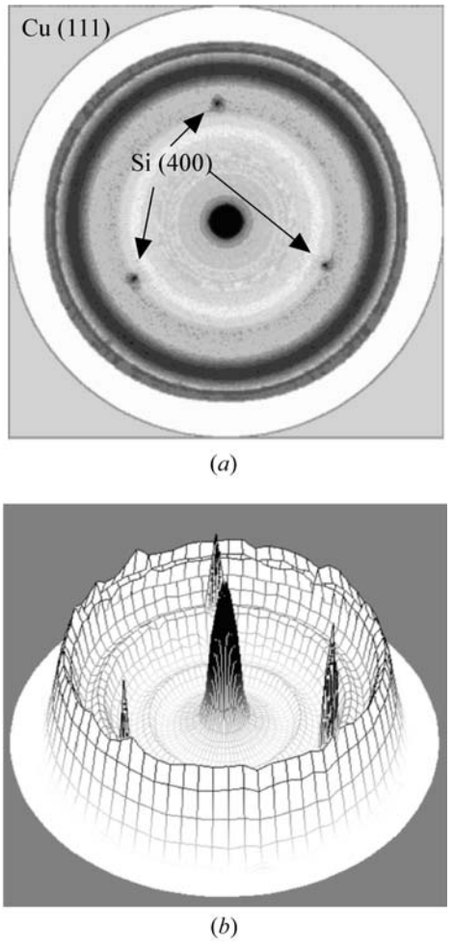

Figure 2.5.23
Combined pole figure of a Cu (111) film on an Si (400) substrate: (*a*) regular 2D projection; (*b*) 3D surface plot.

mized in the centre of the pole figure shows a strong (111) fibre texture. The orientation relationship between the film fibre axis and the substrate is clearly described by the combined pole figures. For samples containing multiple thin-film layers, the orientation relationships between the different layers of the films and substrate can be revealed by superimposing their pole figures.

2.5.4.3. *Stress measurement*

When a solid material is elastically deformed by a force, each crystallite in it changes shape or size. Assuming that the stresses in each crystallite represent the stresses in the solid, the stresses can be measured by measuring the lattice *d*-spacing changes in the crystallites. These *d*-spacing changes can be measured by the changes in diffraction-peak positions based on Bragg's law. In this case, the *d*-spacing serves as a gauge of the deformation. Stress measurement by X-ray diffraction is typically done using a point detector or line detector (Walter, 1971; James & Cohen, 1980; Noyan & Cohen, 1987; Lu, 1996); this will be referred to as the conventional method. The stress or stress tensor is calculated from many strain measurements from diffraction-peak 2θ shifts of a specific lattice-plane family. With a point or line detector, only a small cross section of the diffraction cone is measured at one sample orientation (ψ, φ). Compared to using a conventional detector, 2D detectors have many advantages in stress measurement (Borgonovi, 1984; Korhonen *et al.*, 1989; Yoshioka & Ohya, 1992; Fujii & Kozaki, 1993; He & Smith, 1997; Kämpfe *et al.*, 1999; Hanan *et al.*, 2004). Since a 2D diffraction pattern covers the whole or a large portion of the diffraction rings, it can be used to measure stress with higher accuracy and can be collected in a shorter time than a conventional diffraction pattern, especially when dealing with highly textured materials, large grain sizes, small sample areas, weak diffraction, stress mapping and stress-tensor measurement. The 2D method for stress measurement is based on the fundamental relationship between the stress tensor and the diffraction-cone distortion (He & Smith, 1997; He, 2000; European Standard, 2008).

There are two kinds of stresses, which depend on the source of the loading forces that produce them. One kind is applied stress, caused by external forces acting on the solid object. Applied stress changes when the loading forces change and it disappears once the forces are removed. The stresses measured by X-ray diffraction method are mostly residual stresses. Residual stress is caused by internal forces between different parts of a solid body. Residual stress exists without external forces or remains after the external forces have been removed. The net force and moment on a solid body in equilibrium must be zero, so the residual stresses in the body must be balanced within the body. This means that a compressive stress in one part of the body must come with a tensile stress in another part of the body. For example, the residual stress in a thin film is balanced by the stresses in the substrate. When residual stress in a solid body is mentioned it typically refers to a specific location.

Residual stresses are generally categorized as macroscopic or microscopic depending on the range over which the stresses are balanced. The macroscopic residual stress is the stress measured over a large number of grains. This kind of stress can be measured by X-ray diffraction through the shift of the Bragg peaks. The microscopic stress is the stress measured over one or a few grains, or as small a range as micro- or nanometres. This kind of stress alone will not cause a detectable shift of diffraction peaks, but is reflected in the peak profiles. In this chapter, we will focus on the X-ray diffraction method for stress measurement at the macroscopic level.

