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PRINCIPLE OF THE DYNAMIC X-RAY DIFFRACTION TECHNIQUE

by

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Introduction

As it is well known, x-ray diffraction study is one of the most useful means to determine crystal orientation. For usualy diffraction measurement, several seconds or minutes are required to accumulate enough counts at each point on the diffraction pattern. Thus it would not be possible to directly follow changes in crystal orientation occurring in short times. The dynamic x-ray diffraction technique was developed as a direct means of determining crystal orientation times[1]. In this technique, the sample is vibrated sinusoidally and the diffraction count is accumulated during specified intervals of the vibration period over many cycles. The principle of this technique will be discussed in the following sections.

Diffraction from Crystalline Polymer

The x-ray diffracted intensity from polymer films at a given Bragg and azimuthal angle is given by a summation of

1. coherent scattering from crystalline phase and amorphous phase of the film,
2. incoherent scattering from the sample, and
3. background scattering.

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That is

$$I_{total}(\theta,\Phi) = I_{cr}(\theta,\Phi) + I_{am}(\theta,\Phi) + I_{incoh}(\theta,\Phi) + I_{back}(\theta,\Phi) \tag{1}$$

where $I_{total}(\theta,\Phi)$ is the total intensity of diffracted x-ray at Bragg angle θ and azimuthal angle Φ. $I_{cr}(\theta,\Phi)$ and $I_{am}(\theta,\Phi)$ are the coherent scattering from the crystalline phase and amorphous phase, respectively. $I_{incoh}(\theta,\Phi)$ is the incoherent scattering. $I_{back}(\theta,\Phi)$ is the background scattering, which includes stray radiations, air scattering and slit scattering.

In the case where experimental geometry is shown by (Fig. 1) $I_{cr}(\theta,\Phi)$ is given by

$$I_{cr}(\theta,\Phi) = k_{cr}\, h(\theta)\, I_o\, P_{cr}(\theta,\Phi)\, d \sec\theta\, e^{-\mu d \sec\theta} \tag{2}$$

Here K_{cr} is a constant. $h(\theta)$ is the polarization factor. I_o is the intensity of incident beam. $P_{cr}(\theta,\Phi)$ is the density of crystal with particular orientation which is capable to contribute to the diffraction at θ and Φ. d is the thickness of the sample film. μ is the absorption coefficient in reciprocal centimeters.

Intensity of the Diffraction from Crystalline Phase

As it is well known, the x-ray diffraction flat film pattern of an unoriented sample consists of complete rings, while with oriented samples diffraction concentrates at certain portions of the rings. The diffraction intensity from stretched samples at a given point is a function of the applied strain. In the following discussion we consider a case where a strain is described by the equation

$$\lambda(t) = \lambda_o + \Delta\lambda \cos \omega t \tag{3}$$

Here λ_o is a static strain, $\Delta\lambda$ is the amplitude of dynamic strain, ω is the angular frequency in the dynamic strain, t is time. When the strain is applied on the sample, the change in sample thickness with time is represented by

$$d(t) = d_o - \Delta d \cos (\omega t + \delta d) \tag{4}$$

where d_o is the sample thickness at the strain of λ_o, $\Delta\lambda$ is the amplitude of dynamic change in thickness, δd is the phase difference between strain and thickness change. When the sample volume is constant independently of strain and Poisson ratio is a real number, Eq. (4) is simplified to

$$d(t) = d_o - d_o \frac{\Delta\lambda}{2} \cos \omega t \tag{5}$$

The crystal distribution function $P_{cr}(\theta,\Phi)$ giving the number of crystals having a given plane oriented at angles between θ and $\theta + d\theta$ and Φ and $\Phi + d\Phi$ may be also expressed by a function of time as

$$P_{cr}(\theta,\Phi,t) = P_{cr}{}^{\circ}(\theta,\Phi) + \Delta P_{cr} \cos (\omega t + \delta P_{cr}) \tag{6}$$

In general, the amplitude ΔP_{cr} and the phase difference δP_{cr} are functions of θ, Φ and ω and may differ for different crystal planes.

By inserting Eqs. (4) and (5) into Eq. (2) we have

$$\begin{aligned} I_{cr}(\theta,\Phi) &= K_{cr}(\theta)\, d_o \sec\theta\, P_{cr}{}^{\circ}(\theta,\Phi) \exp(-\mu d_o \sec\theta) \\ &\times \left[1 + \frac{\Delta P_{cr}}{P_{cr}{}^{\circ}(\theta,\Phi)} \cos(\omega t + \delta P_{cr})\right] \\ &\times \left[1 - \frac{\Delta d}{d_o} \cos(\omega t + \delta d)\right] \\ &\times \exp[\mu\, \Delta d \sec\theta \cos(\omega t + \delta d)] \end{aligned}$$

$$K_{cr}(\theta) = k_{cr}\, h(\theta)\, I_0$$

In most cases of experiments with polymer samples, the relationship

$$\mu \, \Delta d \sec\theta \ll 1 \tag{7}$$

holds. The exponential term of the above equation may be expanded as a series and higher terms of $\Delta P_{cr}/P_{cr}^{\circ}$, $\Delta d/d_o$ and $\mu \, \Delta d \sec\theta$ may be neglected. Then

$$I_{cr}(\theta,\phi) = I_{cr}^{\circ}(\theta,\phi) + \Delta I_{cr} \cos(\omega t + \delta_{cr}) \tag{8}$$

where

$$I_{cr}^{\circ}(\theta,\phi) = K_{cr}(\theta) \, d_o \sec\theta \, P_{cr}^{\circ}(\theta,\phi) \exp(-\mu \, d_o \sec\theta)$$

$$= K_{cr}(\theta) \, P_{cr}^{\circ}(\theta,\phi) \tag{9}$$

$$K_{cr}(\theta) = k_{cr} \, h(\theta) \, I_o \, d_o \sec\theta \exp(-\mu \, d_o \sec\theta) \tag{10}$$

and

$$\Delta I_{cr} \cos \delta_{cr} = K_{cr}(\theta) \, \Delta P_{cr} \cos \delta P_{cr} + I_{cr}^{\circ}(\theta,\phi) \left[-\frac{\Delta d}{d_o} \cos \delta_d + \mu \, \Delta d \sec\theta \cos \delta_d \right] \tag{11}$$

$$\Delta I_{cr} \sin \delta_{cr} = K_{cr}(\theta) \, \Delta P_{cr} \sin \delta P_{cr} + I_{cr}^{\circ}(\theta,\phi) \left[-\frac{\Delta d}{d_o} \sin \delta_d + \mu \, \Delta d \sec\theta \sin \delta_d \right] \tag{12}$$

Expression for $I_{am}(\theta,\phi)$ and $I_{incoh}(\theta,\phi)$

In the same way as for $I_{cr}(\theta,\phi)$ the intensity of diffraction from the amorphous phase is represented by

$$I_{am}(\theta,\phi) = I_{am}^{\circ}(\theta,\phi) + \Delta I_{am} \cos(\omega t + \delta_{am}) \tag{13}$$

Here $I_{am}^{\circ}(\theta,\phi)$ is the diffraction intensity from the amorphous phase of the sample with static strain of λ_o, and expressed by

$$I_{am}^{\circ}(\theta,\phi) = K_{am}(\theta)\, P_{am}^{\circ}(\theta,\phi) \tag{14}$$

where $K_{am}(\theta)$ is a function of θ corresponding to $K_{cr}(\theta)$ for tne crystalline phase. $P_{am}^{\circ}(\theta,\phi)$ is the distribution function of the amorphous elements which contribute to the diffraction at the point (θ,ϕ). ΔI_{am} is the amplitude, δ_{am} is the phase different between strain and diffraction intensity of the amorphous phase. Then

$$\Delta I_{am} \cos \delta_{am} = K_{am}(\theta)\, \Delta P_{am} \cos \delta P_{am} + I_{am}^{\circ}(\theta,\phi) \left[- \frac{\Delta d}{d_o} \cos \delta_d + \mu\, (\Delta d) \sec \theta \cos \delta d \right] \tag{15}$$

$$\Delta I_{am} \sin \delta_{am} = K_{am}(\theta)\, \Delta P_{am} \sin \delta P_{am} + I_{am}^{\circ}(\theta,\phi) \left[- \frac{\Delta d}{d_o} \sin \delta d + \mu\, (\Delta d) \sec \theta \sin \delta d \right] \tag{16}$$

just as in the case of $I_{cr}(\theta,\phi)$. ΔP_{am} is the amplitude of the dynamic component of density function $P_{am}(\theta,\phi)$. δP_{am} is the phase difference between the strain and change in distribution function of the amorphous elements.

