Interpretation of Rocking Curves Measured by γ-ray Diffractometry

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Investigations of many imperfect single crystals of different materials by means of a γ-diffractometer show that the mosaic structure of large single crystals is often very inhomogeneous: the mosaic distribution function has neither a Gaussian nor a Lorentzian shape and the shapes differ remarkably for different volume elements in the sample. Current extinction theories must be considered with reservation because Darwin's intensity transport equations are solved assuming the scattering length for a given angle of incidence to be constant all over the irradiated crystal volume. This is not true for samples with inhomogeneous mosaic structure.

Introduction

Rocking curves measured on relatively large imperfect single crystals by means of neutron spectrometers very often have a compact and smooth shape. In most cases the curves are interpreted in terms of Darwin’s mosaic model assuming a Gaussian or Lorentzian mosaic distribution function.

The mosaic structure of target and monochromator crystals for neutron scattering experiments was studied by means of a γ-diffractometer described in the previous paper (Schneider, 1974). Within the limits of the instrumental resolution power of 10″ the rocking curves measured with 0.03 Å γ-radiation are proportional to the mosaic distribution function \( W(\omega) \), supposing the diffraction process to be extinction-free. Owing to the small cross section of the incident γ-ray beam, very detailed investigations of the mosaic structure could be performed and it turns out that the mosaic structure of most of the investigated samples is much more inhomogeneous than is indicated by neutron measurements.

Based on Darwin’s mosaic model, the question why neutron and γ-ray measurements lead to different conclusions concerning the crystal structure of the sample will be discussed. Examples will be given showing that, in general, one cannot assume the mosaic distribution function \( W(\omega) \) to have Gaussian or Lorentzian shape.

Darwin’s mosaic model

Whereas in kinematical theory it is assumed that a scattered wave does not interact again with the crystal, dynamical theory, which is valid for perfect crystals, treats all waves existing within the sample as a coupled system, the so-called optical field. This leads to an eigenvalue problem which has been solved only for a plane-parallel crystal plate of infinite lateral extension. Zachariasen (1945, § III.11) defines a quantity \( A \) in order to distinguish three special cases:

1. \( A \gg 1 \): the crystal is called ‘thick for theory’,
2. \( A \ll 1 \): the crystal is called ‘thin for theory’,
3. \( A \sim 1 \): crystal of ‘medium thickness’.

For negligible absorption and symmetrical Laue geometry with small Bragg angles \( \theta_B \) (\( \cos \theta_B \sim 1 \)) one obtains

\[
A = \frac{r_0}{V} F^2 \lambda t_0
\]

where \( r_0 \)=classical electron radius; \( V \)=volume of the unit cell, \( F \)=structure factor, \( \lambda \)=wavelength, \( t_0 \)=thickness of the crystal plate.

The integrated reflecting power \( R_{\text{dyn}} \), calculated by means of the dynamical theory for a ‘thick crystal’, is much smaller than the kinematical value \( R_{\text{kin}} \). For a normal imperfect crystal the relation \( R_{\text{kin}} > R_{\text{meas}} > R_{\text{dyn}} \) is valid, where \( R_{\text{meas}} \) represents the measured value of the integrated reflecting power. Only for extremely thin crystals does the quantity \( R_{\text{kin}} \) become equal to \( R_{\text{dyn}} \). On the other hand, in order to show dynamical effects, the crystal must be thicker than the so-called extinction length \( t_{\text{ext}} \) which will be defined as the thickness of the crystal plate corresponding to \( A = 1 \):

\[
t_{\text{ext}} = \frac{V}{r_0} \frac{1}{F\lambda}.
\]

The most frequently used model for describing the diffraction in imperfect crystals is Darwin’s (1914, 1922) mosaic model. The mean thickness \( \bar{t}_0 \) of a mosaic block is much smaller than the thickness \( T_0 \) of the whole crystal; \( \bar{t}_0 \) is normally assumed to be of the order of several microns. The deviation of the lattice-plane orientation in one block from the mean lattice-plane orientation for the whole crystal is described by the mosaic distribution function \( W(\omega) \) which is a probability function:

\[
\int W(\omega) d\omega = 1.
\]