2.5.4.3.1. *Stress and strain relation*

Stress is a measure of the deforming force applied to a solid per unit area. The stress on an elemental volume in the sample coordinates S_1, S_2, S_3 contains nine components, given by

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}. \qquad (2.5.63)$$

A component is normal stress when the two indices are identical, or shear stress when the two indices differ. The group of the nine stress components is called the stress tensor. The stress tensor is a tensor of the second order. Under equilibrium conditions, the shear components must maintain the following relations:

$$\sigma_{12} = \sigma_{21},\ \ \sigma_{23} = \sigma_{32} \text{ and } \sigma_{31} = \sigma_{13}. \qquad (2.5.64)$$

Therefore, only six independent components define the stress state in a solid. The following stress states are typically measured:

Uniaxial: all stress components are zero except one normal stress component.

Biaxial: all nonzero components are within the S_1S_2 plane.

Biaxial with shear: $\sigma_{33} = 0$, all other components are not necessarily zero.

Equibiaxial: a special case of biaxial stress where $\sigma_{11} = \sigma_{22} = \sigma$.

Triaxial: all components are not necessarily zero.

Equitriaxial: a special case of triaxial stress where $\sigma_{11} = \sigma_{22} = \sigma_{33} = \sigma$.

Strain is a measure of the resulting deformation of a solid body caused by stress. Strain is calculated from the change in the size and shape of the deformed solid due to stress. Analogous to normal stresses and shear stresses are normal strains and shear strains. The normal strain is calculated from the change in length of the solid body along the corresponding normal stress direction. Like the stress tensor, the strain tensor contains nine components:

$$\varepsilon_{ij} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{bmatrix}. \tag{2.5.65}$$

The directions of all strain components are defined in the same way as for the stress tensor. Similarly, there are six independent components in the strain tensor. Strictly speaking, X-ray diffraction does not measure stresses directly, but strains. The stresses are calculated from the measured strains based on the elasticity of the materials. The stress–strain relations are given by the generalized form of Hooke's law:

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}, \tag{2.5.66}$$

where C_{ijkl} are elastic stiffness coefficients. The stress–strain relations can also be expressed as

$$\varepsilon_{ij} = S_{ijkl}\sigma_{kl}, \tag{2.5.67}$$

where S_{ijkl} are the elastic compliances. For most polycrystalline materials without texture or with weak texture, it is practical and reasonable to consider the elastic behaviour to be isotropic and the structure to be homogeneous on a macroscopic scale. In these cases, the stress–strain relationship takes a much simpler form. Therefore, the Young's modulus E and Poisson's ratio ν are sufficient to describe the stress and strain relations for homogeneous isotropic materials:

$$\begin{aligned} \varepsilon_{11} &= \frac{1}{E}[\sigma_{11} - \nu(\sigma_{22} + \sigma_{33})], \\ \varepsilon_{22} &= \frac{1}{E}[\sigma_{22} - \nu(\sigma_{33} + \sigma_{11})], \\ \varepsilon_{33} &= \frac{1}{E}[\sigma_{33} - \nu(\sigma_{11} + \sigma_{22})], \\ \varepsilon_{12} &= \frac{1+\nu}{E}\sigma_{12}, \quad \varepsilon_{23} = \frac{1+\nu}{E}\sigma_{23}, \quad \varepsilon_{31} = \frac{1+\nu}{E}\sigma_{31}. \end{aligned} \tag{2.5.68}$$

It is customary in the field of stress measurement by X-ray diffraction to use another set of macroscopic elastic constants, S_1 and $\frac{1}{2}S_2$, which are given by

$$\tfrac{1}{2}S_2 = (1+\nu)/E \ \text{ and } \ S_1 = -\nu/E. \tag{2.5.69}$$

Although polycrystalline materials on a macroscopic level can be considered isotropic, residual stress measurement by X-ray diffraction is done by measuring the strain in a specific crystal orientation of the crystallites that satisfies the Bragg condition. The stresses measured from diffracting crystallographic planes may have different values because of their elastic anisotropy. In such cases, the macroscopic elasticity constants should be replaced by a set of crystallographic plane-specific elasticity constants, $S_1^{\{hkl\}}$ and $\frac{1}{2}S_2^{\{hkl\}}$, called X-ray elastic constants (XECs). XECs for many materials can be found in the literature, measured or calculated from microscopic elasticity constants (Lu, 1996). In the case of materials with cubic crystal symmetry, the equations for calculating the XECs from the macroscopic elasticity constants $\frac{1}{2}S_2$ and S_1 are

$$\begin{aligned} \tfrac{1}{2}S_2^{\{hkl\}} &= \tfrac{1}{2}S_2[1 + 3(0.2 - \Gamma(hkl))\Delta] \\ S_1^{\{hkl\}} &= S_1 - \tfrac{1}{2}S_2[0.2 - \Gamma(hkl)]\Delta, \end{aligned} \tag{2.5.70}$$

where

$$\Gamma(hkl) = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2} \ \text{ and } \ \Delta = \frac{5(A_{\rm RX} - 1)}{3 + 2A_{\rm RX}}.$$

In the equations for stress measurement hereafter, either the macroscopic elasticity constants $\frac{1}{2}S_2$ and S_1 or the XECs $S_1^{\{hkl\}}$ and $\frac{1}{2}S_2^{\{hkl\}}$ are used in the expression, but either set of elastic constants can be used depending on the requirements of the application. The factor of anisotropy ($A_{\rm RX}$) is a measure of the elastic anisotropy of a material (He, 2009).