For the incoherent scattering the effects of orientation may be ignored. Then the intensity of incoherent scattering is expressed by

$$I_{incoh}(\theta,\phi) = I_{incoh}(\theta,\phi) + \Delta I_{incoh} \cos(\omega t + \delta_{incoh}) \tag{17}$$

Here $I_{incoh}^{o}(\theta,\Phi)$ is the intensity of incoherent scattering at a strain of λ_o, and

$$\Delta I_{incoh} \cos \delta_{incoh} = I_{incoh}^{o}(\theta,\Phi) \left[- \frac{\Delta d}{d_o} \cos \delta d + \mu\ (\Delta d) \sec \theta \cos \delta d \right] \tag{18}$$

$$\Delta I_{incoh} \sin \delta_{incoh} = I_{incoh}^{o}(\theta,\Phi) \left[- \frac{\Delta d}{d_o} \sin \delta d + \mu\ (\Delta d) \sec \theta \sin \delta d \right] \tag{19}$$

Relation between $I_{total}(\theta,\Phi)$ and $P_{cr}(\theta,\Phi)$

Insertin. :qs. (8), (13) and (17) into Eq. (1) we have

$$I_{total}(\theta,\Phi) = I_{total}^{o}(\theta,\Phi) + \Delta I_{total} \cos (\omega t + \delta_{total}) \tag{20}$$

where

$$I_{total}^{o}(\theta,\Phi) = I_{cr}^{o}(\theta,\Phi) + I_{am}^{o}(\theta,\Phi) + I_{incoh}^{o}(\theta,\Phi) + I_{back}(\theta,\Phi) \tag{21}$$

$$\Delta I_{total} \cos \delta_{total} = \left[I_{total}^{o}(\theta,\Phi) - I_{back}(\theta,\Phi) \right] \left[- \frac{\Delta d}{d_o} \cos \delta d + \mu\ (\Delta d) \sec \theta \cos \delta d \right] + \left[K_{cr}(\theta)\ \Delta P_{cr} \cos \delta P_{cr} + K_{am}(\theta)\ \Delta P_{am} \cos \delta P_{am} \right] \tag{22}$$

$$\Delta I_{total} \sin \delta_{total} = \left[I_{total}^{o}(\theta,\Phi) - I_{back}(\theta,\Phi) \right] \left[- \frac{\Delta d}{d_o} \sin \delta d + \mu\ (\Delta d) \sec\theta \sin \delta d \right] + \left[K_{cr}(\theta)\ \Delta P_{cr} \sin \delta P_{cr} + K_{am}(\theta)\ \Delta F_{am} \sin \delta P_{am} \right] \tag{23}$$

The first terms in Eqs. (22) and (23) arise from the change in the sample thickness. The second terms show the effect of the change in orientation. From these equations we can get the expressions for the dynamic components of the crystal orientation distribution function ΔP. That is, by using Eqs. (15), (16), (22) and (23) we have

$$K_{cr}(\theta)\ \Delta P_{cr} \cos \delta P_{cr} = \Delta I_{total} \cos \delta_{total} - \Delta I_{am} \cos \delta_{am}$$
$$- \left[I_{total}^{\circ}(\theta,\Phi) - I_{am}^{\circ}(\theta,\Phi) - I_{am}(\theta,\Phi) \right] \left[- \frac{\Delta d}{d_o} \cos \delta d + \mu\ (\Delta d) \sec \theta \cos \delta d \right] \quad (24)$$

and

$$K_{cr}(\theta)\ \Delta P_{cr} \sin \delta P_{cr} = \Delta I_{total} \sin \delta_{total} - \Delta I_{am} \sin \delta_{am}$$
$$- \left[I_{total}^{\circ}(\theta,\Phi) - I_{am}^{\circ}(\theta,\Phi) - I_{am}(\theta,\Phi) \right] \left[- \frac{\Delta d}{d_o} \sin \delta d + \mu\ (\Delta d) \sec \theta \sin \delta d \right] \quad (25)$$

When Poisson's ratio is a real number and the sample volume remains constant independently of strain, the sample thickness changes in phase with the external strain and Eqs. (24) and (25) simplify to

$$K_{cr}(\theta)\ \Delta P_{cr} \cos \delta P_{cr} = \Delta I_{total} \cos \delta_{total} - \Delta I_{am} \cos \delta_{am}$$
$$- \left[- \frac{\Delta\lambda}{2} + \frac{\Delta\lambda}{2}\ \mu\ d_o \sec \theta \right] \left[I_{total}^{\circ}(\theta,\Phi) - I_{am}(\theta,\Phi) \right] \quad (26)$$

and

$$K_{cr}(\theta)\ \Delta P_{cr} \sin \delta P_{cr} = \Delta I_{total} \sin \delta_{total} - \Delta I_{am} \sin \delta_{am} \quad (27)$$

In the above expressions all quantities on the right hand side can be evaluated experimentally.

Orientation Functions

The orientation function of a given crystal axis is defined by the following equation

$$f = \frac{3\,\overline{\cos^2\gamma} - 1}{2} \qquad (28)$$

Here γ is the angle between the crystal axis and the stretching direction. In the case of experiments for which the geometry is shown by Fig. 1. The angle γ obeys following relationship

$$\cos\gamma = \sin\phi \qquad (29)$$

The quantity $\overline{\cos^2\gamma}$ is an average value and given by

$$\overline{\cos^2\gamma} = \frac{\int_0^{\pi/2} \cos^2\gamma \; N(\gamma) \sin\gamma \, d\gamma}{\int_0^{\pi/2} N(\gamma) \sin\gamma \, d\gamma} \qquad (30)$$

where $N(\gamma) \sin\gamma \, d\gamma$ is the number of the crystals oriented between γ and $\gamma + d\gamma$. One can show that the function $N(\gamma)$ is proportional to the function $P_{cr}(\theta,\phi)$ previously introduced. Taking into account the condition of Eq. (29) we can show the relation by

$$N(\alpha) \sin\gamma \, d\gamma = - \text{const. } P_{cr}(\theta,\phi) \cos\phi \, d\phi \qquad (31)$$

By inserting Eqs. (29), (31) into (30) we have

$$\overline{\cos^2\gamma} \quad \frac{\int_0^{\pi/2} \sin^2\Phi \; P_{cr}(\theta,\Phi) \cos\Phi \; d\Phi}{\int_0^{\pi/2} P_{cr}(\theta,\Phi) \cos\Phi \; d\Phi} \tag{32}$$

If for $P_{cr}(\theta,\Phi)$ we substitute the quantity for the dynamic state expressed by Eq. (6) we have

$$\overline{\cos^2\gamma} = \frac{\int_0^{\pi/2} \left[\sin^2\Phi \; P_{cr}^{o}(\theta,\Phi) + \Delta P_{cr} \cos\left(\omega t + \delta P_{cr}\right)\right] \cos\Phi \; d\Phi}{\int_0^{\pi/2} \left[P_{cr}^{o}(\theta,\Phi) + \Delta P_{cr} \cos\left(\omega t + \delta P_{cr}\right)\right] \cos\Phi \; d\Phi}$$

$$= \frac{I_{11} + I_{12} \cos \omega t - I_{13} \sin \omega t}{I_{21} + I_{22} \cos \omega t - I_{23} \sin \omega t} \tag{33}$$

where I_{ij} represents the following integrations

$$I_{11} = \int_0^{\pi/2} \sin^2\Phi \; P_{cr}^{o}(\theta,\Phi) \cos\Phi \; d\Phi \tag{34}$$

$$I_{12} = \int_0^{\pi/2} \sin^2\Phi \; \Delta P_{cr} \cos \delta P_{cr} \cos\Phi \; d\Phi \tag{35}$$

$$I_{13} = \int_0^{\pi/2} \sin^2\Phi \; \Delta P_{cr} \sin \delta P_{cr} \cos\Phi \; d\Phi \tag{36}$$

$$I_{21} = \int_0^{\pi/2} P_{cr}^{o}(\theta,\Phi) \cos\Phi \; d\Phi \tag{37}$$

$$I_{22} = \int_0^{\pi/2} \Delta P_{cr} \cos \delta_{cr} \cos\Phi \; d\Phi \tag{38}$$

$$I_{23} = \int_0^{\pi/2} \Delta P_{cr} \sin \delta_{cr} \cos\Phi \, d\Phi \tag{39}$$

Usually I_{12}, I_{13}, I_{22}, and I_{23} are far smaller than I_{11} and I_{21} so if small dynamic strain is used, one may rewrite Eq. (33) as

$$\overline{\cos^2\gamma} = \frac{I_{11}}{I_{21}} \left[1 + \left(\frac{I_{12}}{I_{11}} - \frac{I_{22}}{I_{21}} \right) \cos \omega t - \left(\frac{I_{13}}{I_{11}} - \frac{I_{23}}{I_{21}} \right) \sin \omega t \right] \tag{40}$$

