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Elimination of the Dispersion Effect in the Analysis of Diffraction Line Profiles

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The dispersion effect can be eliminated in the analysis of X-ray diffraction lines by transforming the true angular scattering distribution $E(\theta)$, which has been corrected in advance for instrumental aberrations, to distribution $P(\sigma_\theta')$ in the parameter

$$\sigma_\theta' = \ln(\sin\theta/\sin\hat{\theta})$$

and expressing the radial interference distribution and the spectral wavelength distributions as functions of

$$\sigma_\varrho' = \ln(\varrho/\hat{\varrho}) ,$$

and

$$\sigma_\lambda' = \ln(\lambda/\hat{\lambda})$$

respectively, where ϱ is the reciprocal lattice spacing, λ is the wavelength and the reference values are related by

$$\hat{\lambda}\,\hat{\varrho} = 2\sin\hat{\theta} .$$

The scattering distribution $E(\theta)$ determined from a single crystal using the ω scan with a narrow detector slit at successive θ positions has the mapping relation

$$P(\sigma_\theta')\alpha\{(\sin\theta)/(1+\cos^2 2\theta)\}E(\theta)$$

while the scattering distribution $E(\theta)$ for the conventional powder diffraction line measurement has the mapping relation

$$P(\sigma_\theta')\alpha\{(\sin^2\theta)/(1+\cos^2 2\theta)\}E(\theta) .$$

The radial interference distribution $i(\sigma_\varrho)$ can be expressed in a general form as the convolute of distributions due to crystal size and imperfections with an elastic strain distribution. The mapped scattering distribution $P(\sigma_\theta')$ is shown to be the exact convolute of this radial interference distribution with a modification of the characteristic wavelength distribution $L'(\sigma_\lambda')$:

$$P(\sigma_\theta') = \int\{(\lambda^3/\hat{\lambda}^3)L'(\sigma_\lambda')\}i(\sigma_\theta' - \sigma_\lambda')d\sigma_\lambda .$$

Unfolding the distribution

$$M(\sigma_\lambda') = (\lambda^3/\hat{\lambda}^3)L'(\sigma_\lambda')$$

gives the true radial interference distribution regardless of the width of either the spectral or the radial interference distribution over the full range of scattering angles. The procedure has a particular application in the measurement of lattice parameters.

Introduction

In the present paper a procedure is described whereby the spectral distribution of the characteristic X-ray line can be unfolded from the scattering distribution for a single crystal or powder specimen. If the measured scattering distribution has been corrected for the effects of instrumental aberrations the distribution obtained after unfolding is the true radial interference distribution defined by crystallite size, imperfections and elastic strain.

Since the present treatment is free of approximations, the results are valid regardless of the width of either the spectral or the radial interference distribution. The spacing of the reciprocal lattice node is determined directly in terms of the reference wavelength and is independent of dispersion effects.

If the X-ray wavelength is sharply defined, the interference function for a reflexion can be determined directly by correcting the scattering distribution for the dependence of intensity on scattering angle and mapping the distribution in reciprocal space.

When, however, the incident beam has a distribution of wavelengths dispersion occurs, since the angular scattering distribution due to a given interference function is wavelength dependent.

Lang (1956) has shown that the dispersion effect for a powder specimen could be treated by transforming

the scattering distribution to a scale of sin θ, which is equivalent to a radial mapping in reciprocal space.

Lang showed that in terms of this parameter the scattering distribution could, to the first approximation, be regarded as the convolute of the spectral distribution and the powder interference function, which could then be extracted by unfolding.

Pike (1959) has treated the dispersion effect exactly for the limiting cases where either the wavelength is sharply defined relative to the single-crystal radial interference distribution, or the interference distribution is sharply defined relative to the spectral distribution. Pike's treatment has the disadvantages that the mapping functions are different for the two cases, and the intermediate case remains unsolved.