\( W(\omega) \) was assumed to be a Gaussian distribution function.
If \( t_0 > t_{\text{ext}} \), the integrated reflecting power calculated for such a block by means of the dynamical theory, \( R_{\text{dyn}}^* \), will be smaller than the corresponding kinematical value \( R_{\text{kin}}^* \). For the whole crystal this leads to a difference between \( R_{\text{meas}} \) and \( R_{\text{kin}} \), and the corresponding part of the extinction is called primary extinction. The increase of extinction due to the attenuation of the primary beam by Bragg scattering in the upper layer of the mosaic crystal is called secondary extinction. For the diffraction of 0.03 \( \AA \) \( \gamma \)-radiation in a copper single crystal, one calculates the dynamical half width \( w_{\text{dyn}} \) for the 111 reflexion as about 0.45°; the mean free path \( \mu \) is of the order of 10 mm. Thus Darwin's fundamental conditions for the applicability of his extinction theory should be fulfilled for a great number of real crystals when they are studied by means of the \( \gamma \)-diffractometer.

The basic intensity transport equations in Darwin's theory represent the law of energy conservation in the diffraction process in the crystal. For the coupling constant \( \sigma \) between primary and secondary beam, one obtains

\[
\sigma(\omega) = W(\omega) \cdot \frac{R_{\text{dyn}}^*}{t_0}
\]

which has to be a function of the scan angle \( \omega \). \( R_{\text{dyn}}^* \) is the integrated reflecting power calculated with the dynamical theory for a perfect plane parallel plate of thickness \( t_0 \).

Normally Darwin's intensity transport equations are solved under the assumption that \( \sigma \) is constant over the whole crystal for a given scan angle \( \omega \). Thus it is assumed that \( t_0 \) and \( W(\omega) \) do not change considerably within the sample. For the X-ray wavelengths normally used in structure work Zachariasen (1967) showed a considerable shortcoming in Darwin's theory. Taking into account the finite lateral extension of the mosaic blocks he suggested a new interpretation of the diffraction process; however, like Darwin he assumes \( \sigma \) to be constant within the sample.

**Coexistence of primary and secondary extinction**

Generally speaking, one of the main difficulties in understanding the diffraction process in crystals with \( R_{\text{kin}} > R_{\text{meas}} > R_{\text{dyn}} \) is the coexistence of primary and secondary extinction, because this means the coexistence of two different coupling mechanisms for waves in the crystal: the amplitude coupling from the dynamical and the intensity coupling from the kinematical theory. To distinguish between the two cases, the following rule of thumb will be useful. If, for instance, the dislocation density in a sample is such that there is much more than one dislocation per square of extinction length, the diffraction process can probably be treated by kinematical principles. On the other hand if the dislocation density is much smaller than one per square of extinction length, dynamical principles must be applied. A mathematical approach to solve the problem of coexistence of primary and secondary extinction does not seem to be very promising because the calculations will in general be based on oversimplified models of the crystal structure. Therefore one should first try to eliminate primary extinction in the actual diffraction process by increasing the number of defects (slight deformation of the sample, irradiation with fast neutrons) or by increasing the extinction length by changing the wavelength of the diffracted radiation to values up to the order of \( 10^{-2} \ \AA \).

Brogren (1969) reports on investigations of single germanium crystals up to sizes of 70 × 100 × 6 mm.
With commercial X-ray tubes having a small focal spot, measurements of the investigated reflecting power at the 220 reflexion gave indications of a perfect crystal. However, 122, 244 and 344 keV γ-rays from $^{152}$Eu gave integrated intensities indicating a mosaic behaviour which increased with increasing energy. Fig. 1 shows the result of similar investigations performed by means of the γ-diffractometer on the (100) lattice planes of a 12 mm thick cylindric copper single crystal. The half-width of the crystal diffraction pattern was less than 10°. The integrated reflecting power was measured with radiation of $\lambda = 0.078$ Å on the 200 reflexion and the 0.03 Å radiation on the 200, 400, and 600 reflexions. With all the different extinction lengths involved, the crystal, if perfect, should be 'thick' according to the dynamical theory. In this case the integrated reflecting power $R_{\text{dyn}}$ is proportional to $(F\lambda)d$ ($d$ being the lattice spacing), because the crystal is studied in symmetrical Laue geometry at small Bragg angles. On the other hand, the kinematical value of the integrated reflecting power $R_{\text{kin}}$ is proportional to $(F\lambda)^2d$. In Fig. 1 log $(R/d)$ is plotted as a function of log $(F\lambda)$.