Inserting Eq. (40) into Eq. (28) we have

$$f = f_o + \Delta f \cos (\omega t + \delta_f) \tag{41}$$

when f_o is the orientation function corresponding to static strain λ_o and given by

$$f_o = \frac{3 \frac{I_{11}}{I_{21}} - 1}{2} \tag{42}$$

The dynamic components of the orientation function is given by

$$\Delta f \cos \delta_f = \frac{3}{2} \frac{I_{11}}{I_{21}} \left(\frac{I_{12}}{I_{11}} - \frac{I_{22}}{I_{21}} \right) \tag{43}$$

$$\Delta f \sin \delta_f = \frac{3}{2} \frac{I_{11}}{I_{21}} \left(\frac{I_{12}}{I_{11}} - \frac{I_{22}}{I_{21}} \right) \tag{44}$$

From Eqs. (9), (20) we have

$$P_{cr}^{\circ}(\theta,\Phi) = \frac{1}{K_{cr}(\theta)} \left[I_{total}^{\circ}(\theta,\Phi) - I_{am}^{\circ}(\theta,\Phi) - I_{incoh}^{\circ}(\theta,\Phi) - I_{back}(\theta,\Phi) \right] \tag{45}$$

Eqs. (26) and (27) then lead to

$$\Delta P_{cr} \cos \delta P_{cr} = \frac{1}{K_{cr}(\theta)} \left\{ \Delta I_{total} \cos \delta_{total} - \Delta I_{am} \cos \delta_{am} + \frac{\Delta\lambda}{2} (1 - \mu d_o \sec\theta) \left[I_{total}^{\circ} (\theta,\Phi) - I_{am}^{\circ} (\theta,\Phi) - I_{back}(\theta,\Phi) \right] \right\} \quad (46)$$

and

$$\Delta P_{cr} \sin \delta P_{cr} = \frac{1}{K_{cr}(\theta)} \left\{ \Delta I_{total} \sin \delta_{total} - \Delta I_{am} \sin \delta_{am} \right\} \quad (47)$$

These three expressions are used to perform the integrations (34) - (39). Since the integrations always come into the expressions of orientation function as the ratio of two of them. The factor $1/K_{cr}(\theta)$ will be eliminated in the performance of the calculation of the orientation function. All quantities appearing in the right hand side of these three expressions may be obtained experimentally as will be shown in the following sections.

Semicircle Sector Technique

In order to obtain the quantities introduced in the preceding section, especially $\Delta I_{total} \cos \delta_{total}$ and $\Delta I_{total} \sin \delta_{total}$, the semicircle sector technique was devised. Details of the principle of this technique will be presented hereinafter.

A photo sector rotates in synchronism with the sample vibration. On the sector four windows are arranged so as to activate the corresponding scalers during the strain period between 0 and π, π and 2π, $\frac{\pi}{2}$ and $\frac{3\pi}{2}$, and $-\frac{\pi}{2}$ and $\frac{\pi}{2}$, respectively. Average intensity of diffraction in these four intervals are easily obtained from the accumulated counts of each scaler. Usually, the diffraction counts are accumulated over many cycles of vibration in order to reduce the statistical error of counting. Now we consider the case where the sample is vibrated with period of T(sec.) and diffraction is accumulated over n cycles. Total time necessary for n cycles is

$$\tau = n\ T \tag{48}$$

Each scaler works during the half of this duration.

Total number of counts accumulated by the scaler corresponding to the window which opens between 0 and π is given by

$$N_{0\sim\pi}(\tau) = n \int_0^{T/2} \left[I_{total}^{\circ}\ (\theta,\phi) + \Delta I_{total} \cos\ (\omega\ \tau + \delta_{total}) \right] d\tau$$

$$= \frac{nT}{2} \left[I_{total}^{\circ}\ (\theta,\phi) - \frac{2}{\pi}\ \Delta I_{total} \sin \delta_{total} \right] \tag{49}$$

The average intensity in the phase range between 0 and π is

$$I_{0\sim\pi}(\theta,\phi) = \frac{N_{0\sim\pi}(\tau)}{1/2\tau} = I_{total}^{\circ}\ (\theta,\phi) - \frac{2}{\pi} \Delta I_{total} \sin \delta_{total} \tag{50}$$

In the same way average intensities in the other phase range is given by

$$I_{\pi\sim2\pi}(\theta,\phi) = \frac{N_{\pi\sim\pi}\ (\tau)}{1/2\tau} = I_{total}^{\circ}(\theta,\phi) + \frac{2}{\pi}\ \Delta I_{total} \sin \delta_{total} \tag{51}$$

$$I_{\frac{\pi}{2}\sim\frac{3\pi}{2}}(\theta,\phi) = N_{\frac{\pi}{2}\sim\frac{3\pi}{2}}(\tau) = I_{total}^{\circ}\ (\theta,\phi) - \frac{2}{\pi}\ \Delta I_{total} \cos \delta_{total} \tag{52}$$

$$I_{\frac{3\pi}{2}\sim\frac{5\pi}{2}}(\theta,\phi) = \frac{N_{\frac{3\pi}{2}\sim\frac{5\pi}{2}}(\tau)}{1/2\tau} = I_{total}^{\circ}\ (\theta,\phi) + \frac{2}{\pi} \Delta I_{total} \cos \delta_{total} \tag{53}$$

From these four expressions we have

$$I_{total}{}^{o}(\theta,\phi) = \frac{1}{2}\left[\frac{2N_{o\sim\pi}(\tau)}{\tau} - \frac{2N_{\pi\sim 2\pi}(\tau)}{\tau}\right] \tag{54}$$

$$= \frac{1}{2}\left[\frac{2N_{\frac{\pi}{2}\sim\frac{3\pi}{2}}(\tau)}{\tau} - \frac{2N_{\frac{3\pi}{2}\sim\frac{5\pi}{2}}(\tau)}{\tau}\right] \tag{55}$$

$$\Delta I_{total} \cos \delta_{total} = \frac{\pi}{4}\left[\frac{2N_{\frac{3\pi}{2}\sim\frac{5\pi}{2}}(\tau)}{\tau} - \frac{2N_{\frac{\pi}{2}\sim\frac{3\pi}{2}}(\tau)}{\tau}\right] \tag{56}$$

$$\Delta I_{total} \sin \delta_{total} = \frac{\pi}{4}\left[\frac{2N_{\pi\sim 2\pi}}{\tau} - \frac{2N_{o\sim\pi}}{\tau}\right] \tag{57}$$

Therefore if we measure $N_{o\sim\pi}(\tau)$, $N_{\pi\sim 2\pi}(\tau)$, $N_{\frac{\pi}{2}\sim\frac{3\pi}{2}}(\tau)$ and $N_{\frac{3\pi}{2}\sim\frac{5\pi}{2}}(\tau)$ by accumulating the diffraction counts for duration of τ, we can get $I_{total}{}^{\circ}(\theta,\phi)$, $(\Delta I_{total} \cos \delta_{total})$ from above relations.

Both the opening angles of the photo sector windows and synchronism of the sector rotation contain some small uncertainty, which may induce a rather serious error in the observed values, especially in the value of $\Delta I_{total} \sin \delta_{total}$ which must be considered.