Using the new variables to be introduced in the present paper in the transformation described here, the scattering distribution can be expressed as the convolute of the single crystal radial interference distribution and a distribution derived from the characteristic wavelength distribution.

The radial interference distribution

The intensity scattered at an angle 2θ from a single crystal irradiated by a monochromatic X-ray beam, due to a family of planes of indices *hkl*, is

$$J(\theta)=\tfrac{1}{2}(e^2/mc^2)^2(1+\cos^2 2\theta)I(\varrho) \qquad (1)$$

per unit solid angle, per unit incident beam intensity, where $I(\varrho)$ is the interference distribution in reciprocal space at a vector distance ϱ from the reciprocal lattice origin, and 2θ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$, the vectors of the incident and diffracted rays.

For the wavelength λ, ϱ is given by

$$\varrho=(\mathbf{k}-\mathbf{k}_0)/\lambda$$

where $\mathbf{k}_0$ and $\mathbf{k}$ are unit vectors, and has the magnitude

$$\varrho=2\sin\theta/\lambda\,.$$

The radial interference distribution about the reciprocal lattice node ϱ_{hkl} is determined by integration of the interference function $I(\varrho)$ over a plane S normal to ϱ_{hkl} and at a distance s from the lattice node.

$$i(s_\varrho)=\iint_S I(\varrho)dS \qquad (2)$$

where for the plane S

$$\varrho=\varrho_{hkl}+\mathbf{s}$$

and $\mathbf{s}=\mathbf{s}_\varrho+\mathbf{u}$, where $\mathbf{s}_\varrho$ is constant, parallel to ϱ_{hkl} and $\mathbf{u}$ lies in the surface of integration.

The effects of crystal size and of a homogeneous distribution of imperfections in a single crystal have been expressed by Wilson (1949) in terms of the radial interference distribution, so that these effects can be studied with either single-crystal or powder specimens. Wilson's treatment can be readily extended to the case of a mosaic crystal or a powder having a distribution of reciprocal lattice parameters as in the case of a specimen having a distribution of elastic strain.

Following Guinier's (1963) treatment of Wilson's theory, the radial interference function $i(s_\varrho)$ can be expressed as the convolution of the function $A(s_\varrho)$ due to crystal shape and $Y(s_\varrho)$ due to a homogeneous distribution of imperfections.

$$i(s_\varrho)=(1/V_c)\int A(s_\varrho-s_i)Y(s_i)ds_i \qquad (3)$$

where V_c is the unit-cell volume.

The crystal shape function $A(s_\varrho)$ has the Fourier transform in object space,

$$V(\mathbf{t})=V_c\int A(s_\varrho)\exp(2\pi i s_\varrho t)dt$$

where $\mathbf{t}$ is a vector perpendicular to the *hkl* planes, and consequently the scalar product

$$\mathbf{s}.\mathbf{t}=s_\varrho t\,.$$

$V(t)$ is the 'image volume' defined by Wilson.

The transform of the imperfection function in object space is

$$y(t)=\int Y(s_\varrho)\exp(2\pi i s_\varrho t)ds_\varrho\,.$$

$y(t)$ is the average of the product of the structure factors for cells m and n separated by the vector $\mathbf{t}$.

$$y(t)=\overline{F_nF_{n+m}^*}\,.$$

In a mosaic crystal having a distribution of reciprocal lattice nodes, where the domains have a small angular orientation about the reference direction, $G(\mathbf{s})$ is the probabilit ydistribution of cells having the reciprocal spacing ϱ_{hkl} where

$$\mathbf{s}=\varrho_{hkl}-\hat{\varrho}_{hkl}$$

is the displacement from the reference node $\hat{\varrho}_{hkl}$, which corresponds to a domain of mean spacing and mean orientation.

The component of $\mathbf{s}$ parallel to $\hat{\varrho}_{hkl}$ is

$$s_e=\varrho_{hkl}-\hat{\varrho}_{hkl}\,,$$

provided the angle between the position vectors is small.

