Acta Cryst. (1977). A33, 235–243

International Union of Crystallography

Commission on Crystallographic Apparatus and Commission on Charge, Spin and Momentum Densities

Extinction Corrections: Theory and Experiment. Results of γ-ray Diffractometry*

By JOCHEN R. SCHNEIDER,† *Institut Max von Laue–Paul Langevin, B.P. 156X Centre de Tri*, 38042 *Grenoble Cedex, France*

(*Received* 14 *February* 1976; *accepted* 5 *August* 1976)

The difficulties in relating any diffraction theory to the defect structure of 'real crystals' used in crystallography are discussed qualitatively and it is shown that most of these problems become less severe in structure factor measurements by means of γ-ray diffractometry. Probably more direct information on the defect structure of the samples used in accurate diffraction experiments is needed in order to improve the situation. At present and probably for the near future it seems best to design experiments where extinction is only of the order of 10% or less.

Introduction

In order to correct for extinction in crystal structure determination from diffraction data most experimentalists use Zachariasen's theory (1967, 1968). Recently improvements in this theory have been made (Becker & Coppens, 1974), and have been of importance in charge density studies. However, from a theoretical point of view these theories are not very satisfying because from the outset they are limited to intensity coupling between incident and diffracted radiation; in particular, the treatment of primary extinction seems to be oversimplified (Werner, 1974).

At the Tenth International Congress of Crystallography in Amsterdam Zigan (1975) and Kato (1975; see also Kato, 1976) presented extinction theories based on Tagaki–Taupin wave equations (Tagaki, 1962, 1969; Taupin, 1964). In principle Kato's theory describes a full transition from dynamical to kinematical behaviour. However, because of the mathematical difficulties in working with correlation lengths τ_n, which describe the assumed statistical nature of the crystal imperfections, of order $n>2$, up till now the theory is valid only when extinction is small. Very recently Kuriyama (1975) has compared a classical derivation of the dynamical diffraction equation for imperfect crystals with his general dynamical theory derived with the aid of quantum-field theory. He shows that a number of assumptions made within the so-called classical approach are not necessary in the deviation based on quantum-field theory.

Whereas apparently a big effort has been made in recent years to develop new diffraction theories for imperfect single crystals it seems that much less has been done to correlate these theories with the defect structure of the samples *via* measurable quantities which describe the degree of imperfection of the crystal. Therefore diffraction theories based on Darwin's (1914, 1922) mosaic model, which in general is a very crude approximation to the defect structure in single crystals, are still widely used in crystallography for the interpretation of diffraction experiments.

In this paper Darwin's (1914, 1922) extinction theory is presented in terms of an 'absorbing-hole mosaic model', because on one hand this theory still represents the basis of the terminology used in the discussion of extinction, and on the other hand it is used in the interpretation of intensity measurements performed by means of γ-ray diffractometry, which will be described afterwards.

Extinction

A single crystal will be called imperfect if the integrated reflecting power R_m measured with radiation of wavelength λ at a given reciprocal lattice point **H** is smaller than the theoretical value $R_{\rm kin}$ calculated on the basis of the kinematical theory, and larger than the value $R_{\rm dyn}$ determined from the dynamical theory for a defect free crystal of thickness t_0 much larger than the extinction length $t_{\rm ext}$ defined below:

$$R_{\rm kin} > R_m > R_{\rm dyn}. \tag{1}$$

If $R_m = R_{\rm dyn}$ the crystal is called perfect, if $R_m = R_{\rm kin}$ the crystal is called ideally imperfect. The difference between $R_{\rm kin}$ and R_m is called extinction and is discussed in terms of an extinction coefficient

$$y = \frac{R_m}{R_{\rm kin}} < 1, \tag{2}$$

which depends on the defect structure of the sample as well as on the wavelength λ of the diffracted radiation, the structure factor $F_{\mathbf{H}}$, the Bragg angle θ_B and on the sample thickness t_0. For simplicity only symmetrical Laue scattering geometry is considered and the radiation is assumed to be unpolarized.

For extremely thin defect-free crystals dynamical and kinematical theories give the same value for the integrated reflecting power:

$$\lim_{t_0 \to 0} R_{\rm dyn} = R_{\rm kin}.$$

On the other hand, in order to show dynamical diffraction behaviour the crystal thickness must at least be of the order of the so-called extinction length

$$t_{\rm ext} = \frac{V}{r_0} \frac{1}{F_H \lambda}, \tag{3}$$

* This paper was originally presented at the Tenth Congress of Crystallography, Amsterdam, August, 1975 at an Open Commission Meeting sponsored jointly by the Commission on Crystallographic Apparatus and the Commission on Charge, Spin and Momentum Densities.

† Present address: Hahn-Meitner-Institut, D-1000 Berlin 39, Glienicker Str. 100, Germany.

with r_0 = classical electron radius and V = volume of the unit cell (Zachariasen, 1945, § III 11: $A=1$). In the dynamical theory a defect-free crystal is called 'thick' if $t^x_{ext} \ll t_0 \sim 3t^x_{ext}$, where t^x_{ext} means the extinction length calculated for X-rays of, for example, $\lambda \sim 1$ Å. For negligible absorption its peak reflectivity is 50%, which is not further increased if $t_0 \sim 10t^x_{ext}$. In other words the dark part of the crystal sketched in Fig. 1 does not contribute to an increase of crystal reflectivity. For the diffraction of γ-radiation of much shorter wavelength ($\lambda \sim 0{\cdot}03$ Å) the same crystal may behave as an ideally imperfect crystal because $t^x_{ext} \ll t^\gamma_{ext} \sim 3t_0 \gg t_0$. This shows that

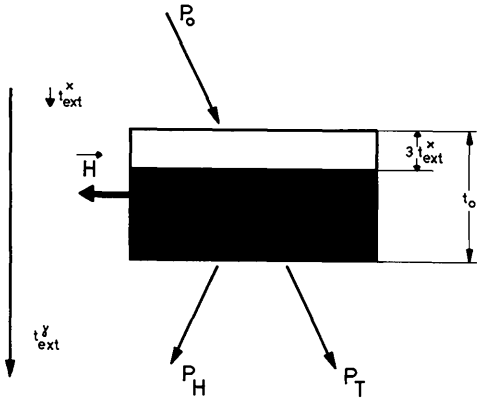

Fig. 1. Schematic representation of the diffraction process in symmetrical Laue geometry in a defect-free single crystal with $t^x_{ext} \ll t_0 \ll t^\gamma_{ext}$. t_0 is the thickness of the sample, t_{ext} and t^γ_{ext} represent the extinction lengths for the diffraction of X-rays and γ-rays respectively. The dark region represents that part of the crystal which does not contribute to an increase of the reflectivity in the case of X-ray diffraction. P_0 = intensity of the incident beam, P_H = Bragg diffracted intensity, P_T = intensity of the primary beam after transmission through the crystal.