If the opening angles of the windows are not just π and a small phase difference exists between sector rotation and sample, initial- and end-point of each window can be indicated as (Fig. 2)

	Initial Point	End Point
window $0\sim\pi$	$0 + \alpha_{11}$	$\pi + \alpha_{12}$
window $\pi\sim 2$	$\pi + \alpha_{21}$	$2\pi + \alpha_{22}$
window $\frac{\pi}{2}\sim\frac{3\pi}{2}$	$\frac{\pi}{2} + \alpha_{31}$	$\frac{3\pi}{2} + \alpha_{32}$
window $\frac{3\pi}{2}\sim\frac{5\pi}{2}$	$\frac{3\pi}{2} + \alpha_{41}$	$\frac{5\pi}{2} + \alpha_{42}$

Then the diffracted counts are accumulated not over a phase duration of π, but over a phase duration of $\pi + (\alpha_{12} - \alpha_{11})$. The accumulated counts of each scaler are given by

$$N_{0-\pi} = \frac{n}{\omega}\int_{\alpha_{11}}^{\pi + \alpha_{12}} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta_{total})\right] dx$$

$$= \frac{n}{\omega} (\pi + \alpha_{12} - \alpha_{11}) I_{total}{}^{o} (\theta,\phi)$$

$$- \frac{n}{\omega} \Delta I_{total} \left[2 \sin \delta_{total} + (\alpha_{11} - \alpha_{12}) \cos \delta_{total}\right] \quad (58)$$

$$N_{\pi-2\pi}(\tau) = \frac{n}{\omega} \int_{\pi + \alpha_{21}}^{\pi + \alpha_{22}} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta_{total})\right] dx$$

$$= \frac{n}{\omega} (\pi + \alpha_{22} - \alpha_{21}) I_{total}{}^{o}(\theta,\phi)$$

$$+ \frac{n}{\omega} \Delta I_{total} \left[2 \sin \delta_{total} + (\alpha_{21} + \alpha_{22}) \cos \delta_{total}\right] \quad (59)$$

$$N_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau) = \frac{n}{\omega}\int_{\frac{\pi}{2} + \alpha_{31}}^{\frac{3\pi}{2} + \alpha_{32}} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta_{total})\right] dx$$

$$= \frac{n}{\omega} (\pi + \alpha_{32} - \alpha_{31}) I_{total}{}^{o}(\theta,\phi)$$

$$- \frac{n}{\omega} \Delta I_{total} \left[2 \cos \delta_{total} - (\alpha_{31} + \alpha_{32}) \sin \delta_{total}\right] \quad (60)$$

$$N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau) = \frac{n}{\omega} \int_{\frac{3\pi}{2}+\alpha_{41}}^{\frac{5\pi}{2}+\alpha_{42}} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta_{total}) \right] dx$$

$$= \frac{n}{\omega} (\pi + \alpha_{42} - \alpha_{41}) I_{total}{}^{o}(\theta,\phi)$$

$$+ \frac{n}{\omega} \Delta I_{total} \left[2 \cos \delta_{total} - (\alpha_{41} + \alpha_{42}) \sin \delta_{total} \right] \quad (61)$$

Here we expand sin α_{ij} and cos α_{ij} into series and neglect higher terms of α_{ij} under the assumption that α_{ij} is small. In this case the time durations over which each scaler works are not $\frac{1}{2}$ nt. They are expressed by the following equations.

$$\tau_{o-\pi} = nt \frac{\pi + \alpha_{12} - \alpha_{11}}{2\pi} = \frac{n}{\omega} (\pi + \alpha_{12} - \alpha_{11}) \quad (62)$$

$$\tau_{\pi-2\pi} = nt \frac{\pi + \alpha_{22} - \alpha_{21}}{2\pi} = \frac{n}{\omega} (\pi + \alpha_{12} - \alpha_{11}) \quad (63)$$

$$\tau_{\frac{\pi}{2}-\frac{3\pi}{2}} = nt \frac{\pi + \alpha_{32} - \alpha_{31}}{2\pi} = \frac{n}{\omega} (\pi + \alpha_{32} - \alpha_{31}) \quad (64)$$

$$\tau_{\frac{3\pi}{2}-\frac{5\pi}{2}} = nt \frac{\pi + \alpha_{42} - \alpha_{41}}{2\pi} = \frac{n}{\omega} (\pi + \alpha_{42} - \alpha_{41}) \quad (65)$$

Here $(\pi + \alpha_{i2} - \alpha_{i1})/2\pi$ show the ratio of the duration over which the i-th scaler works. Hereinafter the ratios will be represented by S_{ij}, that is

$$S_{0\sim\pi} \equiv \frac{\pi + \alpha_{12} - \alpha_{11}}{2\pi} \tag{66}$$

$$S_{\pi\sim 2\pi} \equiv \frac{\pi + \alpha_{22} - \alpha_{21}}{2\pi} \tag{67}$$

$$S_{\frac{\pi}{2}\sim\frac{3\pi}{2}} \equiv \frac{\pi + \alpha_{32} - \alpha_{31}}{2\pi} \tag{68}$$

$$S_{\frac{3\pi}{2}\sim\frac{5\pi}{2}} \equiv \frac{\pi + \alpha_{42} - \alpha_{41}}{2\pi} \tag{69}$$

Now the average intensities of diffraction in each duration are given by

$$\frac{N_{0\sim\pi}(\tau)}{\tau_{0\sim\pi}} \equiv \frac{N_{0\sim\pi}(\tau)}{\tau\, S_{0\sim\pi}}$$

$$= I_{total}^{\circ}(\theta,\phi) - \frac{\Delta I_{total}}{\pi + \alpha_{12} - \alpha_{11}} \left[2\sin\delta_{total} + (\alpha_{11} + \alpha_{12})\cos\delta_{total}\right]$$

$$= I_{total}^{\circ}(\theta,\phi) - \frac{\Delta I_{total}}{\pi} \left[2\sin\delta_{total}\left(1 - \frac{\alpha_{22} + \alpha_{21}}{\pi}\right) + (\alpha_{21} + \alpha_{22})\cos\delta_{total}\right]$$

(70)

$$\frac{N_{\pi-2\pi}(\tau)}{\tau_{\pi-2\pi}} = \frac{N_{\pi-2\pi}(\tau)}{\tau\, S_{\pi-2\pi}}$$

$$= I_{total}^{o}(\theta,\phi) + \frac{\Delta I_{total}}{\pi}\left[2 \sin \delta_{total}\left(1 - \frac{\alpha_{22} - \alpha_{21}}{\pi}\right) + (\alpha_{21} + \alpha_{22}) \cos \delta_{total}\right] \qquad (71)$$

$$\frac{N_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau)}{\tau_{\frac{\pi}{2}-\frac{3\pi}{2}}} = \frac{N_{\frac{\pi}{2}-\frac{3\pi}{2}}}{\tau\, S_{\frac{\pi}{2}-\frac{3\pi}{2}}}$$

$$= I_{total}^{o}(\theta,\phi) - \frac{\Delta I_{total}}{\pi}\left[2 \cos \delta_{total}\left(1 - \frac{\alpha_{32} - \alpha_{31}}{\pi}\right) - (\alpha_{31} + \alpha_{32}) \sin \delta_{total}\right] \qquad (72)$$

$$\frac{N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{\tau_{\frac{3\pi}{2}-\frac{5\pi}{2}}} = \frac{N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{\tau\, S_{\frac{3\pi}{2}-\frac{5\pi}{2}}}$$

$$= I_{total}^{o}(\theta,\phi) + \frac{\Delta I_{total}}{\pi}\left[2 \cos \delta_{total}\left(1 - \frac{\alpha_{42} - \alpha_{41}}{\pi}\right) - (\alpha_{41} + \alpha_{42}) \sin \delta_{total}\right] \qquad (73)$$

From these relations we have the following equations corresponding to Eqs. (56) and (57)

$$I_{\frac{3\pi}{2}-\frac{5\pi}{2}} - I_{\frac{\pi}{2}-\frac{3\pi}{2}} = \frac{N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{\tau\, S_{\frac{3\pi}{2}-\frac{5\pi}{2}}} - \frac{N_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau)}{\tau\, S_{\frac{\pi}{2}-\frac{5\pi}{2}}}$$

$$= \frac{4}{\pi}\,\Delta I_{total}\cos\delta_{total}$$

$$= \frac{4}{\pi}\,\Delta I_{total}\cos\delta_{total}\left(1 - S_{\frac{\pi}{2}-\frac{3\pi}{2}} - S_{\frac{3\pi}{2}-\frac{5\pi}{2}}\right)$$

$$= \frac{1}{\pi}\,\Delta I_{total}\sin\delta_{total}\left(\alpha_{31} + \alpha_{32} + \alpha_{41} + \alpha_{42}\right) \qquad (74)$$

and

$$I_{\pi-2\pi} - I_{0-\pi} = \frac{N_{\pi-2\pi}(\tau)}{\tau\, S_{\pi-2\pi}} - \frac{N_{0-\pi}(\tau)}{\tau\, S_{0-\pi}}$$

$$= \frac{4}{\pi}\,\Delta I_{total}\sin\delta_{total}$$

$$= \frac{4}{\pi}\,\Delta I_{total}\sin\delta_{total}\left(1 - S_{0-\pi} - S_{\pi-2\pi}\right)$$

$$= \frac{1}{\pi}\,\Delta I_{total}\cos\delta_{total}\left(\alpha_{11} + \alpha_{12} + \alpha_{21} + \alpha_{22}\right) \qquad (75)$$

In the right side of the expression of the above equations, the first terms correspond to those in Eqs. (56) and (57). The second terms arise from the uncertainties in the opening angles of the sector windows, and vanish when the opening angles of all windows are just π. The last terms in both expressions are mostly due to the uncertainty in the phase relation between the sector and sample vibration. Since $\sin \delta_{total}$ is usually a quantity of the order of 0.1 or less, these two additional terms show a relatively large influence on evaluating $\Delta I_{total} \sin \delta_{total}$ from Eq. (75).