The radial reciprocal lattice strain function is

$$g(s_e)=\iint G(\mathbf{s})dS\,.$$

The resultant radial interference distribution is obtained by integrating the interference function for the strained lattice over a surface at a distance

$$s_c=s_\varrho-s_e=\varrho-\varrho_{hkl}$$

from the node ϱ_{hkl} and then integrating over the lattice strain distribution. The resultant can be expressed as the double convolution.

$$i(s_\varrho)=1/V_c\iint A(s_c-s_i)Y(s_i)ds_i\,.\,g(s_\varrho-s_c)ds_c\,. \qquad (4)$$

The line integral of the radial interference distribution is equal to the volume integral of the interference function about the reciprocal lattice node.

$$\int i(s_\varrho)ds_\varrho = \int I(\mathbf{s})dV_s = \overline{F_{hkl}^2}V/V_c^2 \qquad (5)$$

where $\overline{F_{hkl}}$ is the mean structure factor and V is the crystal volume.

Relation between the scattering and interference distributions

The radial interference distribution for the single crystal can be determined using the 'ω scan' with a narrow detector slit.

The total energy recorded by a fixed detector when the crystal is rotated about an axis normal to the plane of incidence, through the lattice node hkl, is

$$E(\theta) = (\varphi_s/\dot{\omega})(e^2/mc^2)^2(1+\cos^2 2\theta)\sin\theta i(s_\varrho)/\varrho^2 \qquad (6)$$

per unit incident beam intensity, as shown in the Appendix, where $\dot{\omega}$ is the angular velocity and φ_s is the angular detector slit width.

A crystalline powder having a random orientation distribution will have a resultant interference distribution in reciprocal space constant over a spherical surface of radius ϱ, of magnitude

$$I_p(s_\varrho) = n_p i(s_\varrho)/4\pi\varrho^2 \qquad (7)$$

where $i(s_\varrho)$ in the radial interference distribution for a single crystal of equal volume, and n_p is the multiplicity of the reflexion.

The power over a detector element of solid angle Ω_s is, from (1)

$$\begin{aligned} E(\theta) &= J(\theta)\Omega_s = \tfrac{1}{2}(e^2/mc^2)^2(1+\cos^2 2\theta)I_p(s_\varrho)\,.\,\Omega_s \\ &= \Omega_s(n_p/8\pi)(e^2/mc^2)^2(1+\cos^2 2\theta)i(s_\varrho)/\varrho^2\,. \end{aligned} \qquad (8)$$

This expression for the powder scattering distribution differs from the corresponding expression for the single-crystal scattering distribution by the factor $\sin\theta$.

Dispersion

The dispersion of the scattering distribution due to the spectral wavelength distribution can be treated initially by introducing the parameter:

$$\sigma_\theta = (\sin\theta - \sin\hat{\theta})/\sin\hat{\theta} \qquad (9)$$

where $\hat{\theta}$ is the scattering angle for the reference wavelength $\hat{\lambda}$ due to lattice node $\hat{\varrho}_{hkl}$, so that

$$\hat{\lambda}\hat{\varrho}_{hkl} = 2\sin\hat{\theta}\,.$$

The radial interference distribution can be expressed in terms of a similar parameter σ_ϱ as

$$i''(\sigma_\varrho) = i(s_\varrho)$$

where $\sigma_\varrho = s_\varrho/\hat{\varrho}_{hkl} = \sigma_\theta(\varrho, \hat{\lambda})$

and the characteristic wavelength distribution as $L(\sigma_\lambda)$ where

$$\sigma_\lambda = (\lambda - \hat{\lambda})/\hat{\lambda} = \sigma_\theta(\hat{\varrho}_{hkl}, \lambda)\,.$$