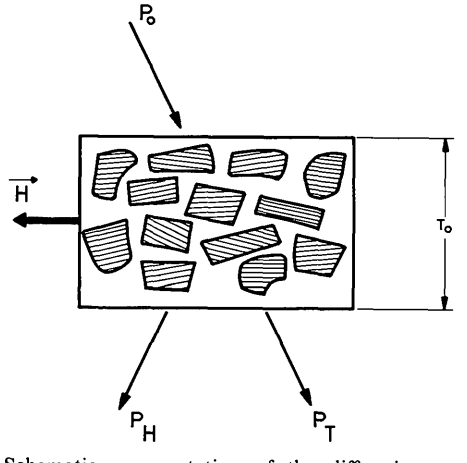

Fig. 2. Schematic representation of the diffraction process in symmetrical Laue geometry in a mosaic crystal. The mean thickness $\bar{t}_0$ of the mosaic blocks is assumed to be much smaller than the thickness T_0 of the sample. P_0 = intensity of the incident beam, P_H = Bragg diffracted intensity, P_T = intensity of the primary beam after transmission through the crystal.

the degree of imperfection as defined above, or the degree of extinction, is extremely wavelength dependent. Freund (1973) found in copper crystals with different dislocation densities a full transition from dynamical to kinematical diffraction behaviour by varying the wavelength from 1·3 to 0·03 Å.

Darwin's mosaic model

The imperfect crystal of thickness T_0 is assumed to be an aggregate of a great number of independently scattering perfect crystal blocks of thickness $t_0 \ll T_0$ as indicated in Fig. 2. The absorption in a perfect block is assumed to be negligible. The deviation of the lattice-plane orientation ω of one block from the mean lattice-plane orientation ω_0 for the whole crystal is described by means of the so-called mosaic distribution function $W(\omega)$, which is a probability function:

$$\int_{-\infty}^{\infty} W(\omega_0 - \omega)\mathrm{d}\omega = 1. \tag{4}$$

$W(\omega)$ was assumed to be a Gaussian distribution function and its full width at half maximum is called the mosaic spread $\Delta\omega_M$. In his diffraction theory Darwin assumes the half-width w^*_{dyn} of the diffraction pattern for the perfect mosaic blocks to be much smaller than the mosaic spread $\Delta\omega_M$, which is a limitation imposed by his mosaic model: adjacent mosaic blocks are separated mainly by dislocations which cause lattice tilts and therefore increase the mosaic spread. If $w^*_{dyn} \sim \Delta\omega_M$ it is difficult to imagine how adjacent blocks are separated from each other and the quantity t_0 looses its physical meaning.

On the basis of this model Darwin formulated the well-known intensity transfer equations:

$$\begin{aligned} \frac{\mathrm{d}P_0}{\mathrm{d}T} &= -\mu_0 P_0 - \sigma P_0 + \sigma P_H \\ \frac{\mathrm{d}P_H}{\mathrm{d}T} &= -\mu_0 P_H - \sigma P_H + \sigma P_0. \end{aligned} \tag{5}$$

$P_0(T)$ and $P_H(T)$ represent the power of the incident and diffracted beams respectively at depth T, μ_0 is the total linear absorption coefficient. For the coupling constant σ, which has to be a function of the rocking angle ω, one obtains

$$\sigma(\omega) = W(\omega)\frac{R^*_{dyn}}{\bar{t}_0}. \tag{6}$$

$\bar{t}_0$ is the mean block thickness, R^*_{dyn} represents the integrated reflecting power calculated with the dynamical theory for a perfect plane parallel plate of infinite lateral extension and thickness $\bar{t}_0$.

Secondary extinction

Some of the basic problems with Darwin's extinction theory and his mosaic model become less important if one can assume $t_{ext} \gg \bar{t}_0$. Then $R^*_{dyn} = Q\bar{t}_0/\cos\theta_B$ and the coupling constant $\sigma(\omega)$ becomes independent of the size of the perfect blocks:

$$\sigma(\omega) = W(\omega)\frac{Q}{\cos\theta_B} \tag{7}$$

$$Q = r_0^2\left|\frac{F}{V}\right|^2 \frac{\lambda^3}{\sin 2\theta_B}\cdot\frac{1+\cos^2 2\theta_B}{2}. \tag{8}$$

The solution of Darwin's intensity transport equations leads to the following expression for the theoretical reflectivity distribution:

$$r_{th}(\omega)=\tfrac{1}{2}\{1-\exp[-2\sigma(\omega)T_0]\}\exp(-\mu_0 T_0/\cos\theta_B). \quad (9)$$

If $W(\omega)$ is assumed to be Gaussian the integrated reflecting power R_{th} is calculated to be

$$R_{th}=\int r_{th}(\omega)\mathrm{d}\omega=y_s R_{kin} \quad (10)$$

$$R_{kin}=Q\frac{T_0}{\cos\theta_B}\exp(-\mu_0 T_0/\cos\theta_B) \quad (11)$$

$$y_s=\exp(-gQT_0/\cos\theta_B);\ g=\text{const.}\frac{1}{\Delta\omega_M}. \quad (12)$$

y_s is the coefficient for secondary extinction. The defect structure of the sample is represented by the mosaic spread $\Delta\omega_M$ alone. In order to measure the mosaic distribution function $W(\omega)$ directly in a diffraction experiment, extinction has to be very small, as can be seen immediately from a first-order approximation to $r_{th}(\omega)$:

$$r_{th}(\omega)\simeq R_{kin}W(\omega)\left[1-W(\omega)Q\frac{T_0}{\cos\theta_B}\right]. \quad (13)$$

Fig. 3 shows a series of rocking curves measured with 0·03 Å γ-radiation in neighbouring volume elements of a tungsten single crystal 0·9 mm thick, 3 mm in width and 15 mm in height. The extinction factor was $y\sim 0{\cdot}85$. The corresponding mosaic distribution functions $W(\omega)$ are of very irregular shape and vary strongly within the sample. Therefore $\sigma(\omega)$ is not constant all over the sample for a given ω as was assumed for the solution of Darwin's intensity transport equations.

