A_2]$

Table 21
The invariant polynomials $J_{k,\,l+2}$ for the cubic Laue classes.

$l = 0$:	1
$l = 2$:	$A_1^4 + A_2^4 + A_3^4, A_2^2A_3^2 + A_1^2A_3^2 + A_1^2A_2^2$
$l = 4$:	$A_1^6 + A_2^6 + A_3^6, A_1^2A_2^2A_3^2,$
$m\bar{3}m$:	$A_1^4A_2^2 + A_2^4A_3^2 + A_3^4A_1^2 + A_1^4A_3^2 + A_2^4A_1^2 + A_3^4A_2^2$
$m\bar{3}$:	$A_1^4A_2^2 + A_2^4A_3^2 + A_3^4A_1^2, A_1^4A_3^2 + A_2^4A_1^2 + A_3^4A_2^2$

6. Alternative approach – corrections for diffraction line shifts

When finding the WSODF and the average strain and stress tensors during the Rietveld refinement is not of interest, one can choose a different approach that corrects only for the line shifts caused by stress. In this case, an alternative representation for I_l, with fewer refinable parameters, is possible. To accomplish this, the orientation angles in the crystal system (Φ, β) are replaced in (18) by the direction cosines (A_1, A_2, A_3). After introducing in (17) and rearranging, one obtains

$$I_l(\mathbf{h}, \mathbf{y}) = \sum_{k=1}^{k_l} M_{kl}(\Psi, \gamma) J_{k,l+2}(A_1, A_2, A_3), \tag{25}$$

where $J_{k,l+2}$ are homogeneous polynomials of degree $l + 2$ in the variables A_1, A_2, A_3, invariant to the Laue class symmetry operations. The functions $M_{kl}(\Psi, \gamma)$ are linear combinations of $A_{il}^m(\Psi, \gamma)$ and $B_{il}^m(\Psi, \gamma)$:

$$M_{kl}(\Psi, \gamma) = \mu_{kl}^0 P_l^0(\Psi) + \sum_{n=1}^{l} (\mu_{kl}^n \cos n\gamma + \nu_{kl}^n \sin n\gamma) P_l^n(\Psi). \tag{26}$$

The coefficients μ_{kl}^n, ν_{kl}^n can be refined in the Rietveld program in the same way as the coefficients α_{il}^{mn}, β_{il}^{mn}, γ_{il}^{mn} and δ_{il}^{mn} from the alternative approach. For sample symmetry higher than triclinic, the coefficients μ_{kl}^n, ν_{kl}^n follow selection rules identical to those for α_{il}^{mn}, β_{il}^{mn} from Tables 2 and 3. The maximum number k_l of functions M_{kl} in the series expansion (25) must be equal to or smaller than the total number of functions A_{il}^m, B_{il}^m in (17) and (18), but for crystal symmetry higher

than triclinic, it is frequently much smaller. For example, for the Laue class 4/m and $l = 4$, the total number of A_{il}^m, B_{il}^m is 14 but $k_4 = 8$. This fact is important in Rietveld refinement, as the total number of refinable parameters is kept to a minimum. On the other hand, if this approach is taken, there is no path to obtain the WSODF and the average strain and stress tensors from the coefficients μ_{kl}^n, ν_{kl}^n. Therefore, the choice of representation for I_l depends on the problem that we have to solve. If one is interested only in correcting for line shifts in the Rietveld refinement caused by residual strain in the specimen, the approach employing (25) and (26) is taken for any value of l. Conversely, if one is interested in the WSODFs $\varepsilon'(\varphi_1, \Phi_0, \varphi_2)$ and $\sigma(\varphi_1, \Phi_0, \varphi_2)$ and the average strain and stress tensors $\bar{e}_i$ and $\bar{s}_i$, then the approach employing (17) to (20) is taken. Because determination of the average strain and stress tensors requires the terms only for $l = 0$, 2, a third 'mixed' representation for $\langle \varepsilon_{\mathbf{h}}(\mathbf{y}) \rangle$ is also possible, which allows for correction of peak shifts and determination of $\bar{e}_i$ and $\bar{s}_i$, but without reconstruction of the WSODF; because the sum terms (16) are independent, I_l can be developed according to (17) to (20) for $l \leq 2$ and according to (25) and (26) for $l \geq 4$.