The measured values indicate a transition between amplitude and intensity coupling. In other words, one should expect the crystal to exhibit perfect behaviour for Cu Kα radiation, whereas the crystal behaves as an imperfect one for the diffraction of 0.03 Å radiation at the 600 reflexion. The difference between the values of the integrated reflecting power measured in neighbouring volume elements disappears for the 400 and 600 reflexions respectively. The distance between positions I and II was 0.5 mm. This result represents an instructive example of the well-known fact that the weaker the extinction the less the diffraction process depends on the degree of perfection in the sample.

Secondary extinction only

With respect to the 0.03 Å γ-radiation, the extinction length in copper is of the order of 300 μm for the 444 and about 60 μm for the 111 reflexion. In tungsten one obtains $t_{\text{ext}} \approx 60$ μm for the 440 and about 30 μm for the 110 reflexion. If the size of the perfect domains in a real crystal can be assumed to be smaller than or of the order of 10 μm, it is reasonable to neglect primary extinction in the interpretation of rocking curves measured by γ-ray diffractometry. In these cases one obtains for the integrated reflecting power of a mosaic block

$$R_{\text{yn}} = R_{\text{kin}} = Qt_0,$$

where $Q$ is the average scattering cross section per unit volume of the crystal calculated within the kinematical theory. For small Bragg angles

$$Q = r_0^2 \left( \frac{F^2}{V} \right) \lambda^2 \cdot d.$$
\( \sigma(\omega) \) becomes equal to \( W(\omega).Q \), the extinction correction depends only on the mosaic distribution function and from the solution of Darwin's intensity transport equations one obtains the following expression for the theoretical reflectivity

\[
\begin{align*}
    r_{\text{th}}(\omega) &= 0.5 \{ 1 - \exp[-2 \cdot W(\omega) \cdot QT] \\ & \quad \approx W(\omega) \cdot QT_0 [1 - W(\omega)QT_0].
\end{align*}
\]

If \( W(\omega)QT_0 \ll 1 \), there is no extinction at all. The reflectivity is proportional to the mosaic distribution function and the integrated reflecting power is equal to

\[
R_{\text{kin}} = \int r_{\text{th}}(\omega) d\omega = QT_0.
\]

The integrated reflecting power \( R_{\text{meas}} \) measured at a certain reflexion in a given sample can be compared with the kinematical value \( R_{\text{kin}} \), and if the two values do not differ more than a few percent, the mosaic distribution function can be deduced directly from the measured reflectivity distribution \( r_{\text{meas}}(\omega) \)

\[
W(\omega) = \frac{r_{\text{meas}}(\omega)}{R_{\text{meas}}}.
\]

For a great many real crystals the kinematical limit can be reached using the 0.03 Å \( \gamma \)-radiation and one obtains a direct insight into the mosaic structure of the sample. On one hand this seems to be an unalterable condition for a correct understanding of secondary extinction and on the other hand detailed knowledge of the mosaic structure provides an experimental check of the validity of the applied extinction theory: The mosaic distribution function \( W(\omega) \) is a crystal property and if Darwin's theory of secondary extinction is applicable, one should deduce the same distribution function \( W(\omega) \) from the reflectivity distributions \( r_{\text{meas}}(\omega) \) measured at different orders of a given reflexion.

**Mosaic structure of a Be, W and a Cu crystal**

Fig. 2 shows a rocking curve of a Be crystal measured by means of the two-axis neutron spectrometer D13 of the Institut Laue-Langevin which is mounted at the end of a curved neutron guide for thermal neutrons. The wavelength of 0.845 Å was selected using the 200 reflexion of a Cu crystal. The monochromator had a
mosaic spread of the order of $2.5'$ and was set in Bragg geometry. The Be crystal was 8 mm thick and we studied the 110 reflexion in symmetrical Laue geometry. The lattice spacing of monochromator and sample did not fit well [$d_{(200)}=1.808$ Å, $d_{(110)}=1.14$ Å] and therefore the diffraction was not free of dispersion. The cross section of the primary neutron beam was 1 cm$^2$ and the measured rocking curve has a smooth and compact shape. By means of the $\gamma$-diffractometer we investigated in the same Be crystal a volume ele-

Fig. 6. Rocking curves of different neighbouring volume elements of a copper crystal labelled (Cu 1-2). Reflexion 111, primary divergence 25$''$.  

Fig. 7. Rocking curves of different volume elements near the surface of the copper crystal (Cu 1-2). Reflexion 220, primary divergence 10$''$. 
ment of 0.5 × 10 × 8 mm out of the 10 × 10 × 8 mm which was studied with neutrons. The rocking curve measured in symmetrical Laue geometry at the 110 reflexion is plotted in Fig. 3. The mosaic distribution function shows very strong fluctuations.