2.5.4.3.2. *Fundamental equations*

Fig. 2.5.24 illustrates two diffraction cones for backward diffraction. The regular diffraction cone (dashed lines) is from the powder sample with no stress, so the 2θ angles are constant at all γ angles. The diffraction ring shown as a solid line is the cross section of a diffraction cone that is distorted as a result of stresses. For a stressed sample, 2θ becomes a function of γ and the sample orientation (ω, ψ, φ), *i.e.* $2\theta = 2\theta(\gamma, \omega, \psi, \varphi)$. This function is uniquely determined by the stress tensor. The strain measured by the 2θ shift at a point on the diffraction ring is $\varepsilon_{(\gamma,\omega,\psi,\varphi)}^{\{hkl\}}$, based on the true strain definition

$$\varepsilon_{(\gamma,\omega,\psi,\varphi)}^{\{hkl\}} = \ln\frac{d}{d_o} = \ln\frac{\sin\theta_o}{\sin\theta} = \ln\frac{\lambda}{2d_o\sin\theta}, \tag{2.5.71}$$

where d_o and θ_o are the stress-free values and d and θ are measured values from a point on the diffraction ring corresponding to (γ, ω, ψ, φ). The direction of $\varepsilon_{(\gamma,\omega,\psi,\varphi)}^{\{hkl\}}$ in the sample coordinates S_1, S_2, S_3 can be given by the unit-vector components h_1, h_2 and h_3. As a second-order tensor, the relationship between the measured strain and the strain-tensor components is then given by

$$\varepsilon_{(\gamma,\omega,\psi,\varphi)}^{\{hkl\}} = \varepsilon_{ij} \cdot h_i \cdot h_j. \tag{2.5.72}$$

The scalar product of the strain tensor with the unit vector in the above equation is the sum of all components in the tensor multiplied by the components in the unit vector corresponding to the first and the second indices. The expansion of this equation for i and j values of 1, 2 and 3 results in

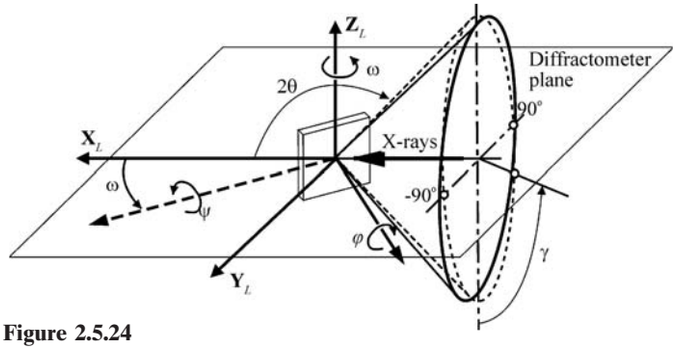

Figure 2.5.24
Diffraction-cone distortion due to stresses.

$$\varepsilon^{\{hkl\}}_{(\gamma,\omega,\psi,\varphi)} = h_1^2\varepsilon_{11} + 2h_1h_2\varepsilon_{12} + h_2^2\varepsilon_{22} + 2h_1h_3\varepsilon_{13} + 2h_2h_3\varepsilon_{23} + h_3^2\varepsilon_{33}. \tag{2.5.73}$$

Or, taking the true strain definition,

$$h_1^2\varepsilon_{11} + 2h_1h_2\varepsilon_{12} + h_2^2\varepsilon_{22} + 2h_1h_3\varepsilon_{13} + 2h_2h_3\varepsilon_{23} + h_3^2\varepsilon_{33} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right), \tag{2.5.74}$$

where θ_o corresponds to the stress-free d-spacing and θ are measured values from a point on the diffraction ring. Both θ and $\{h_1, h_2, h_3\}$ are functions of $(\gamma, \omega, \psi, \varphi)$. By taking γ values from 0 to 360°, equation (2.5.74) establishes the relationship between the diffraction-cone distortion and the strain tensor. Therefore, equation (2.5.74) is the fundamental equation for strain measurement with two-dimensional X-ray diffraction.