The resultant scattering distribution due to the spectral distribution $L(\sigma_\lambda)$ is derived from relation (6) for the single crystal and relation (8) for the powder as

$$P_L(\sigma_\theta) = \int i''(\sigma_\varrho)/\varrho^2)\,.\,L(\sigma_\lambda)d\sigma_\lambda\,; \qquad (10)$$

where for the single crystal

$$P_L(\sigma_\theta) = k_s E(\theta)/[(1+\cos^2 2\theta)\,.\,\sin\theta]$$

and

$$k_s = (\dot{\omega}/\varphi_s)/(e^2/mc^2)^2\,,$$

and for the powder

$$P_L(\sigma_\theta) = k_p E(\theta)/(1+\cos^2 2\theta)$$

where

$$k_p = 8\pi/n_p[\Omega_s(e^2/mc^2)^2]\,.$$

The transformation of $E(\theta)$ to the σ_θ scale is equivalent to Lang's (1956) tranformation to the $\sin\theta$ scale. The $P_L(\sigma_\theta)$ distribution for single-crystal and powder specimens includes the correction for the θ dependence of the scattering distribution.

Lang carried out the dispersion correction for the powder case by replacing the scattering integral by the convolute, using the approximation that the equation

$$d\lambda/\hat{\lambda} + d\varrho/\hat{\varrho} = d(\sin\theta)/\sin\hat{\theta}$$

is valid over finite increments in λ and ϱ.

On the σ scale this approximation gives

$$\sigma_\theta = \sigma_\lambda + \sigma_\varrho$$

and the scattering integral

$$P_L(\sigma_\theta) = 4\pi\int I_P(\sigma_\theta - \sigma_\lambda)L(\sigma_\lambda)d\sigma_\lambda\,. \qquad (11)$$

Unfolding $L(\sigma_\lambda)$ gives the powder interference distribution.

In order to avoid the approximation involved in the convolute Pike (1959) has evaluated the scattering integral in the limiting cases. He has treated the special case of a powder having relatively large perfect grains and a distribution of lattice spacings, but as shown in (4) this does not impose a restriction on his result.

The integral can be evaluated directly when the wavelength is sharply determined so that the interference function is slowly varying and effectively constant over the spectral range:

$$\begin{aligned} P_L(\sigma_\theta) &= [i(\sigma_\varrho)/4\sin^2\theta]\int \lambda^2 L(\sigma_\lambda)d\sigma_\lambda \\ P_L(\sigma_\theta) &\propto i(\sigma_\varrho)/\sin^2\theta\,. \end{aligned} \qquad (12)$$

Similarly when the interference function is sharply determined relative to the wavelength integration over σ_ϱ gives, with the use of relation (5),

$$\begin{aligned} P_L(\sigma_\theta) &= (1/\overline{\varrho}_{hkl})^2(\sin\theta/\sin\overline{\theta})(\overline{F_{hkl}})^2(V/V_c^2)L(\sigma_\lambda) \\ P_L(\sigma_\theta) &\propto L(\sigma_\lambda)\sin\theta\,. \end{aligned} \qquad (13)$$

The resultant distributions in the limiting cases have a dependence differing by a factor $\sin^3\theta$. The intermediate case remains unsolved.

Exact treatment of the dispersion effect

The approximation involved in forming the convolution (11) can be avoided by introducing the parameters

$$\sigma'_\theta = \ln(\sin\theta/\sin\hat{\theta})$$
$$\sigma'_\lambda = \ln(\lambda/\hat{\lambda})$$
$$\sigma'_\varrho = \ln(\varrho/\hat{\varrho})\,. \qquad (14)$$

It can be seen that for small differences $\sigma'_\theta \simeq \sigma_\theta$ and these parameters approach those of relation (9). These parameters have the property that $\sigma'_\theta = \sigma'_\varrho + \sigma'_\lambda$ which is required for the formation of the convolute.