Secondary extinction in crystals with inhomogeneous mosaic structure

Systematic investigations of a large number of imperfect single crystals by means of γ-ray diffractometry have shown that an inhomogeneous mosaic structure of the type depicted in Fig. 3 is not unusual. In order to estimate the influence of these inhomogeneities on the extinction correction it is useful to distinguish between two types of inhomogeneities (Schneider, 1975*a*). As indicated in Fig. 4 the irradiated

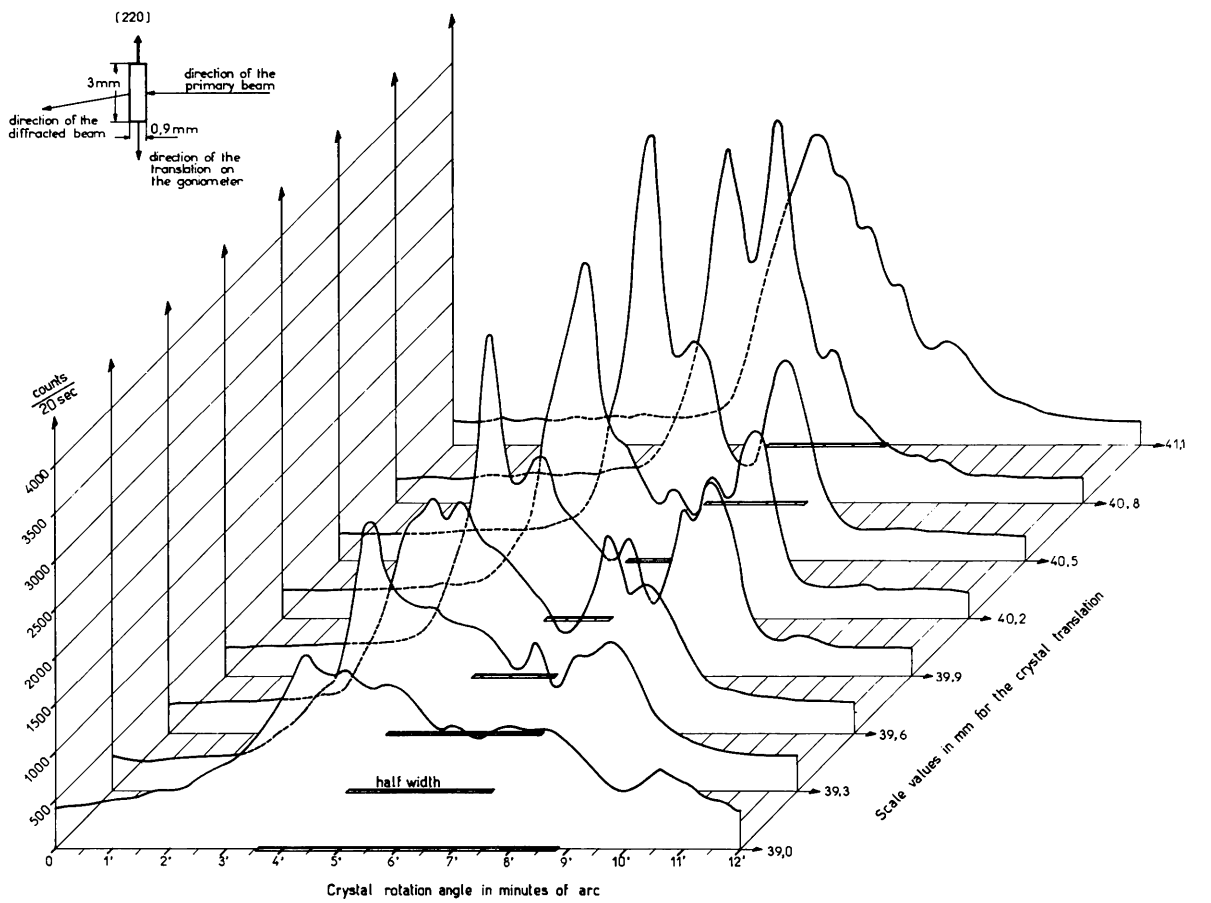

Fig. 3. Rocking curves measured with 0·03 Å γ-radiation in neighbouring volume elements of a tungsten single crystal. Reflexion 220. Cross section of the incident beam 0·2 × 10 mm, angular resolution in the scattering plane, 10″. Distance between neighbouring volume elements, 0·3 mm.

crystal volume v is assumed to consist of two parts v_1 and v_2 with different values of $\sigma(\omega)$ for ω = constant. The inhomogeneity is of type A if the interface between v_1 and v_2 is perpendicular to the diffracting lattice planes and parallel to the surface of the plane parallel crystal plate. The inhomogeneity is of type B if the interface between v_1 and v_2 is perpendicular to the crystal surface and parallel to the lattice planes.

It can be shown that type A inhomogeneities will not have an important influence on the diffraction properties of the crystal (Schneider, 1975*a*). The inhomogeneities in the mosaic structure shown in Fig. 3 are at least partly of type B and the theoretical reflectivity distribution $r_{th}(\omega)$ can be calculated in two different ways: After averaging over the local $W(\omega)$ one obtains a mean mosaic distribution function

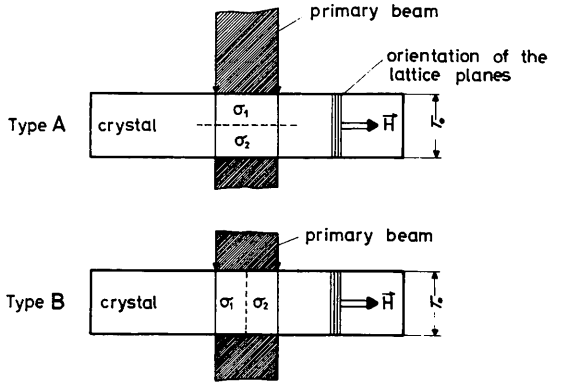

Fig. 4. Schematic representation of type A and type B inhomogeneities in the mosaic structure of real crystals. σ is the coupling constant in Darwin's energy transfer equations.