Introducing the elasticity of materials, one obtains

$$-\frac{\nu}{E}(\sigma_{11}+\sigma_{22}+\sigma_{33}) + \frac{1+\nu}{E}(\sigma_{11}h_1^2 + \sigma_{22}h_2^2 + \sigma_{33}h_3^2 + 2\sigma_{12}h_1h_2 + 2\sigma_{13}h_1h_3 + 2\sigma_{23}h_2h_3) = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right) \tag{2.5.75}$$

or

$$S_1(\sigma_{11}+\sigma_{22}+\sigma_{33}) + \tfrac{1}{2}S_2(\sigma_{11}h_1^2 + \sigma_{22}h_2^2 + \sigma_{33}h_3^2 + 2\sigma_{12}h_1h_2 + 2\sigma_{13}h_1h_3 + 2\sigma_{23}h_2h_3) = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right). \tag{2.5.76}$$

It is convenient to express the fundamental equation in a clear linear form:

$$p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{13}\sigma_{13} + p_{23}\sigma_{23} + p_{33}\sigma_{33} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right), \tag{2.5.77}$$

where p_{ij} are stress coefficients given by

$$p_{ij} = \begin{cases} (1/E)[(1+\nu)h_i^2 - \nu] = \tfrac{1}{2}S_2h_i^2 + S_1 & \text{if } i = j, \\ 2(1/E)(1+\nu)h_ih_j = 2\tfrac{1}{2}S_2h_ih_j & \text{if } i \neq j. \end{cases} \tag{2.5.78}$$

In the equations for the stress measurement above and hereafter, the macroscopic elastic constants $\frac{1}{2}S_2$ and S_1 are used for simplicity, but they can always be replaced by the XECs for the specific lattice plane $\{hkl\}$, $S_1^{\{hkl\}}$ and $\frac{1}{2}S_2^{\{hkl\}}$, if the anisotropic nature of the crystallites should be considered. For instance, equation (2.5.76) can be expressed with the XECs as

$$S_1^{\{hkl\}}(\sigma_{11}+\sigma_{22}+\sigma_{33}) + \tfrac{1}{2}S_2^{\{hkl\}}(\sigma_{11}h_1^2 + \sigma_{22}h_2^2 + \sigma_{33}h_3^2 + 2\sigma_{12}h_1h_2 + 2\sigma_{13}h_1h_3 + 2\sigma_{23}h_2h_3) = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right). \tag{2.5.79}$$

The fundamental equation (2.5.74) may be used to derive many other equations based on the stress–strain relationship, stress state and special conditions. The fundamental equation and the derived equations are referred to as 2D equations hereafter to distinguish them from the conventional equations. These equations can be used in two ways. One is to calculate the stress or stress-tensor components from the measured strain (2θ-shift) values in various directions. The fundamental equation for stress measurement with 2D-XRD is a linear function of the stress-tensor components. The stress tensor can be obtained by solving the linear equations if six independent strains are measured or by linear least-squares regression if more than six independent measured strains are available. In order to get a reliable solution from the linear equations or least-squares analysis, the independent strain should be measured at significantly different orientations. Another function of the fundamental equation is to calculate the diffraction-ring distortion for a given stress tensor at a particular sample orientation (ω, ψ, φ) (He & Smith, 1998). The fundamental equation for stress measurement by the conventional X-ray diffraction method can also be derived from the 2D fundamental equation (He, 2009).

2.5.4.3.3. *Equations for various stress states*

The general triaxial stress state is not typically measured by X-ray diffraction because of low penetration. For most applications, the stresses in a very thin layer of material on the surface are measured by X-ray diffraction. It is reasonable to assume that the average normal stress in the surface-normal direction is zero within such a thin layer. Therefore, $\sigma_{33} = 0$, and the stress tensor has five nonzero components. In some of the literature this stress state is denoted as triaxial. In order to distinguish this from the general triaxial stress state, here we name this stress state as the 'biaxial stress state with shear'. In this case, we can obtain the linear equation for the biaxial stress state with shear:

$$p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{13}\sigma_{13} + p_{23}\sigma_{23} + p_{\rm ph}\sigma_{\rm ph} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right), \tag{2.5.80}$$

where the coefficient $p_{\rm ph} = \frac{1}{2}S_2 + 3S_1$ and $\sigma_{\rm ph}$ is the pseudo-hydrostatic stress component introduced by the error in the stress-free d-spacing. In this case, the stresses can be measured without the accurate stress-free d-spacing, since this error is included in $\sigma_{\rm ph}$. The value of $\sigma_{\rm ph}$ is considered as one of the unknowns to be determined by the linear system. With the measured stress-tensor components, the general normal stress (σ_φ) and shear stress (τ_φ) at any arbitrary angle φ can be given by

$$\sigma_\varphi = \sigma_{11}\cos^2\varphi + \sigma_{12}\sin 2\varphi + \sigma_{22}\sin^2\varphi, \tag{2.5.81}$$

$$\tau_\varphi = \sigma_{13}\cos\varphi + \sigma_{23}\sin\varphi. \tag{2.5.82}$$

Equation (2.5.81) can also be used for other stress states by removing the terms for stress components that are zero. For instance, in the biaxial stress state $\sigma_{33} = \sigma_{13} = \sigma_{23} = 0$, so we have

$$p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{\rm ph}\sigma_{\rm ph} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right). \tag{2.5.83}$$