These uncertainties will be eliminated in the following way. When the apparatus is driven in the reverse direction, the phase range of each window changes from that for the rotation to forward direction. For example, the window that previously opened over the phase range between 0 and π now opens over the period between π and 2π. The opening ranges of each window are shown in the next table.

	Initial Point	End Point
window 0_π	$0 - \alpha_{22}$	$\pi - \alpha_{21}$
window π_2	$\pi - \alpha_{12}$	$2\pi - \alpha_{11}$
window $\frac{\pi}{2}\_\frac{3\pi}{2}$	$\frac{\pi}{2} - \alpha_{32}$	$\frac{3\pi}{2} - \alpha_{31}$
window $\frac{3\pi}{2}\_\frac{5\pi}{2}$	$\frac{3\pi}{2} - \alpha_{42}$	$\frac{5\pi}{2} - \alpha_{41}$

By comparing Table II to Table I and referring Eqs. (74) and (75), we have expressions for the case of reverse rotation.

$$\frac{N_{\frac{3\pi}{2}\_\frac{5\pi}{2}}(\tau)}{\tau \; S_{\pi-2\pi}} - \frac{N_{\frac{\pi}{2}\_\frac{3\pi}{2}}(\tau)}{\tau \; S_{0-\pi}}$$

$$= \frac{4}{\pi} \Delta I_{total} \sin \delta_{total}$$

$$+ \frac{4}{\pi} \Delta I_{total} \sin \delta_{total} \left(1 - S_{o\ \pi} - S_{\pi\ 2\pi}\right)$$

$$- \frac{1}{\pi} \Delta I_{total} \cos \delta_{total} \left(\alpha_{11} + \alpha_{12} + \alpha_{21} + \alpha_{22}\right) \qquad (76)$$

$$\frac{N_{\pi-2\pi}(\tau)}{\tau\, S_{\pi-2\pi}} - \frac{N_{0-\pi}(\tau)}{\tau\, S_{0-\pi}}$$

$$= \frac{4}{\pi}\,\Delta I_{total}\sin\delta_{total} + \frac{4}{\pi}\,\Delta I_{total}\sin\delta_{total}\left(1 - S_{0-\pi} - S_{\pi-2\pi}\right) - \frac{1}{\pi}\,\Delta I_{total}\cos\delta_{total}\left(\alpha_{11} + \alpha_{12} + \alpha_{21} + \alpha_{22}\right) \qquad (77)$$

From Eqs. (74), (75), (76) and (77) we have

$$\Delta I_{total}\cos\delta_{total} = \frac{\pi}{8}\,\frac{1}{2 - S_{\frac{\pi}{2}-\frac{3\pi}{2}} - S_{\frac{3\pi}{2}-\frac{5\pi}{2}}}\left\{\left|\frac{N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{\tau\, S_{\frac{3\pi}{2}-\frac{5\pi}{2}}} - \frac{N_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau)}{\tau\, S_{\frac{\pi}{2}-\frac{3\pi}{2}}}\right|_{forward} + \left|\frac{N_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{\tau\, S_{\frac{3\pi}{2}-\frac{5\pi}{2}}} - \frac{N_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau)}{\tau\, S_{\frac{\pi}{2}-\frac{3\pi}{2}}}\right|_{reverse}\right\} \qquad (78)$$

and

$$\Delta I_{total}\sin\delta_{total} = \frac{\pi}{8}\,\frac{1}{2 - S_{0-\pi} - S_{\pi-2\pi}}\left\{\left|\frac{N_{\pi-2}(\tau)}{\tau\, S_{\pi-2\pi}} - \frac{N_{0-\pi}(\tau)}{\tau\, S_{0-\pi}}\right|_{forward} + \left|\frac{N_{\pi-2\pi}(\tau)}{\tau\, S_{\pi-2\pi}} - \frac{N_{0-\pi}(\tau)}{\tau\, S_{0-\pi}}\right|_{reverse}\right\} \qquad (79)$$

As is shown by the above expressions, the sector constants play a significant role in experiments for obtaining the values of $\Delta I_{total} \cos \delta_{total}$ and $\Delta I_{total} \sin \delta_{total}$ accurately.

Determination of the Sector Constants

To determine the sector constants experimentally, a pulse signal of constant frequency is used as an input to the counters. In this case, the counts accumulated by the counters are exactly proportional to the duration over which each counter is activated. According to the Eqs. (58) through (61) the accumulated numbers of pulses are

$$C_{0-\pi}(\tau) = (\pi + \alpha_{12} - \alpha_{11})\, C_0 = \tau\, S_{0-\pi}\, C_0 \qquad (80)$$

$$C_{\pi-2\pi}(\tau) = (\pi + \alpha_{22} - \alpha_{21})\, C_0 = \tau\, S_{\pi-2\pi}\, C_0 \qquad (81)$$

$$C_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau) = (\pi + \alpha_{32} - \alpha_{31})\, C_0 = \tau\, S_{\frac{\pi}{2}-\frac{2\pi}{2}}\, C_0 \qquad (82)$$

$$C_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau) = (\pi + \alpha_{42} - \alpha_{41})\, C_0 = \tau\, S_{\frac{3\pi}{2}-\frac{5\pi}{2}}\, C_0 \qquad (83)$$

for forward rotation. Here , n and w are the same quantities as those defined previously. C_0 is the cycle of the input pulse signal. When the values of C_0 is known, the sector constants are given by

$$S_{0-\pi} = \frac{C_{0-\pi}(\tau)}{C_0\, \tau} \qquad (84)$$

$$S_{\pi-2\pi} = \frac{C_{\pi-2\pi}(\tau)}{C_o\ \tau} \tag{85}$$

$$S_{\frac{\pi}{2}-\frac{3\pi}{2}} = \frac{C_{\frac{\pi}{2}-\frac{3\pi}{2}}(\tau)}{C_o\ \tau} \tag{86}$$

$$S_{\frac{3\pi}{2}-\frac{5\pi}{2}} = \frac{C_{\frac{3\pi}{2}-\frac{5\pi}{2}}(\tau)}{C_o\ \tau} \tag{87}$$

When the value of C_o is unknown, the following equations can be used with good precision so far as α_{ij} are small.

$$S_{o-\pi} = \frac{C_{o-\pi}}{2\left(C_{o-\pi} + C_{\pi-2\pi} + C_{\frac{\pi}{2}-\frac{3\pi}{2}} + C_{\frac{3\pi}{2}-\frac{5\pi}{2}}\right)} \tag{88}$$

$$S_{\pi-2\pi} = \frac{C_{\pi-2\pi}}{2\left(C_{o-\pi} + C_{\pi-2} + C_{\frac{\pi}{2}-\frac{3\pi}{2}} + C_{\frac{3\pi}{2}-\frac{5\pi}{2}}\right)} \tag{89}$$

$$S_{\frac{\pi}{2}-\frac{3\pi}{2}} = \frac{C_{\frac{\pi}{2}-\frac{3\pi}{2}}}{2\left(C_{o-\pi} + C_{\pi-2\pi} + C_{\frac{\pi}{2}-\frac{3\pi}{2}} + C_{\frac{3\pi}{2}-\frac{5\pi}{2}}\right)} \tag{90}$$

$$S_{\frac{3\pi}{2}-\frac{5\pi}{2}} = \frac{C_{\frac{3\pi}{2}-\frac{5\pi}{2}}}{2\left(C_{o-\pi} + C_{\pi-2\pi} + C_{\frac{\pi}{2}-\frac{3\pi}{2}} + C_{\frac{3\pi}{2}-\frac{5\pi}{2}}\right)} \tag{91}$$

The sector constants for reverse rotation will easily be given by the same equations.

Resolution of Overlapping

In order to evaluate the quantities such as $I_{cr}^{o}(\theta,\phi)$, $\Delta I_{cr} \cos \delta_{cr}$ and $\Delta I_{cr} \sin \delta_{cr}$ for a particular diffraction peak, it is necessary to correct for overlap. One method of resolution is to assume that each peak may be represented by a Lorenzian function to give[2)3)]

$$I(2\theta,\phi) = \sum_j \frac{I_{oj}(\phi)}{1 + \left(\frac{2\theta - 2\theta_{oj}(\phi)}{\beta_j(\phi)}\right)^2} \qquad (92)$$

where $I(2\theta,\phi)$ is diffraction intensity corrected for background, polarization, absorption, and incoherent scattering. $I_{oj}(\phi)$, $2\theta_{oj}(\phi)$ and $\beta_j(\phi)$ are, respectively, the height, angular position of the maximum and half-width of the j^{th} component of the composit diffraction pattern at azimuthal angle of ϕ.