The resolution in the neutron-diffraction experiment could be improved considerably but in general it will remain much worse than the resolution of the γ-diffractometer. Additionally, for instance in a neutron monochromator crystal, the diffraction of neutrons will be strongly affected by extinction, so that the measured reflectivity distribution differs remarkably from the mosaic distribution function. Fig. 4 shows rocking curves measured by means of the γ-diffractometer at different orders of the 111 reflexion of a copper single crystal. Because the Bragg angles are small, the irradiated sample volume does not change considerably when the diffraction with higher momentum transfer is studied at the same lattice planes. On the other hand, the atomic form factor changes and because Q is proportional to $F^2\alpha$ the degree of extinction occurring in the diffraction process decreases with increasing momentum transfer. For the whole rocking curve – Fig. 4 represents only a cut – we showed that the diffraction at the 444 reflexion is extinction-free. So the mosaic distribution function $W(\omega)$ is proportional only to the 444 reflectivity distribution and there is an important deformation of the true shape of $W(\omega)$ as derived from the lower orders of reflexion due to extinction.

The 15 mosaic distribution functions $W(\omega)$ shown in Fig. 5 were measured from the 110 reflexion of a 0.51 mm thick tungsten single crystal. They represent a very inhomogeneous mosaic structure. The cross section of the primary beam was 0.5 mm in width and 2 mm in height. We investigated in symmetrical Laue geometry neighbouring volume elements of dimension 0.5 × 2 × 0.51 mm which were arranged in three superposed layers. The diffraction process was not extinction free and the angular resolution was only 25″. Thus the mosaic structure is probably still more inhomogeneous than is indicated in Fig. 5.

Finally we shall discuss the mosaic structure of a copper crystal which seemed to be as homogeneous as is often assumed a priori in theoretical work. Fig. 6 shows a series of smooth rocking curves of nearly the same shape. They were measured at the 111 reflexion with a primary γ-beam of 25″ of arc divergence. We tried to understand where the flat tails of the rocking curves, giving them a Lorentzian shape, came from. Therefore, the crystal was rotated 90° and a series of rocking curves were measured at the 220 reflexion in volume elements near the surface of the sample. The cross section of the primary beam was 0.2 × 10 mm². The results are shown in Fig. 7. The half-widths of the curves increased and the peak reflectivity decreased when the investigated volume element approached the surface. The integrated reflecting power increased, too, and this indicates that the diffraction process was not extinction-free. Therefore we studied the Bragg dif-

![Fig. 8. Rocking curves of different volume elements near the surface of the copper crystal (Cu 1-2). Reflexion 440, primary divergence 10″.](image-url)
fraction at the 440 reflection in the same volume elements and, as can be seen from Fig. 8, the effect became much clearer. Obviously the crystal consists of several layers having different mosaic spreads. The increase of the mosaic spread was observed at both surfaces and therefore we believe that the effect is due to surface damage. The crystal was cut by spark erosion.

Reflectivity of neutron monochromators

One of the first problems which we encountered when investigating neutron monochromator crystals using the $\gamma$-diffractometer was the explanation of the result that most of the crystals had a reflectivity much smaller than that predicted by commonly used diffraction theories. Most of the investigated monochromator crystals had an inhomogeneous mosaic structure and with the aid of Fig. 9 it is shown that these inhomogeneities are to a great extent responsible for the small neutron reflectivity of the crystals.

On the 111 reflexion of a 1 cm thick copper crystal a reflectivity distribution $r_{\text{kin}}(\omega)$ was measured with $\gamma$-radiation of $\lambda_{\text{kin}} = 0.03 \text{ Å}$. The structure factor will be called $F_{\text{kin}}$ and the lattice spacing $d_{\text{kin}}$. We assumed that the diffraction is extinction free. A theoretical reflectivity distribution $r_{\text{th}}(\omega)$ is calculated for the diffraction of radiation of wavelength $\lambda$ at a reflexion characterized by the structure factor $F$ and the lattice spacing $d$ by means of the following formula:

$$r_{\text{th}}(\omega) = 0.5 \left[ 1 - \exp \left( -2r_{\text{kin}}(\omega)C \right) \right]$$

$$C = \frac{F}{F_{\text{kin}}} \left( \frac{\lambda}{\lambda_{\text{kin}}} \right)^2 \frac{d}{d_{\text{kin}}}.$$