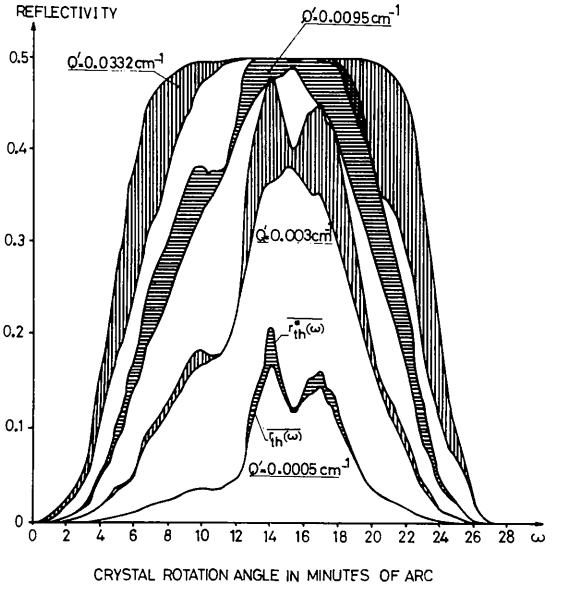

Fig. 5. Reflectivity distributions of a copper single crystal calculated for different values of $Q' = Q/\cos\theta_B$ by means of Darwin's extinction theory for negligible primary extinction. $r_{th}(\omega)$ = calculated diffraction pattern when inhomogeneities in the mosaic structure of type B are taken into account, $r^*_{th}(\omega)$ = diffraction pattern calculated assuming the mosaic structure to be homogeneous.

$\overline{W(\omega)}$ from which one can calculate a theoretical reflectivity distribution $\overline{r^*_{th}(\omega)}$ for the whole crystal. On the other hand from the different $W(\omega)$ one can first calculate local reflectivity distributions, which are averaged afterwards as done by the detector in a diffraction experiment in order to get the mean reflectivity distribution $\overline{r_{th}(\omega)}$. As shown in Fig. 5 for a copper crystal where 24 local mosaic distributions were measured, $\overline{r_{th}(\omega)} \leq \overline{r^*_{th}(\omega)}$ for all rocking angles ω, which leads to the relation

$$R_{kin} \geq R^*_{th} \geq R_{th} \tag{14}$$

for the corresponding values of the integrated reflecting power. Type B inhomogeneities cause an increase of the amount of secondary extinction and the extinction factor y_s can be split in two parts:

$$y_s = \frac{R_{th}}{R_{kin}} = y'_s y''_s. \tag{15}$$

$y'_s = R^*_{th}/R_{kin}$ is related to the amount of secondary extinction occuring in the crystal if the mosaic structure is assumed to be homogeneous. $y''_s = R_{th}/R^*_{th}$ represents the increase in secondary extinction due to inhomogeneities of type B. It seems difficult to develop a generally applicable diffraction theory for imperfect single crystals having an inhomogeneous mosaic structure, and at present it therefore seems more promising either to do diffraction experiments with a radiation of very short wavelength, so that extinction becomes a small effect, or to improve the defect structure of the sample. Measurements where only small extinction was encountered are discussed below, and an example of the latter approach is the study of the change that occured in Nb single crystals, when they were loaded with deuterium gas (Schneider & Stump, 1975). Thirteen rocking curves were measured by means of γ-ray diffractometry in different volume elements of a cylindrical Nb crystal 1·3 cm in diameter and 2·8 cm in length. The two local mosaic distributions $W_1(\omega)$ and $W_2(\omega)$ plotted in Fig. 6 show the degree of inhomogeneity in the mosaic structure of the sample. $\overline{W(\omega)}$, the average over all local distributions, shows that the overall mosaic spread is $\Delta\omega_M \sim 3'$. Pure niobium has a b.c.c. structure and can absorb large quantities of hydrogen and deuterium. From the phase diagram one knows that at room temperature the deuterium can be dissolved in the cubic α phase up to an atomic ratio of D/Nb ~ 0·02. For larger D/Nb atomic ratios a β phase precipitates which has an orthorhombic structure. This has been studied extensively by Schober, Linke & Wenzl (1974; Schober, 1975*a*, *b*). The occurrence of a β metal hydride seems to be responsible for the drastic changes in the mosaic structure of the niobium crystals, as shown in Fig. 7 for five samples containing different amounts of deuterium. The mosaic structure of the samples appeared to be very homogeneous for all the different concentrations of deuterium. The local mosaic distributions $W(\omega)$ differ only slightly from the mean distributions $\overline{W(\omega)}$, which are plotted in Fig. 7. They show an increase in the overall mosaic spread up to 71′ for an atomic ratio D/Nb ~ 0·6.

Primary extinction – absorbing-hole mosaic model

As discussed above, part of a defect-free mosaic block of thickness $\bar{t}_0$ does not contribute to an increase of crystal reflectivity if $t_{ext} \ll \bar{t}_0$, which is indicated by the dark region in Fig. 1. This causes an increase of extinction, called primary extinction, because the kinematical theory assumes that all atoms contribute equally well to the Bragg scattered inten-