For the diffraction intensity in the dynamic state, we make the additional assumption that the half-width and angular position of the maximum remain unaltered. Then we have

$$I_{diff}(2\theta,\phi) \equiv I_{total}^{o}(2\theta,\phi) - I_{back}(2\theta,\phi)\,\frac{\exp(+\mu d_o \sec\theta)}{h(\theta)\, d_o \sec\theta} - I_{incoh}(2\theta,\phi)$$

$$= \sum_j \frac{I_{oj}(\phi)}{1 + \left(\frac{2\theta - 2\theta_{oj}(\phi)}{\beta_j(\phi)}\right)^2} \qquad (93)$$

and

$$\Delta I_{diff}'(2\theta,\phi) \equiv \left\{\Delta I_{total} \cos \delta_{total} + \frac{\Delta\lambda}{2} (1 - \mu d_o \sec\theta) \left[I_{total}^{o}(2\theta,\phi) - I_{backgr}(2\theta,\phi)\right]\right\}$$

$$\times \frac{\exp(\mu d_o \sec\theta)}{h(\theta)\, d_o \sec\theta}$$

$$= \sum_j \frac{\Delta I_{oj}(\phi)}{1 + \left(\frac{2\theta - 2\theta_{oj}(\phi)}{\beta_j(\phi)}\right)^2} = \sum_j \frac{I_j(2\theta,\phi)}{I_{oj}(\phi)} \Delta I_{oj}'(\phi) \qquad (94)$$

$$\Delta I_{diff}''(2\theta,\phi) \equiv \left\{\Delta I_{total} \sin \delta_{total}\right\} \frac{\exp(\mu d_o \sec\theta)}{h(\theta)\, d_o \sec\theta}$$

$$= \sum_j \frac{\Delta I_{oj}''(\phi)}{1 + \left(\frac{2\theta - 2\theta_{oj}(\phi)}{\beta_j(\phi)}\right)^2} = \sum_j \frac{I_j(2\theta,\phi)}{I_{oj}(\phi)} \Delta I_{oj}''(\phi) \qquad (95)$$

where $\Delta I_{oj}'(\phi)$ and $\Delta I_{oj}(\phi)$ are the in-phase and out-of-phase component of the dynamic diffraction intensity of j-th component at the angular position of its peak. $I_j(2\theta,\phi)$ is the intensity of the j-th component which is expected from the assumption of Lorenzian form for diffraction intensity. That is

$$I_j(2\theta,\phi) = \frac{I_{oj}(\phi)}{1 + \left(\dfrac{2\theta - 2\theta_{ij}(\phi)}{\beta_j(\phi)}\right)^2} \tag{96}$$

$h(\theta)$ is the polarization factor defined by

$$h(\theta) = \frac{1 + \cos^2(2\theta)}{2} \quad : \text{filter monochromatizing} \tag{97}$$

$$h(\theta) = \frac{1 + \cos^2(2\theta_m)\cos(2\theta)}{1 + \cos^2(2\theta_m)} \quad : \text{for crystal monochromatizing}$$

θ_m: Bragg angle for the monochromatizing capital (98)

Actually, resolution of the overlapping is made as follows: First the quantity $I_{diff}(2\theta,\phi)$ is obtained at a particular azimuthal angle as a function of the Bragg angle for the sample with static strain λ_o. Then the intensity curve is separated into each component peak by the usual process[3,4], and we get the maximum values $I_{oj}(\phi)$, the angular positions of the j-th maximum $(2\theta_{oj}(\phi))$, and the half-widths $\beta_j(\phi)$ at azimuthal angle ϕ. The same procedures are repeated at various azimuthal angles.

We then fix the azimuthal angle at particular points and measure the in-phase and out-of-phase components of the dynamic diffraction at the angular positions of the component peaks. We have the simultaneous equations

$$\Delta I_{diff}'(2\theta_i,\phi) = \sum_j C_{ij}(\phi)\,\Delta I_{oj}'(\phi) \tag{99}$$

and

$$\Delta I_{diff}''(2\theta_i,\phi) = \sum_j C_{ij}(\phi)\ \Delta I_{oj}''(\phi) \tag{100}$$

where

$$C_{ij} = \frac{1}{1 + \left(\dfrac{2\theta_{ij}(\phi) - 2\theta_{oj}(\phi)}{\beta_j}\right)^2} \tag{101}$$

which give $\Delta I_{oj}'(\phi)$ and $\Delta I_{oj}''(\phi)$ for all component peaks. The same procedures are repeated at various azimuthal angles, and finally we get $\Delta I_{oj}'(\phi)$ and $\Delta I_{oj}''(\phi)$ as functions of ϕ.

When $I_{oj}(\phi)$, $\Delta I_{oj}'(\phi)$ and $\Delta I_{oj}''(\phi)$ have been determined for each component peak, we substitute them for $P_{cr}(\theta,\phi)$, $\Delta P_{cr}\cos\delta_{cr}$ and $\Delta P_{cr}\sin\delta_{cr}$, respectively, in equations (34) - (39). Thus we have the following integrations.

$$I^j_{11} = \int_0^{\pi/2} \sin^2\phi\ I_{oj}(\phi)\cos\phi\ d\phi \tag{102}$$

$$I^j_{12} = \int_0^{\pi/2} \sin^2\phi\ \Delta I_{oj}'(\phi)\cos\phi\ d\phi \tag{103}$$

$$I^j_{13} = \int_0^{\pi/2} \sin^2\phi\ \Delta I_{oj}''(\phi)\cos\phi\ d\phi \tag{104}$$

$$I^j_{21} = \int_0^{\pi/2} I_{oj}(\phi)\cos\phi\ d\phi \tag{105}$$

$$I^j_{22} = \int_0^{\pi/2} \Delta I_{oj}'(\phi) \cos\phi \, d\phi \qquad (106)$$

$$I^j_{23} = \int_0^{\pi/2} \Delta I_{oj}''(\phi) \cos\phi \, d\phi \qquad (107)$$

By integrations graphically and using Eqs. (41) through (44) we can get the orientation function for crystal planes corresponding to j-th diffraction peak.

Narrow Slit Sector Technique

When one choses phase ranges between $-\varepsilon$ and ε, $\frac{\pi}{2} - \varepsilon$ and $\frac{\pi}{2} + \varepsilon$, $\pi - \varepsilon$ and $\pi + \varepsilon$, $\frac{3\pi}{2} - \varepsilon$ and $\frac{3\pi}{2} + \varepsilon$ as the phase duration over which counts are accumulated, then total counts accumulated during n cycles of the sample vibration are

$$N_o = n \int_{-\varepsilon}^{\varepsilon} \left[I_{total}{}^{\circ}(\theta,\phi) + \Delta I_{total} \cos(x + \delta) \right] \frac{dx}{\omega}$$

$$= \frac{n}{\omega} \cdot 2\varepsilon \, I_{total}{}^{\circ}(\theta,\phi) + \frac{n}{\omega} \Delta I_{total} \, 2 \sin\varepsilon \cos\delta \qquad (108)$$

$$N_{\frac{\pi}{2}} = n \int_{\frac{\pi}{2} - \varepsilon}^{\frac{\pi}{2} + \varepsilon} \left[I_{total}{}^{\circ}(\theta,\phi) + \Delta I_{total} \cos(x + \delta) \right] \frac{dx}{\omega}$$

$$= \frac{n}{\omega} \cdot 2\varepsilon \, I_{total}{}^{\circ}(\theta,\phi) - \frac{n}{\omega} \Delta I_{total} \, 2 \sin\varepsilon \sin\delta \qquad (109)$$

$$N_\pi = n \int_{\pi - \varepsilon}^{\pi + \varepsilon} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta) \right] \frac{dx}{\omega}$$

$$= \frac{n}{\omega} 2\varepsilon \; I_{total}{}^{o}(\theta,\phi) - \frac{n}{\omega} \Delta I_{total} \; 2 \sin \varepsilon \cos\delta \tag{110}$$

$$N_{\frac{3\pi}{2}} = n \int_{\frac{3\pi}{2} \quad \varepsilon}^{\frac{3\pi}{2} + \varepsilon} \left[I_{total}{}^{o}(\theta,\phi) + \Delta I_{total} \cos (x + \delta) \right] \frac{dx}{\omega}$$

$$= \frac{n}{\omega} \cdot 2 \quad I_{total}{}^{o}(\theta,\phi) + \frac{n}{\omega} \Delta I_{total} \; 2 \sin \varepsilon \sin\delta \tag{111}$$