Fig. 9 represents the result of such a calculation. One sees that the shape of the rocking curve is smoothed by secondary extinction. The cross section of the primary $\gamma$-ray beam was $0.5 \times 10 \text{ mm}$. The shape of the rocking curves measured in neighbouring volume elements varied considerably. Only one curve $r_{\text{kin}}(\omega)$ from one particular volume element is shown. The cross section of an incident neutron beam is at least of the order of $10 \times 10 \text{ mm}$ so that with neutrons the measured rocking curve would be further smoothed owing to the spatial averaging over a relatively big sample volume. The holes in the curves plotted in Fig. 9 at $\omega$ equal to 7 and 18° respectively will probably not show up; thus the neutron rocking curve would lead us to believe that the crystal has a homogeneous mosaic structure. For reasons of simplicity, the deconvolution of the measured neutron curve is often done assuming a Gaussian-shaped mosaic distribution, and in the given example this would lead to a mosaic spread of about 35°. From this value and the crystal thickness $T_0$ one estimates a reflectivity which will have to be higher than the one which was measured. In this case the discrepancy would be caused by the model assumed for mosaicity and could not only be due to the fact that primary extinction was neglected in the calculation.
In a first approximation each point of the irradiated monochromator crystal will see neutrons of all directions within the limits given by the dimensions of the beam tube or the neutron guide respectively. In the example discussed here we may assume an angular divergence of the primary beam of about 30'. Because of the holes in the mosaic structure of the crystal, part of the incoming neutrons cannot be accepted by the crystal; it is as if part of the primary beam passes beside the sample. In order to obtain the reflectivity distribution, the Bragg-reflected intensity is normalized with the intensity of the primary beam and therefore one never obtains maximum reflectivity for crystals with holes in their mosaic structure.

**Conclusion**

In real crystals with inhomogeneous mosaic structure the reflecting properties change within the sample. Therefore the scattering length \( \sigma(\omega) \) cannot be assumed to be constant all over the irradiated crystal volume when Darwin’s intensity transport equations, the basis of the general extinction theories (Becker & Coppens, 1974), are to be solved. For a plane-parallel crystal the author showed experimentally (Schneider, 1973) that a change in \( \sigma(\omega) \) perpendicular to the surface, as shown for the copper crystal in Figs. 6–8, will not affect the correction for secondary extinction, provided the true mosaic distribution function is known. On the other hand, inhomogeneities in the mosaic structure as shown in Fig. 5 for the tungsten crystal create serious problems. At least for large imperfect single crystals, a mathematical approach for solving the extinction problem in general does not seem very promising because of the large variety in the samples and the experimental conditions. As far as the diffraction of electromagnetic radiation is concerned, a possible way to surmount the difficulties is to select the wavelength of the radiation used in the diffraction experiment in such a way that primary extinction may be neglected and that the error in Darwin's correction for secondary extinction due to the inhomogeneities in the mosaic structure become sufficiently small. This is one reason why precise absolute measurements of structure factors should be done using \( \gamma \)-rays (Maier-Leibnitz & Schneider, 1972). Furthermore, \( \gamma \)-rays have an obvious advantage when measurements have to be done with the target contained in ovens, cryostats or high-pressure devices.

On one hand, the \( \gamma \)-diffractometer seems to be a unique tool in the characterization of the mosaic structure of target crystals for neutron scattering experiments because one obtains an unadulterated crystal property. On the other hand, if the diffraction properties of a given neutron monochromator crystal have to be improved, it is important to know if a low reflectivity is due to primary extinction that is caused by the existence of perfect domains, or if it is due to inhomogeneities in the mosaic structure. When the mosaic structure of a sample is changed by elastic or plastic deformations in order to obtain better diffraction properties, the process can be monitored easily by means of the \( \gamma \)-diffractometer. When crystals are bent, one can check additionally if the mean orientation of the lattice planes follows the macroscopic curvature.

It was shown that one can find samples which behave like perfect crystals for X-rays or neutrons of a wavelength of about 1 Å, whereas the diffraction of 412 keV \( \gamma \)-radiation in these crystals should be treated by means of kinematical principles. Thus one can apply X-ray topography or other direct methods in order to obtain an idea of the type of imperfections contained in the crystal and then study their influence on the diffraction process in the kinematical approximation using \( \gamma \)-ray diffractometry. This should be very useful on the diffraction process in the kinematical approximation using \( \gamma \)-ray diffractometry. This should be very useful in a systematic investigation of the influence of defects on the diffraction process in general and especially of their influence on primary extinction.

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**References**