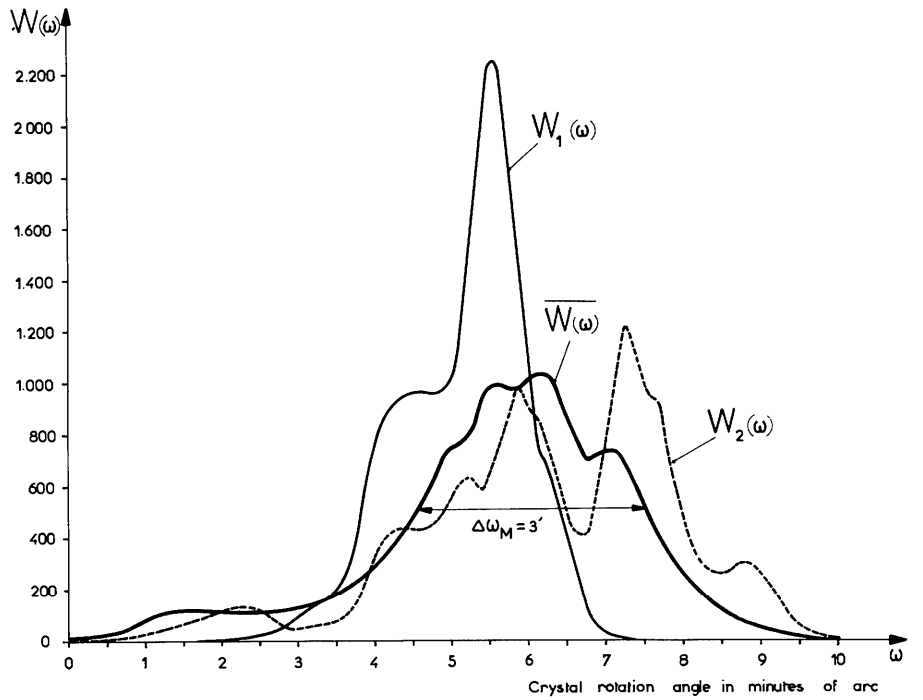

Fig. 6. Local mosaic distributions $W_1(\omega)$, $W_2(\omega)$, and averaged distribution $\overline{W(\omega)}$ of a pure niobium single crystal, determined by γ-ray diffractometry ($\lambda = 0{\cdot}03$ Å, primary divergence 30″, reflexion 110).

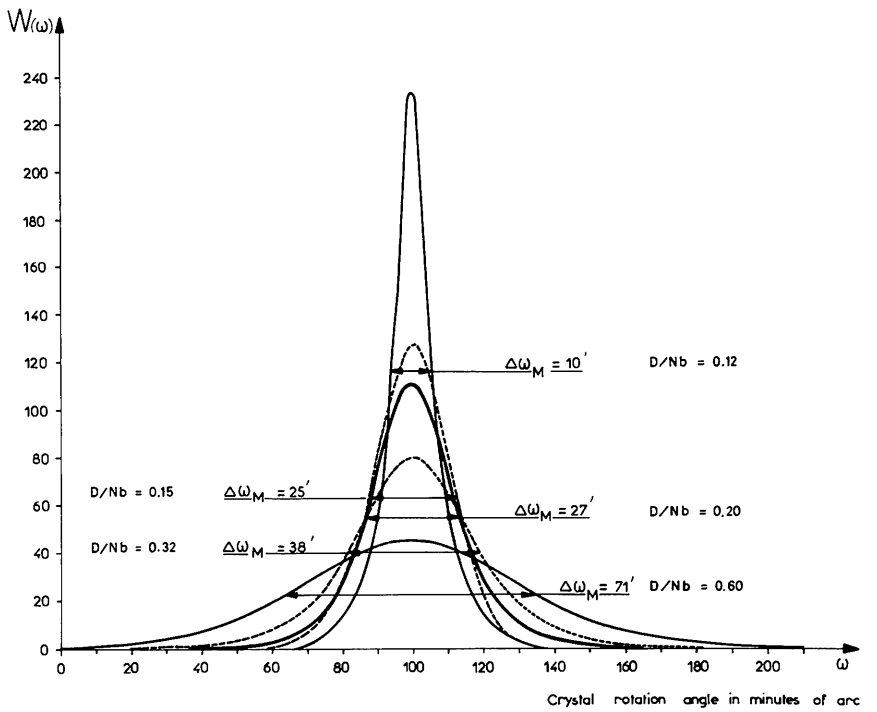

Fig. 7. Averaged mosaic distributions determined by γ-ray diffractometry at the 110 reflexion of niobium crystals containing different amounts of deuterium ($\Delta\omega_M$ = mosaic spread).

sity. Neighbouring mosaic blocks are separated by an arrangement of dislocations which create a long-range displacement or strain field decreasing only with $1/r$, where r represents the distance from the defect centre. Therefore perfect blocks do not touch each other but are separated by a distorted region which cannot be treated with the dynamical theory for a defect-free crystal. Both aspects are summarized in Fig. 8 which represents what may be called an absorbing-hole mosaic model.

The 'absorbing holes', which are due to primary extinction, represent a decrease of the effective crystal volume, which can be taken into account by using an effective sample thickness $T_{\text{eff}} \leq T_0$ in the expression for the extinction coefficient:

$$y = \exp(-gQT_{\text{eff}}/\cos\theta_B). \tag{16}$$

Because $T_{\text{eff}} = T_0 - (T_0 - T_{\text{eff}})$ the extinction coefficient can be split in two parts:

$$y = y_s y_p, \tag{17}$$

where y_s is the coefficient for secondary extinction defined above, and

$$y_p = \exp[-gQ(T_0 - T_{\text{eff}})/\cos\theta_B] \tag{18}$$

represents the coefficient for primary extinction. The difference $(T_0 - T_{\text{eff}})$ depends essentially on the mean block thickness $\bar{t}_0$ and on the extinction length t_{ext}. In X-ray diffraction the atomic scattering factor decreases rather rapidly with scattering angle and therefore the extinction length increases and the absorbing holes have the tendency to vanish for increasing scattering angles. The existence of absorbing holes may therefore be discussed in terms of an angular-dependent pseudo absorption.

In general it will be very difficult to relate any diffraction theory to a model like that shown in Fig. 8 and even this model probably only represents a very crude approximation to the defect structure of 'real crystals' used in single-crystal diffraction experiments. Therefore it was decided to measure structure factors with 0·03 Å γ-radiation (Maier-Leibnitz & Schneider, 1972); primary extinction will in general be negligible and secondary extinction will be rather small for samples of reasonable size.

γ-ray diffractometry

The three γ-ray diffractometers installed at the Institut Max von Laue–Paul Langevin in Grenoble were constructed for investigations of the mosaic structure of rather big single crystals by means of Bragg diffraction of the 412 keV γ-radiation from radioactive gold (Schneider, 1974*a*). These crystals were intended for use as samples or monochromators in neutron scattering experiments. The principle of the experimental set up is shown in Fig. 9. No monochromator is needed to obtain a highly collimated monochromatic γ-ray beam ($\lambda = 0{\cdot}0302$ Å, $\Delta\lambda/\lambda \sim 10^{-6}$, angular divergence in the scattering plane $\Delta\omega_{\text{Ap}} \sim 10''$), and the integrated reflecting power can be measured on an absolute scale. Because the absorption of the 412 keV γ-radiation is small (the mean free path for example being about 11 mm for copper), measurements with targets contained in ovens, cryostats, or high-pressure devices can be easily performed.