In the 2D stress equations for any stress state with $\sigma_{33} = 0$, we can calculate stress with an approximation of d_o (or $2\theta_o$). Any error in d_o (or $2\theta_o$) will contribute only to a pseudo-hydrostatic term $\sigma_{\rm ph}$. The measured stresses are independent of the input d_o (or $2\theta_o$) values (He, 2003). If we use d_0' to represent the initial input, then the true d_o (or $2\theta_o$) can be calculated from $\sigma_{\rm ph}$ with

$$d_0 = d_0'\exp\left(\frac{1-2\nu}{E}\sigma_{\rm ph}\right), \tag{2.5.84}$$

$$\theta_0 = \arcsin\left[\sin\theta_0'\exp\left(\frac{1-2\nu}{E}\sigma_{\rm ph}\right)\right]. \tag{2.5.85}$$

Care must be taken that the $\sigma_{\rm ph}$ value also includes the measurement error. If the purpose of the experiment is to

determine the stress-free d-spacing d_o, the instrument should be first calibrated with a stress-free standard of a similar material.

2.5.4.3.4. *Data-collection strategy*

The practice of stress analysis with 2D-XRD involves the selection of the diffraction-system configuration and the data-collection strategy, frame correction and integration, and stress calculation from the processed data points. Most concepts and strategies developed for a conventional diffractometer are still valid for 2D-XRD. We will focus on the new concepts and practices due to the nature of the 2D detectors.

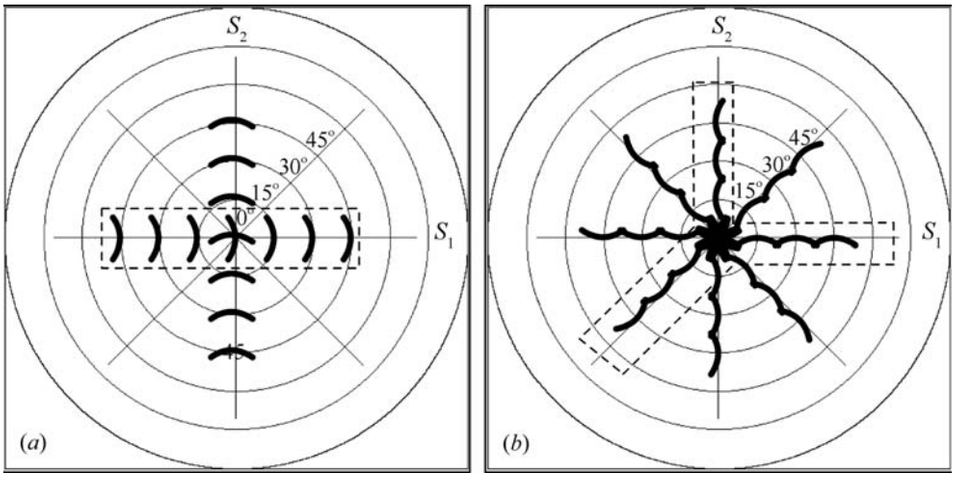

Figure 2.5.25
Data-collection strategy schemes: (*a*) $\omega + \varphi$ scan; (*b*) $\psi + \varphi$ scan.

The diffraction vector is in the normal direction to the measured crystalline planes. It is not always possible to have the diffraction vector in the desired measurement direction. In reflection mode, it is easy to have the diffraction vector normal to the sample surface, or tilted away from the normal, but impossible to have the vector on the surface plane. The stress on the surface plane, or biaxial stress, is calculated by elasticity theory from the measured strain in other directions. The final stress-measurement results can be considered as an extrapolation from the measured values. In the conventional $\sin^2\psi$ method, several ψ-tilt angles are required, typically at 15° steps from −45° to +45°. The same is true with a 2D-XRD system. The diffraction vectors corresponding to the data scan can be projected onto a 2D plot in the same way as the pole-density distribution in a pole figure. The 2D plot is called a data-collection strategy scheme.

By evaluating the scheme, one can generate a data-collection strategy suitable for the measurement of the intended stress components. Fig. 2.5.25 illustrates two schemes for data collection. In the bisecting condition ($\omega = \theta$ or $\theta_1 = \theta$ and $\psi = 0^\circ$), the trace of the diffraction vector falls in the vicinity of the scheme centre. Either an ω tilt or a ψ tilt can move the vectors away from the centre. The circles on the scheme are labelled with the tilt angle of 15°, 30° and 45°. Scheme (*a*) is for an ω tilt of 0°, ±15°, ±30° and ±45° with the φ angle at 0° and 90°. It is obvious that this set of data would be suitable for calculating the biaxial-stress tensor. The data set with $\varphi = 0^\circ$, as shown within the box enclosed by the dashed lines, would be sufficient on its own to calculate σ_{11}. Since the diffraction-ring distortion at $\varphi = 0^\circ$ or $\varphi = 90^\circ$ is not sensitive to the stress component σ_{12}, strategy (*a*) is suitable for the equibiaxial stress state, but is not able to determine σ_{12} accurately. In scheme (*b*), the ψ scan covers 0° to 45° with 15° steps at eight φ angles with 45° intervals. This scheme produces comprehensive coverage on the scheme chart in a symmetric distribution. The data set collected with this strategy can be used to calculate the complete biaxial-stress tensor components and shear stress (σ_{11}, σ_{12}, σ_{22}, σ_{13}, σ_{23}). The scheme indicated by the boxes enclosed by the dashed lines is a time-saving alternative to scheme (*b*). The rings on two φ angles are aligned to S_1 and S_2 and the rings on the third φ angle make 135° angles to the other two arrays of rings. This is analogous to the configuration of a stress-gauge rosette. The three φ angles can also be separated equally by 120° steps. Suitable schemes for a particular experiment should be determined by considering the stress components of interest, the goniometer, the sample size, the detector size and resolution, the desired measurement accuracy and the data-collection time.