Substituting for ϱ in the integral and changing the variables gives the convolution integral

$$P_M(\sigma'_\theta) = \int M(\sigma'_\lambda) i'(\sigma'_\theta - \sigma'_\lambda) d\sigma'_\lambda \qquad (15)$$

where

$$M(\sigma'_\lambda) = (\lambda/\hat{\lambda})^3 L'(\sigma'_\lambda)$$

and

$$i'(\sigma'_\varrho) = i''(\sigma_\varrho) = i(s_\varrho)\,.$$

From (15) and the definition of M it is at once obvious why the correction factors calculated by Pike in the extreme cases, leading to $i''(\sigma_\varrho)$ and $L(\sigma_\lambda)$ respectively, differ by a factor $\sin^3\theta$.

$P_M(\sigma'_\theta)$ is obtained from the scattering distribution $E(\theta)$ for the single crystal by using the relation

$$P_M(\sigma'_\theta) = (k_s/\hat{\lambda}^2)(\sin\theta/(1+\cos^2 2\theta))E(\theta)\,, \qquad (16)$$

and for the powder as

$$P_M(\sigma'_\theta) = (4k_p/\hat{\lambda}^2)\{\sin^2\theta/(1+\cos^2 2\theta)\}E(\theta); \qquad (17)$$

by using the mapping given by relation (14).

The wavelength function $M(\sigma'_\lambda)$ can be derived directly from the characteristic wavelength distribution, and unfolding this function from the transformed scattering distribution $P_M(\sigma'_\theta)$ gives the exact radial interference function for the crystal, which can then be expressed as a distribution $i(s_\varrho)$ in reciprocal space, about the lattice node.

Conclusion

The procedure enables the dispersion effect to be eliminated and the radial interference distribution to be determined within the accuracy of the measurements of scattering intensity and scattering angle, provided the instrumental aberrations have been corrected in advance within these limits.

It should be particularly useful in measurements in the region of scattering near 180°. Here the dispersion effect is large, but the theoretical limit of accuracy is high since the angular range of the scattering distribution is a maximum and the distortion due to the majority of instrumental aberrations approaches zero.

APPENDIX

Measurement of the single-crystal radial interference distribution

The radial interference distribution for a single crystal is measured by scanning about the axis $\boldsymbol{\omega}$ normal to the plane of incidence with the scattering angle 2θ fixed and defined by a narrow detector slit.

The energy received over a solid angle Ωs of the detector in scanning at an angular velocity $\dot{\omega}$ is

$$E(\theta) = (1/\dot{\omega}) \int J\Omega_s d\omega\,.$$

The area of reciprocal space normal to the lattice vector $\boldsymbol{\varrho}$ swept out by rotation through an angle $d\omega$ by a detector element normal to the plane of incidence is

$$dS = (\varrho/\lambda)\xi d\omega\,,$$

where ξ is the angle normal to the incident plane subtended by the detector element, and φ_s is the angular slit width in the incident plane:

$$\xi = \Omega_s/\varphi_s\,.$$

The energy

$$E(\theta) = (\lambda/\varrho)(\varphi_s/\dot{\omega}) \int J dS$$
$$= (\varphi/\dot{\omega})(e^2/mc^2)^2 \sin\theta(1+\cos^2 2\theta)[i(s_\varrho)/\varrho^2]\,,$$

which is equivalent to (6).

The integrated intensity is obtained by allowing φ_s to increase to include the full scattering distribution in the ω scan.

By use of the relation

$$d\varphi = \lambda ds_\varrho/(\cos\theta)$$

the integrated intensity is obtained as

$$E_T\dot{\omega} = Q\,.\,V$$

per unit incident beam intensity, with the usual meaning for Q.

References

LANG, A. R. (1956). *J. Appl. Phys.* **27**, 485.
PIKE, E. R. (1959). *Acta Cryst.* **12**, 87.
WILSON, A. J. C. (1949). *X-Ray Optics*. London: Methuen.
GUINIER, A. (1963). *X-Ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies*. San Francisco: Freeman.