The total activity of the gold source is about 75 Ci. Its half-life is $T_{1/2} = 2{\cdot}7$ d, so in general the source is changed after 10 d. The maximum counting rate measured with the NaI(Tl) scintillation counter for a beam cross section of $0{\cdot}2 \times 10$ mm is of the order of 5000 c.p.s. The ratio of peak to background intensities for a γ rocking curve of a crystal with 1% peak reflectivity is at least of the order of ten.

Owing to the short wavelength, the Bragg angles are of the order of 1° and therefore only lattice tilts contribute to the width of a γ rocking curve, which makes the γ-ray diffractometer complementary to backscattering instruments (Freund & Schneider, 1972). Furthermore, the scattering geometry becomes very simple. Crystals are studied in Laue geometry. In spite of the fact that the Ewald sphere is very large, possible effects of multiple Bragg scattering on the measured diffraction pattern can be avoided (Schneider, 1975*b*). If the fine structure in the shape of the measured rocking curve is not smaller than the instrumental resolution of 10″, no deconvolution problem exists and the rocking curve is directly proportional to the mosaic distribution function $W(\omega)$, provided $R_m \simeq R_{\text{kin}}$ (Schneider, 1974*b*).

Absolute structure factors measured by means of 0·03 Å γ-radiation

Because no monochromator is needed, the γ-ray beam incident on the sample is unpolarized and so the polarization factor is well known. The intensity distribution over the cross section of the primary γ-ray beam is homogeneous and stable in time. Each individual Bragg reflexion is measured on an absolute scale. Rather thick imperfect single crystals can be used, so that the crystal surface can be prepared carefully and the sample thickness is determined very precisely with a micrometer screw. Because for most atoms the γ-ray energy of 412 keV is much bigger than the binding energy of the electrons, anomalous dispersion does not occur. If the γ-ray measurement is performed at very low temperature, structure factors, *e.g.* of transition metals, can be determined absolutely with an accuracy of the order of 0·5% (Schneider, 1976).

A series of rocking curves was measured by means of a γ-ray diffractometer at the $2\bar{2}0$ reflexion of a copper single crystal 0·82 cm in thickness. The extinction length for the reflexion is $t_{\text{ext}} = 92$ μm and much larger than the expected size of perfect domains. Therefore primary extinction was assumed to be negligible in the interpretation of that diffraction experi-

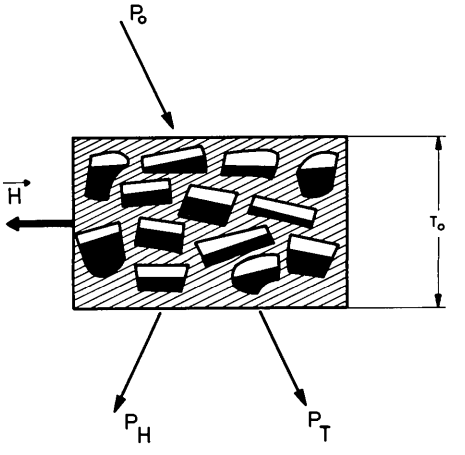

Fig. 8. 'Absorbing-hole mosaic model': The dark regions, which do not contribute to an increase in reflectivity of the mosaic blocks, are called 'absorbing holes' and are related to primary extinction. The shadowed area between the blocks represents the imperfect crystal region between mosaic blocks.

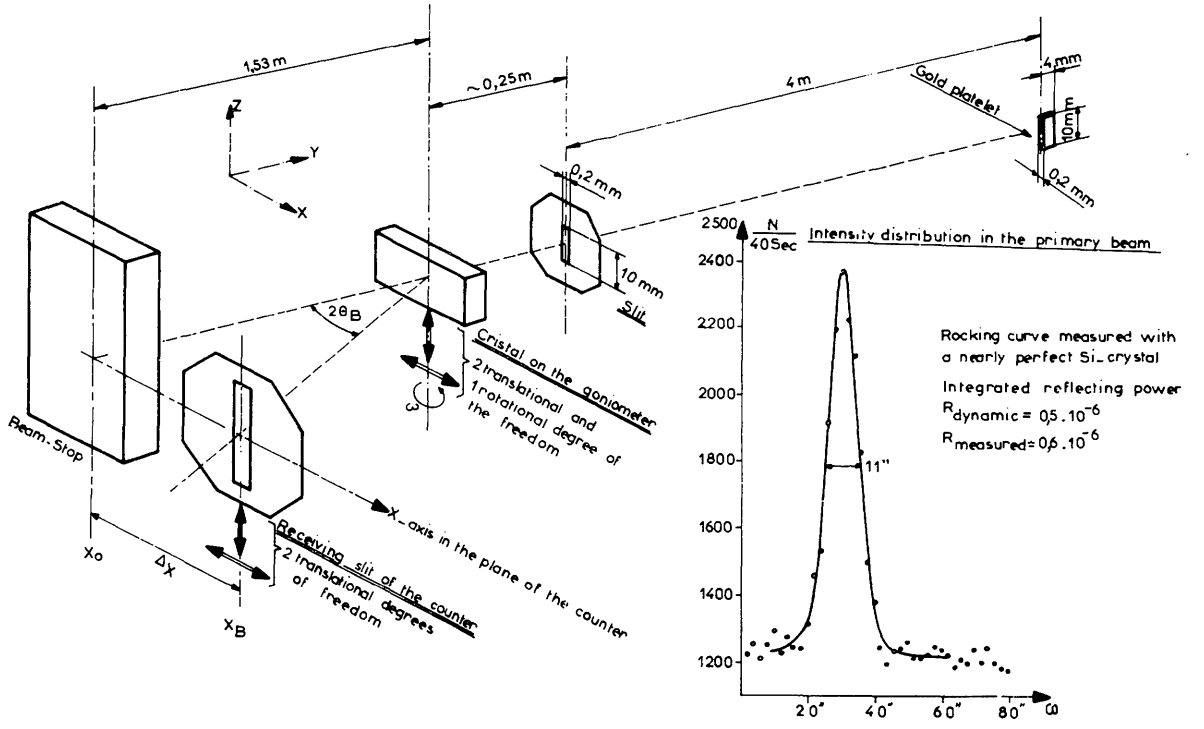

Fig. 9. Schematic set up of the γ-diffractometer and the profile of the intensity distribution in the primary beam.