2.5.4.3.5. *Data integration and peak evaluation*

The purpose of data integration and peak evaluation is to generate a set of data points along distorted diffraction rings. Data integration for stress analysis is γ integration over several defined segments so as to generate diffraction profiles representing the corresponding segments. The peak position can be determined by fitting the diffraction profile to a given analytic function. Fig. 2.5.26 illustrates data integration over a diffraction frame. The total integration region is defined by $2\theta_1$, $2\theta_2$, γ_1 and γ_2. The integration region is divided into segments given by $\Delta\gamma$. One data point on the distorted diffraction ring is generated from each segment. The γ value in the centre (denoted by the dot-dashed line) of each segment is taken as the γ value of the data point. γ integration of the segment produces a diffraction profile and the 2θ value is determined from the profile. The number of segments and the segment size ($\Delta\gamma$) are selected based on the quality of the data frame. The larger the segment size $\Delta\gamma$ is, the better the integrated diffraction profile as more counts are being integrated. γ integration also produces a smearing effect on the diffraction-ring distortion because the counts collected within the segment size $\Delta\gamma$ are considered as a single γ value at the segment

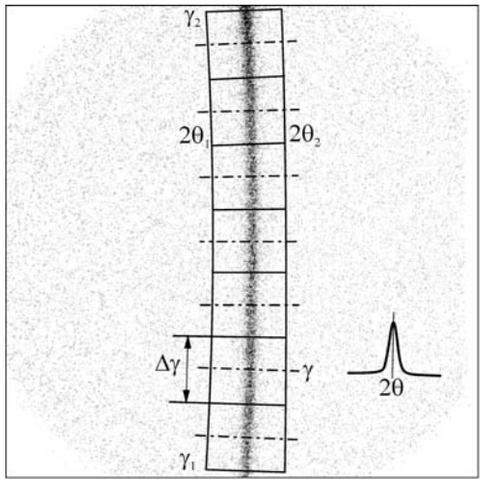

Figure 2.5.26
Data integration for stress measurement.

centre. The 2θ shift in the segment is averaged. The segment size $\Delta\gamma$ should be sufficient to produce a smooth diffraction profile, but not so large as to introduce too much smearing. For data frames containing high pixel counts, the integration segment can be small, *e.g.* $\Delta\gamma \leq 2^\circ$, and still have a smooth profile for each segment. For data frames having low pixel counts, for example the frames collected from a micron-sized area, from a sample with large grains or with a short data-collection time, it is critical to choose a sufficiently large segment size. The segment size can be determined by observing the smoothness of the integrated profile.

Peak evaluation in each segment can be done using the same algorithm used in the conventional method. The corrections to the integrated profiles are performed before or during the peak evaluation. Absorption correction eliminates the influence of the irradiated area and the diffraction geometry on the measured intensity distribution. The absorption for a given material and radiation level depends on the incident angle to the sample and the reflected angle from the sample. For 2D-XRD, the reflected angle is a function of γ for each frame. The polarization effect is also a function of γ. Therefore, the correction for polarization and absorption should be applied to the frame before integration. (Details of these corrections were discussed in Section 2.5.4.3.4.) The polarization and absorption correction is not always necessary if the error caused by absorption can be tolerated for the application, or if the data-collection strategy involves only ψ and φ scans.

In most cases, $K\alpha$ radiation is used for stress measurement, in which case the weighted average wavelength of $K\alpha_1$ and $K\alpha_2$ radiation is used in the calculations. For samples with a broad peak width, diffraction of $K\alpha_1$ and $K\alpha_2$ radiation is merged together as a single peak profile, and the profile can be evaluated as if there is a single $K\alpha$ line without introducing much error to the measured d-spacing. For samples with a relatively narrow peak width, the diffraction profile shows strong asymmetry or may even reveal two peaks corresponding to the $K\alpha_1$ and $K\alpha_2$ lines, especially at high 2θ angles. In this case the profile fitting should include contributions from both the $K\alpha_1$ and $K\alpha_2$ lines. It is common practice to use the peak position from the $K\alpha_1$ line and the $K\alpha_1$ wavelength to calculate the d-spacing after $K\alpha_2$ stripping.