The invariant polynomials $J_{k,l+2}(A_1, A_2, A_3)$ are given in Tables 17 to 21 for all Laue groups for $l \leq 4$. For higher values of l, one can calculate the polynomials in the same way as for $l \leq 4$. Alternatively, taking into account that the general form of $J_{k,l+2}$ in (25) is already known, we can adopt another simpler procedure: the invariance conditions are set on the general expression $I_l(A_1, A_2, A_3, \mathbf{y}) = \sum_{i=0}^{l+2} \sum_{j=0}^{l+2-i} M'_{ij,l}(\mathbf{y}) A_1^i A_2^j A_3^{l+2-i-j}$ and the system of linear homogenous equations is solved for $M'_{ij,l}(\mathbf{y})$. Finally, by rearranging all the terms with a common factor, which we denote by $M_{kl}(\mathbf{y})$, one obtains (25).

7. Conclusions

A method for the determination of the texture-weighted strain orientation distribution function (WSODF) and average strain and stress tensors is presented. It is based on the development of the texture-weighted strain tensor in a series of generalized spherical harmonics. The difference between this approach and recent descriptions of the strain/stress orientation distribution function (SODF) (Wang *et al.*, 1999, 2000; Behnken, 2000) is fourfold: (i) this approach directly determines WSODF instead of SODF, which is in accord with the fact that a diffraction experiment yields the texture-weighted strain measure, which is also used to calculate the average strain and stress tensors; (ii) it assumes that only observable strain is invariant to the symmetry operations of a crystal point group; (iii) the approach is extended for arbitrary crystalline symmetry; (iv) it is adopted specifically for implementation in Rietveld refinement programs. Implementation in a Rietveld refinement program can be made in two ways: one set of refinable parameters allows calculation of strain and stress values, while the alternative approach corrects only for diffraction peak shifts, with generally fewer refinable parameters, but without the possibility of estimating strains and stresses.

References

Balzar, D., Von Dreele, R. B., Bennett, K. & Ledbetter, H. (1998). *J. Appl. Phys.* **84**, 4822–4833.
Balzar, D. & Popa, N. C. (2001). In preparation.
Behnken, H. (2000). *Phys. Status Solidi A*, **177**, 401–418.
Bunge, H. J. (1982). *Texture Analysis in Material Science*. London: Butterworth.
Christenson, A. L. & Rowland, E. S. (1953). *Trans. ASM*, **45**, 638–676.
Ferrari, M. & Lutterotti, L. (1994). *J. Appl. Phys.* **76**, 7246–7255.
Hauk, V. (1997). *Structural and Residual Stress Analysis by Nondestructive Methods*. Amsterdam: Elsevier.
Noyan, I. C. & Cohen, J. B. (1987). *Residual Stress*. New York: Springer-Verlag.
Popa, N. C. (1992). *J. Appl. Cryst.* **25**, 611–616.
Popa, N. C. (2000). *J. Appl. Cryst.* **33**, 103–107.
Reuss, A. (1929). *Z. Angew. Math. Mech.* **9**, 49–58.
Rietveld, H. (1969). *J. Appl. Cryst.* **2**, 65–71.
Voigt, W. (1928). *Lehrbuch der Kristallphysik*. Leipzig: Teubner.
Von Dreele, R. B. (1997). *J. Appl. Cryst.* **30**, 517–525.
Wang, Y. D., Lin Peng, R. & McGreevy, R. (1999). *Proceedings of the Twelfth International Conference on Textures of Materials ICOTOM-12*, Canada, August 9–13, pp. 553–559. Ottawa: NRC Research Press.
Wang, Y. D., Lin Peng, R., Zeng, X. H. & McGreevy, R. (2000). *Mater. Sci. Forum*, **347–349**, 66–73.