In this case the duration over which the scalers are actually activated is

$$n \; T \frac{2\varepsilon}{2\pi} = \tau \; S \tag{112}$$

where τ is the total time which is necessary for vibrations of n cycles. S is the sector constant defined by the ratio of opening angle of the window to 2π. The average intensity of each duration is then given by

$$I_o(\theta,\phi) \equiv \frac{N_o(\theta,\phi)}{\tau \; S} = I_{total}{}^{o}(\theta,\phi) + \frac{\sin \varepsilon}{\varepsilon} \Delta I_{total} \cos\delta \tag{113}$$

$$I_{\frac{\pi}{2}}(\theta,\phi) \equiv \frac{N_{\frac{\pi}{2}}(\theta,\phi)}{\tau \; S} = I_{total}{}^{o}(\theta,\phi) - \frac{\sin \varepsilon}{\varepsilon} \Delta I_{total} \sin\delta \tag{114}$$

$$I_{\pi}(\theta,\phi) \equiv \frac{N_{\pi}(\theta,\phi)}{\tau\ S} = I_{total}{}^{\circ}(\theta,\phi) - \frac{\sin\varepsilon}{\varepsilon}\,\Delta I_{total}\cos\delta \qquad (115)$$

$$I_{\frac{3\pi}{2}}(\theta,\phi) \equiv \frac{N_{\frac{3\pi}{2}}(\theta,\phi)}{\tau\ S} = I_{total}{}^{\circ}(\theta,\phi) + \frac{\sin\varepsilon}{\varepsilon}\,\Delta I_{total}\sin\delta \qquad (116)$$

The semicircle sector technique corresponds to a special case where ε is $\pi/2$. If we put ε equal to $\pi/2$, the above expressions reduce to Eqs. (50) - (53).

Another extreme case is the narrow slit sector technique, which was devised by Kawai et. al.[1]. In the extreme in which sector windows are narrowed, Eqs. (113) - (116) are rewritten as follows

$$I_{o}(\theta,\phi) = I_{total}{}^{\circ}(\theta,\phi) + \Delta I_{total}\cos\delta \qquad (117)$$

$$I_{\frac{\pi}{2}}(\theta,\phi) = I_{total}{}^{\circ}(\theta,\phi) - \Delta I_{total}\sin\delta \qquad (118)$$

$$I_{\frac{\pi}{2}}(\theta,\phi) = I_{total}{}^{\circ}(\theta,\phi) - \Delta I_{total}\cos\delta \qquad (119)$$

$$I_{\frac{3\pi}{2}}(\theta,\phi) = I_{total}{}^{\circ}(\theta,\phi) + \Delta I_{total}\sin\delta \qquad (120)$$

In general, if a narrow slit window opening between $\gamma - \varepsilon$ and $\gamma + \varepsilon$ is used, the average intensity is given by

$$I_\gamma(\theta,\phi) = I_{total}^\circ(\theta,\phi) + \Delta I_{total} \cos(\gamma + \delta) \qquad (121)$$

As it has been shown above, there is not any restriction about the opening angle of the sector window so far as the diffraction intensity changes linearly with strain. In this case, the quantities that we have to know are $I_{total}^\circ(\theta,\phi)$, ΔI_{total} and δ. Thus we have only to use a sector which has at least three windows. The opening angle of the windows is determined so as to reduce the experimental error.

As shown by Eq. (121), the narrow slit technique is superior to other wide window sector techniques in giving a diffraction intensity at a particular point of strain directly. However, as it has been seen, the diffraction intensity is always given by a ratio of the accumulated counts to the duration of accumulation. The statistical error of the accumulated counts is inversely proportional to the square root of the total number of counts, which is proportional to the opening angle of the window. Thus the statistical error of counting is reduced by widening the window of the sector. Widening of the opening angle also reduces the experimental error in determining the sector constant. Therefore, the wide window technique is superior to narrow slit sector technique in reducing the experimental error.

Measurement of the Crystal Spacing in Dynamic State

When the diffraction peak is high and sharp enough, the diffraction intensity is usually symmetrical about the top of the peak. It is then easy to find a Lorenzian function by which the intensity near the top is represented. Thus the intensity is shown as a function of Bragg angle as follow

$$I(2\theta,\phi) = \frac{I_o(\phi)}{1+\left(\frac{2\theta - 2\theta_o(\phi)}{\beta(\phi)}\right)^2} \qquad (122)$$

When the sample is deformed, the diffraction intensity at a given point changes with strain. The intensity-strain coefficient at a certain point in the vicinity of the top may be given by

$$\frac{\partial I(2\theta,\phi)}{\partial\alpha} = \frac{1}{1+\left(\frac{2\theta - 2\theta_o(\phi)}{\beta(\phi)}\right)^2}\frac{\partial I_o(\phi)}{\partial\alpha}$$

$$+ \frac{\partial I(2\theta,\phi)}{\partial(2\theta)}\left[-\frac{\partial(2\theta_o)}{\partial\alpha} - \frac{2\theta - 2\theta_o}{\beta(\phi)}\frac{\partial\beta(\phi)}{\partial\alpha}\right]$$

$$= \frac{I(2\theta,\phi)}{I_o(\phi)}\frac{I_o(\phi)}{\partial\alpha}$$

$$\frac{\partial I(2\theta,\phi)}{\partial(2\theta)}\left[\frac{\partial(2\theta_o)}{\partial\alpha} + \frac{2\theta-2\theta_o}{\beta(\phi)}\frac{\partial\beta(\phi)}{\partial\alpha}\right] \qquad (123)$$

where α is strain.

Since the relations

$$I(2\theta_o + \varepsilon,\phi) = I(2\theta_o - \varepsilon,\phi) \tag{124}$$

and

$$\frac{\partial I(2\theta_o + \varepsilon,\phi)}{\partial(2\theta)} = -\frac{\partial I(2\theta_o - \varepsilon,\phi)}{\partial(2\theta)} \tag{125}$$

hold in the vicinity of the top, we have

$$\frac{\partial I(2\theta_o + \varepsilon,\phi)}{\partial\alpha} - \frac{\partial I(2\theta_o - \varepsilon,\phi)}{\partial\alpha} = -2\,\frac{\partial I(2\theta_o + \varepsilon,\phi)}{\partial(2\theta)}\,\frac{\partial(2\theta_o)}{\partial\alpha} \tag{126}$$

This relation will be generally independent of the assumption of the Lorenzian representation of the diffraction intensity so far as the intensity changes symmetrically around the top of the peak.

The Bragg angle is related to the crystal spacing by

$$\sin\theta = \frac{n\lambda}{2d} \tag{127}$$

where λ is the x-ray wavelength, d is the distance between successive crystal planes, n whole number. From this relation we have

$$\frac{\Delta d}{d} = -\frac{\cos\theta_o}{\sin_{\ o}}\,\Delta\theta_o$$

By combining this equation with Eq. (115) we have

$$\frac{\Delta d}{d} = \frac{1}{2}\,\frac{\cos\theta_o}{\sin\theta_o}\,\frac{1}{\dfrac{\partial I(2\theta_o - \varepsilon,\phi)}{\partial(2\theta)}}\left[\Delta I(2\theta_o - \varepsilon,\phi) - \Delta I(2\theta_o + \varepsilon,\phi)\right] \tag{128}$$

where Δd and $\Delta I(\theta,\phi)$ are changes in crystal spacing and intensity at the point of (θ,ϕ) induced by change in strain $(\Delta\alpha)$, respectively. $\partial I(2\theta_o - \varepsilon,\phi)/ \partial(2\theta)$ is the slope of the intensity curve at point of $(2\theta - \varepsilon,\phi)$.

When a dynamic strain $\alpha_o + \Delta\alpha \cos \omega t$ is applied on the sample, $\partial I(2\theta_o - \varepsilon,\phi)/ \partial(2\theta)$ is given by the slope of the intensity curve obtained by radial scanning for the sample with static strain α_o. Dynamic diffraction intensities $\Delta I^*(2\theta_o - \varepsilon,\phi)$ and $\Delta I^*(2\theta_o + \varepsilon,\phi)$ are obtained by the dynamic x-ray technique. We can then get the spacing change in dynamic state from Eq. (127).

This technique will be applicable especially on a highly stretched sample, because, in this case, diffraction peaks separate each other and sharp enough.