Background correction is necessary if there is a strong background or the peak-evaluation algorithms are sensitive to the background, such as in $K\alpha_2$ stripping, peak fitting, and peak-intensity and integrated-intensity evaluations. Background correction is performed by subtracting a linear intensity distribution based on the background intensities at the lower 2θ side and the higher 2θ side of the diffraction peak. The background region should be sufficiently far from the 2θ peak so that the correction will not truncate the diffraction profile. The 2θ ranges of the low background and high background should be determined based on the width of the 2θ peak and available background in the profile. Based on a normal distribution, a 2θ range of 2 times the FWHM covers 98% of the peak intensity, and 3 times the FWHM covers more than 99.9%, so the background intensity should be determined at more than 1 to 1.5 times the FWHM away from the peak position. The background correction can be neglected for a profile with a low background or if the error caused by the background is tolerable for the application. The peak position can be evaluated by various methods, such as gravity, sliding gravity, and profile fitting by parabolic, pseudo-Voigt or Pearson-VII functions (Lu, 1996; Sprauel & Michaud, 2002).

2.5.4.3.6. *Stress calculation*

The final data set after integration and peak evaluation should contain many data points describing the diffraction-ring shape for all collected frames. Each measured data point contains three goniometer angles (ω, ψ, φ) and the diffraction-ring position (γ, 2θ). The peak intensity or integrated intensity of the diffraction profile is another value to be determined and may be used in the stress calculation. In most cases the number of data points is more than the number of unknown stress components, so a linear least-squares method can be used to calculate the stresses. In a general least-squares regression, the residual for the ith data point is defined as

$$r_i = y_i - \hat{y}_i, \tag{2.5.86}$$

where y_i is the observed response value, $\hat{y}_i$ is the fitted response value and r_i is the residual, which is defined as the difference between the observed value and the fitted value. The summed square of residuals is given by

$$S = \sum_{i=1}^{n} r_i^2 = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2, \tag{2.5.87}$$

where n is the number of data points and S is the sum-of-squares error to be minimized in the least-squares regression. For stress calculation, the observed response value is the measured strain at each data point,

$$y_i = \ln\left(\frac{\sin\theta_0}{\sin\theta_i}\right), \tag{2.5.88}$$

and the fitted response value is given by the fundamental equation as

$$\hat{y}_i = p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{13}\sigma_{13} + p_{23}\sigma_{23} + p_{33}\sigma_{33} + p_{\rm ph}\sigma_{\rm ph}, \tag{2.5.89}$$

where all possible stress components and stress coefficients are listed as a generalized linear equation. Since the response-value function is a linear equation of unknown stress components, the least-squares problem can be solved by a linear least-squares regression. In order to reduce the impact of texture, large grains or weak diffraction on the results of the stress determination, the standard error of profile fitting and the integrated intensity of each profile may be introduced as a weight factor for the least-squares regression (He, 2009).

2.5.4.3.7. *Comparison between the 2D method and the conventional method*

Stress measurement on a polycrystalline material by X-ray diffraction is based on the strain measurements in a single or in several sample orientations. Each measured strain is calculated from the average d-spacing of specific lattice planes $\{hkl\}$ over many crystallites (grains). A larger number of contributing crystallites gives better accuracy and sampling statistics (also referred to as particle statistics). The sampling statistics are determined by both the crystal structure and the instrumentation. The instrument window is mainly determined by the divergence of the incident X-ray beam. Lattice-plane families with high multiplicity will also effectively improve the sampling statistics. The number of contributing crystallites measured by a conventional diffractometer is limited by the sizes and divergences of the incident and diffracted beams to the point detector. In a two-