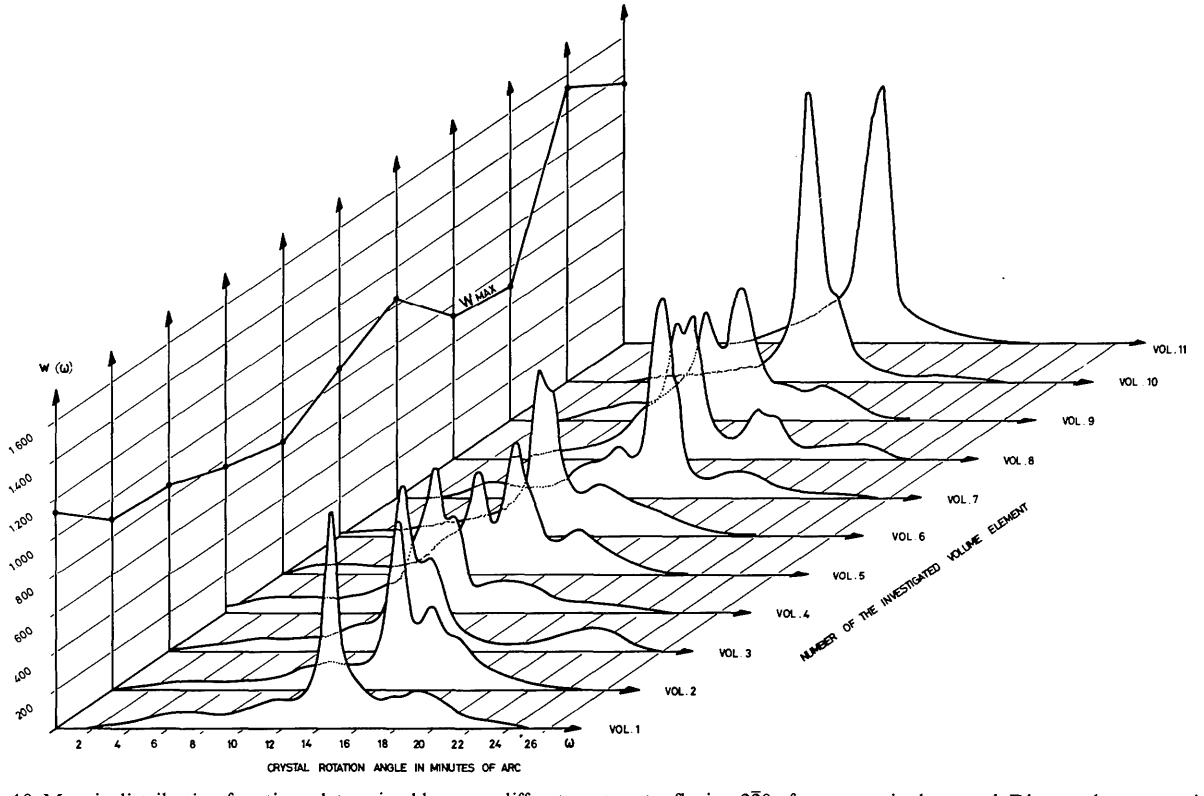

Fig. 10. Mosaic distribution functions determined by γ-ray diffractometry at reflexion $2\bar{2}0$ of a copper single crystal. Distance between neighbouring volume elements 0·5 cm. Cross section of the incident beam 0·5 × 5 mm, angular resolution in the scattering plane 30″.

ment. If there is no deconvolution problem involved in the interpretation of the measured reflectivity distribution $r_m(\omega)$,

$$r_m(\omega) = \frac{P_{\mathbf{H}}(\omega)}{P_0 \exp(-\mu_0 T_0/\cos\theta_B)} = r_{\text{th}}(\omega) \exp(\mu_0 T_0/\cos\theta_B)$$

and one obtains from formula (9)

$$W(\omega) = \frac{\cos\theta_B}{2QT_0} \ln\left(\frac{1}{1-2r_m(\omega)}\right). \tag{19}$$

Because $\int W(\omega)\mathrm{d}\omega = 1$:

$$Q = \frac{\cos 2\theta_B}{2T_0} \int \ln\left(\frac{1}{1-2r_m(\omega)}\right) \mathrm{d}\omega. \tag{20}$$

In terms of an ω step scan the mosaic distribution function can be written as a function of $r_m(\omega)$, where ω_ν is the rocking angle running from ω_1 to ω_N in steps of $\Delta\omega$:

$$W(\omega_\nu) = \frac{\ln\left(\frac{1}{1-2r_m(\omega_\nu)}\right)}{\sum_{\nu=1}^{N} \ln\left(\frac{1}{1-2r_m(\omega_\nu)}\right) \Delta\omega}. \tag{21}$$

Furthermore one obtains a formula for the direct calculation of the structure factor $F_{\mathbf{H}}$ from the measured reflectivity distribution $r_m(\omega_\nu)$:

$$|F_{\mathbf{H}}| = \left[\frac{V^2}{r_0^2 \lambda^3 T_0} \frac{\sin 2\theta_B \,.\, \cos\theta_B}{(1+\cos^2 2\theta_B)} \times \sum_{\nu=1}^{N} \ln\left(\frac{1}{1-2r_m(\omega_\nu)}\right) \Delta\omega\right]^{1/2}. \tag{22}$$