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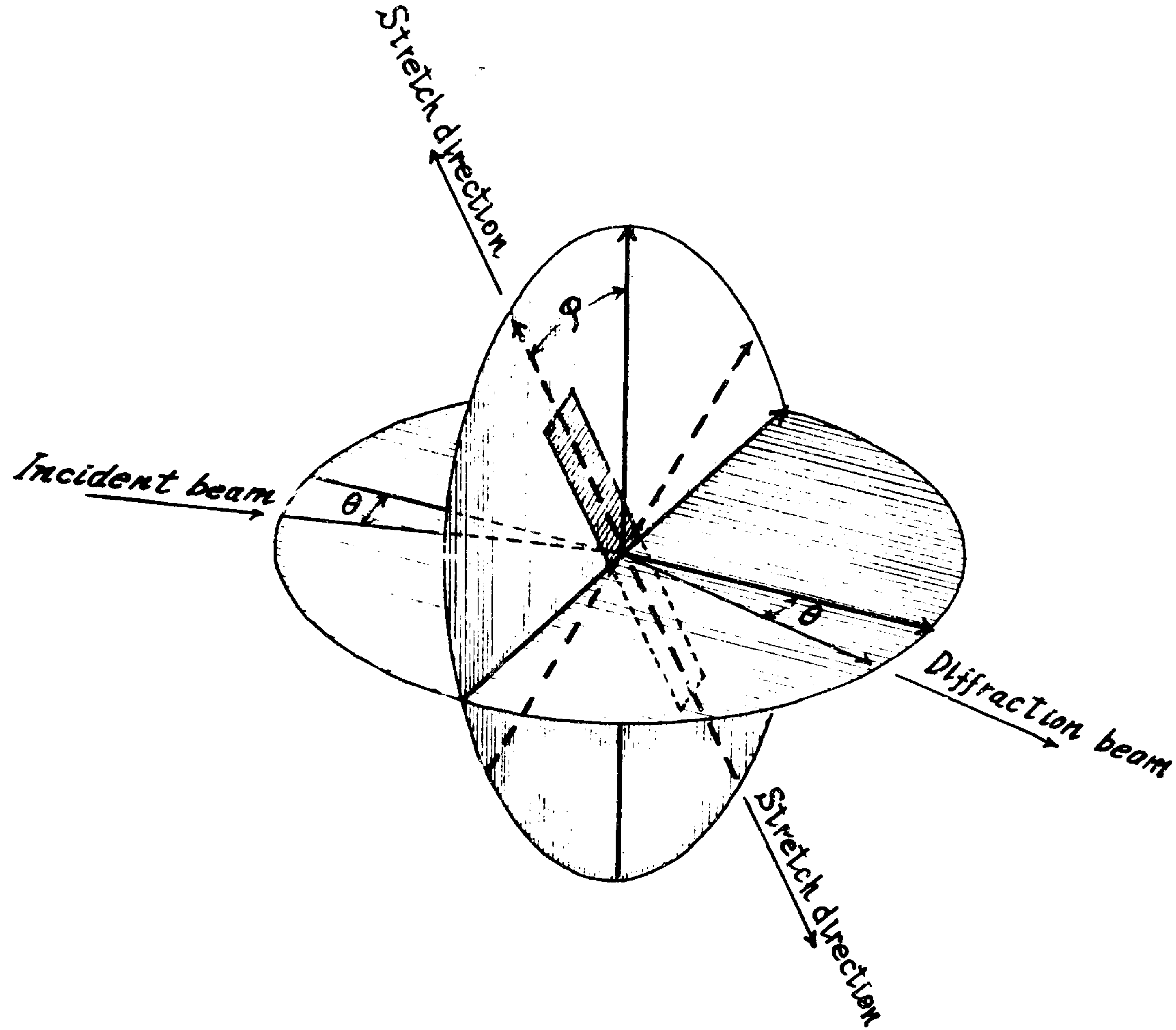
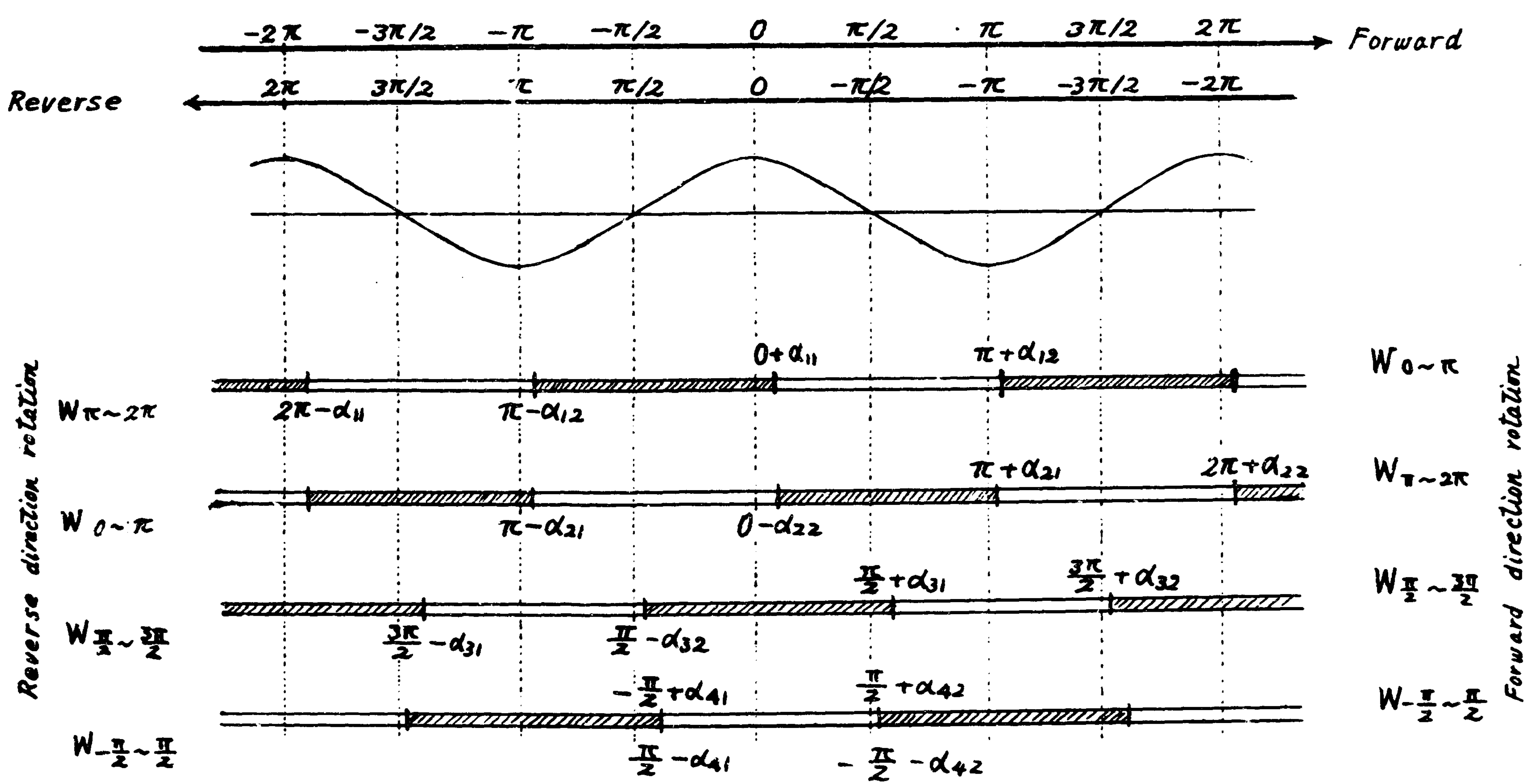

Stretch direction
Incident beam
θ
φ
θ
Diffraction beam
Stretch direction

FIGURE 1



-2π -3π/2 -π -π/2 0 π/2 π 3π/2 2π
Forward
2π 3π/2 π π/2 0 -π/2 -π -3π/2 -2π
Reverse
0+α11
π+α12
W0~π
Wπ~2π
2π-α11
π-α12
π+α21
2π+α22
Wπ~2π
W0~π
π-α21
0-α22
π/2+α31
3π/2+α32
Wπ/2~3π/2
Wπ/2~3π/2
3π/2-α31
π/2-α32
-π/2+α41
π/2+α42
W-π/2~π/2
W-π/2~π/2
π/2-α41
-π/2-α42
Reverse direction rotation
Forward direction rotation

FIGURE 2

Unclassified

Security Classification

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13 ABSTRACT

A mathematical analysis is made of data obtained by the dynamic x-ray diffraction technique. It is shown how by measuring the integrated diffraction intensity over a given interval of the strain cycle and accumulating results over many cycles of strain, the portion of the change in diffracted intensity which is in phase ($\Delta I'$) and out of phase ($\Delta I''$) with the applied sinusoidal strain may be obtained. The means for separating contributions of overlapping crystalline and amorphous peaks is discussed as is the determination of the dynamic orientation function by graphical integration of the change in diffracted intensity with azimuthal angle.

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