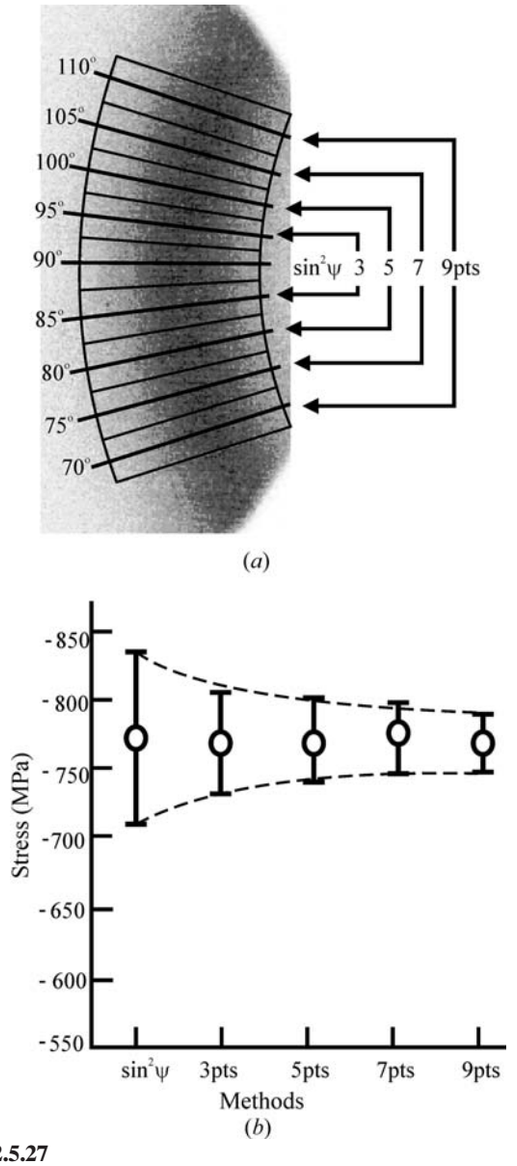

Figure 2.5.27
Stress calculation with the 2D method and the $\sin^2\psi$ method: (*a*) nine data points (abbreviated as pts) on the diffraction ring; (*b*) measured stress and standard deviation by different methods.

dimensional diffraction system, more crystallites can contribute to the diffraction because of the larger γ range.

An example of a stress calculation is provided by the measurement of the residual stress on the end surface of a carbon steel roller. One of the seven frames taken with an ω scan is shown in Fig. 2.5.27(*a*). The (211) ring covering the γ range 67.5 to 112.5° was used for stress analysis. First, the frame data were integrated along γ with an interval of $\Delta\gamma = 5°$. A total of nine diffraction profiles were obtained from γ integration. The peak position 2θ for each γ angle was then obtained by fitting the profile with a Pearson-VII function. A total of 63 data points can be obtained from the seven frames. The data points at $\gamma = 90°$ from seven frames, a typical data set for an ω diffractometer, were used to calculate the stress with the conventional $\sin^2\psi$ method. In order to compare the gain from having increased data points with the 2D method, the stress was calculated from 3, 5, 7 and 9 data points on each frame. The results from the conventional $\sin^2\psi$ method and the 2D method are compared in Fig. 2.5.27(*b*). The measured residual stress is compressive and the stress values from different methods agree very well. With the data taken from the same measurement (seven frames), the 2D method gives a lower standard error and the error decreases with increasing number of data points from the diffraction ring.

2.5.4.4. *Quantitative analysis*

2.5.4.4.1. *Crystallinity*

The crystallinity of a material influences many of its characteristics, including mechanical strength, opacity and thermal properties. Crystallinity measurement provides valuable information for both materials research and quality control in materials processing. The diffraction pattern from a material containing both amorphous and crystalline solids has a broad feature from the amorphous phase and sharp peaks from the crystalline phase. The weight percentage of the crystalline phases in a material containing both crystalline and amorphous phases can be determined by X-ray diffraction (Chung & Scott, 1973; Alexander, 1985; Murthy & Barton, 2000; Kasai & Kakudo, 2005). Assuming that the X-ray scattering intensity from each phase in such a material is proportional to its weight percentage, and that the scattering intensities from all phases can be measured within a given 2θ range, the per cent crystallinity is given by

$$x_{\rm pc} = 100\% \frac{I_{\rm crystal}}{I_{\rm crystal} + I_{\rm amorphous}}, \qquad (2.5.90)$$

where $x_{\rm pc}$ is the per cent crystallinity, $I_{\rm crystal}$ is the integrated intensity of all crystalline peaks and $I_{\rm amorphous}$ is the integrated intensity of the amorphous scattering. The accuracy of the measured per cent crystallinity depends on the integrated diffraction profile. Since most crystalline samples have a preferred orientation, it is very difficult to obtain a consistent measurement of crystallinity with a conventional diffractometer. Fig. 2.5.28 shows a 2D diffraction frame collected from an oriented polycrystalline sample. The diffraction is in transmission mode with the X-ray beam perpendicular to the plate sample surface. Fig. 2.5.28(*a*) shows a diffraction profile integrated from a horizontal region analogous to a profile collected with a conventional diffractometer. Only one peak from the crystalline phase can be observed in the profile. It is also possible that a different peak or no peak is measured if the sample is loaded in other orientations. Fig. 2.5.28(*b*) is the diffraction profile integrated from the region covering all peaks from the crystalline phase over almost all azimuthal angles. A total of four peaks from the crystalline phase are observed. This shows that a 2D-XRD system can measure per cent crystallinity more accurately and with more consistent results (Pople *et al.*, 1997; Bruker, 2000) than a conventional system.

2.5.4.4.2. *Crystallite size*

The size of the crystallites in a polycrystalline material has a significant effect on many of its properties, such as its thermal, mechanical, electrical, magnetic and chemical properties. X-ray diffraction has been used for crystallite-size measurement for many years. Most methods are based on diffraction-line broadening and line-profile analysis (Wilson, 1971; Klug & Alexander, 1974; Ungár, 2000). Another approach to crystallite-size measurement is based on the spotty diffraction rings collected with two-dimensional detectors when a small X-ray beam is used (Cullity, 1978; He, 2009). Line-profile analysis is based on the diffraction profile in the 2θ direction, while crystallite-size analysis with a spotty 2D diffraction pattern is based on the diffraction profile in the γ direction. The latter may be referred to as γ-profile analysis.