Fig. 10 shows a series of mosaic distribution functions deduced by means of formula (21) from the γ rocking curves measured in different volume elements of the copper single crystal. Apparently the mosaic structure of the sample is very inhomogeneous. The peak reflectivity $r_{\max}$ varied between 8 and 10%. For each volume element structure factors were calculated by means of formula (22). The atomic scattering factors obtained after correction for thermal motion are plotted in Fig. 10. The experimental values are significantly smaller than the Hartree–Fock free-atom value and oscillate around a theoretical value, which is the average of two different values obtained from band calculations by Arlinghaus (1967) and Wakoh & Yamashita (1971). This theoretical value was also used to calculate the kinematical integrated reflecting power R_{kin} for the estimation of the degree of extinction $(1-y)$ which occurs in the different volume elements and which is also shown in Fig. 11. The statistical error in the atomic scattering factors f_m measured in different volume elements is about $\pm 0{\cdot}25\%$. The average value over the first nine volume elements is $\overline{f_m} = 16{\cdot}46 \pm 0{\cdot}07$ and the error is about $\pm 0{\cdot}5\%$. The measurements performed in volume elements 10 and 11 are affected by more than 10% extinction and the corresponding f_m values are too small in comparison with the whole series of measurements. Therefore it was assumed that extinction was significantly underestimated for these two measurements, which were excluded from all further considerations.

Conclusions

An important number of corrections necessary to deduce atomic scattering factors from X-ray intensities measured on imperfect single crystals do not need to be considered in the interpretation of diffraction patterns measured by γ-ray diffractometry, which therefore opens new possibilities for the measurements of accurate structure factors in simple crystals with relatively small unit cells. Because the absorption of the 412 keV γ-radiation is small, measurements with the specimen in ovens, cryostats, or high-pressure devices can be easily performed.

If extinction is less than 10%, the determination of structure factors from rocking curves measured by γ-ray diffractometry is in general independent of the defect structure of the sample. Therefore accurate structure factors can be measured in crystals which undergo structural phase transitions as a function of pressure or temperature, which often are accompanied by changes in the defect structure of the samples.

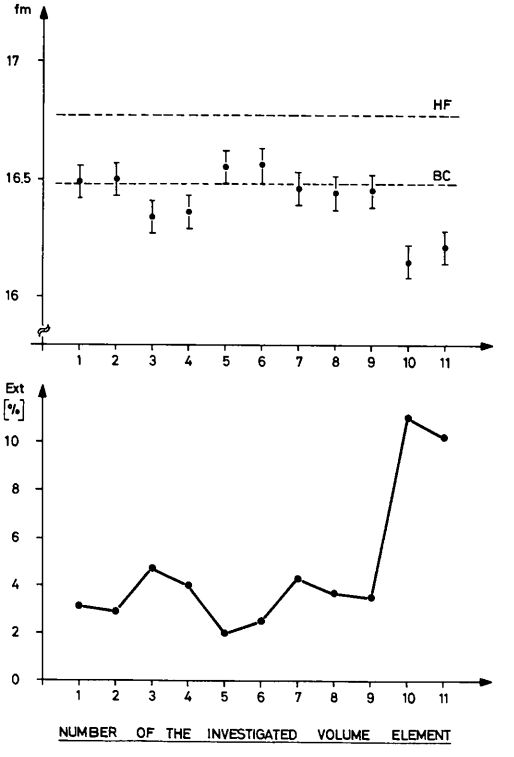

Fig. 11. Experimental atomic scattering factors f_m of the $2\bar{2}0$ reflexion of copper and the degree of extinction $(1-y)$ as determined from γ-ray rocking curves measured in different volume elements of the sample.

The author thanks Dr M. S. Lehmann for reading the manuscript and for valuable comments.

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International Union of Crystallography

Commission on Crystallographic Apparatus and Commission on Charge, Spin and Momentum Densities

The Theoretical Models of Extinction. Their Domain of Applicability*

BY PIERRE BECKER, *Centre de Mécanique Ondulatoire Appliquée, CNRS, and Université Paris* VI, 23 *Rue du Maroc*, 75019 *Paris, France*

(*Received* 22 *March* 1976; *accepted* 5 *August* 1976)

The various theoretical models of extinction are critically reviewed. It is shown that the Darwin energy transfer equations are valid as long as the mean coherence distance in the sample is smaller than the extinction length, as demonstrated recently by Kato. The available solution is correct when the entrance and exit surface do not overlap and the approximation is seen to be reasonable for more complicated cases. The correlation between primary and secondary extinction is discussed. It is emphasized, in practical applications, that many tests, both theoretical and experimental (when possible) of the correctness of the correction should be made. Only samples that fit a given diffraction theory should be used for accurate studies like charge density determination.

I. Introduction

The problem of extinction is one of the major obstacles to the accuracy of coherent X-ray or neutron diffraction experiments. Various methods of correction have been proposed, both experimental and theoretical. Those methods have been all criticized in the literature and many crystallographers may be believe that no serious progress has been made in this field.

In the present article, a review is given of the basic physical assumptions used in the extinction theories. Several tests are described that tell whether an extinction correction can be applied to a given data set. The main purpose of this article is to give some confidence in the actual correction of extinction.

There exist two theories of the diffraction of X-rays or neutrons:

(*a*) The kinematical theory is based on the Born approximation which is supposed to be applicable to the whole sample under diffraction. It is therefore assumed that the interaction between radiation and matter is small enough for the incident beam not to be perturbed (except in a classical absorption process) within the sample.

This theory is believed to be valid for the diffraction by gaseous molecules but the translational symmetry of a crystal does impose constraints on the structure of the waves that can travel inside the crystal. The kinematical theory is only valid in the limit of thin crystals.

(*b*) The dynamical theory is the study of the waves that are compatible with the periodic nature of the crystal. It can be developed with 'quasi-geometrical' arguments, taking into account all the possible rescatterings of the incident and diffracted beams (Darwin, 1914; James, 1957; Warren, 1969). The problem can be formulated in a more general way, in terms of the electromagnetic theory (James, 1963; Batterman & Cole, 1964; Authier, 1970; Kato, 1974), in either the plane-wave or the spherical-wave approximation. A major difficulty comes from the boundary conditions: no general solution has been found that is valid for every diffraction geometry.

The dynamical theory leads to the kinematical theory in the limit of thin crystals. The frontier can be calculated from

* This paper was originally presented at the Tenth Congress of Crystallography, Amsterdam 1975, at an Open Commission Meeting sponsored jointly by the Commission on Crystallographic Apparatus and the Commission on Charge, Spin and Momentum Densities.