New Experimental Methods for Perturbation Crystallography.
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Part B

Multilayer

5.8 Theory

An alternative, and more standard, way to generate a broad-energy X-ray band is by using a multilayer. A multilayer can be grown on curved surfaces to produce focusing elements, their thickness can be graded in-depth and/or laterally, and the constituent materials can be varied over a wide range to achieve optimum performance for a given application. For reflection of X-rays, layers of high and low Z should alternate with no interdiffusion between the layers. Furthermore, the two materials must be chemically compatible and withstand the high power of synchrotron X-ray beams. The main problems encountered are interface roughness and variations of layer thickness, which both affect the reflectivity and become very important when the d-spacing is decreased which is necessary for monochromators for X-rays of higher energies.

A brief overview of the multi-layer theory will be given.

5.8.1 Bragg’s law

The monochromator property of a multi-layer is governed by Bragg’s law that, corrected for refraction, is given by [23]:

\[ n\lambda = 2d \sin \theta \sqrt{1 - \frac{2<\alpha> - <\alpha>^2}{\sin^2 \theta}} \]  

(5-8)

where \(<\alpha>\), the deviation of the real part of the refractive index from 1, is the mean over the two components of the bilayer with thicknesses \(t_A\) and \(t_B\)

\[ <\alpha> = \frac{t_A \alpha_A + t_B \alpha_B}{d}. \]

Here the \(\alpha_A\) and \(\alpha_B\) are defined as

\[ \alpha_{\lambda,B} = \frac{\lambda^2}{r_e} \sum_i (Z_i + f_i) N_i, \]

where \(r_e\) is the classical electron radius.
with \( Z \), the atomic number, \( r \), the classical Thomson radius of the electron, \( N \), the number of atoms of type \( i \) per unit volume, and \( f' \) the real part of the anomalous atomic scattering factor. The \( d \)-spacing corresponds to the local spacing between layer pairs of the multi-layer.

However, in practice Bragg’s law is still applicable since the correction factor in Equation 5-8 is in general a few percent.

### 5.8.2 Focusing

The same focusing conditions as for mirrors apply\(^{[21]} \). However, in contrast to the bent-Laue monochromator, a multi-layer is bent elliptically. For focusing the local bending radius \( R \) is given by

\[
R = \frac{-2pq}{\theta(p+q)}, \tag{5-9}
\]

where \( p \) and \( q \) are the source to multi-layer and multi-layer to sample distances, respectively.

In practice, the focus will be broadened. The perfection of the surface of the multi-layer is mainly limited by the polishing errors\(^{[21]} \) with typical slope errors of 1 \( \mu \)rad (r.m.s).

### 5.8.3 Energy dispersion and rocking curve width

The energy dispersion of the X-ray beam produced by a multi-layer scales approximately as

\[
\frac{\Delta E}{E} = \frac{1.8}{nm_{\text{eff}}}, \tag{5-10}
\]

where \( m_{\text{eff}} \) is the effective number of layer pairs participating in the reflection process. The half width of the Bragg peak is related to Equation 5-9 as

\[
\Delta \theta = \theta \frac{\Delta E}{E}. \tag{5-11}
\]

### 5.9 Optics Set-up

The multi-layer used consisted of alternating W and B\(_4\)C (boron carbide) layers, with a laterally graded \( d \)-spacing of 13\% over 200 mm (average \( d \)-spacing: 25 Å), on a pyrex wafer substrate.

#### 5.9.1 Multi-layer bender set-up

The multi-layer is connected to the bender set-up by using weak-links as is shown in Figure 5-20. The bending of the multi-layer is achieved by exerting a torque at both ends of the multi-layer. The whole set-up rests on a tripod with two legs being fixed to translation tables. One translation table is used for a rotation in \( \theta \) while the other one can be used for horizontal alignment of the set-up.
Figure 5-20: The multi-layer bender set-up. It should be noted that the horizontal alignment system is not drawn (courtesy Dr U. Lienert).

5.10 Software Development

Obtaining $\Delta I$ from the multi-layer method is less obvious than just measuring one point on the flat plateau as in the bent-Laue method, since the broad-energy X-ray band produced by the multi-layer is more or less Gaussian shaped and has thus no flat region. This means that one single measurement can not give the $\Delta II$. However, the $\Delta II$ and $\Delta \theta$ can be calculated by a mathematical analysis.

The multi-layer will generate a Gaussian-like shaped broad-energy X-ray band-pass as is shown in Figure 5-21a (solid line). When an electric field is applied, the same peak will be shifted by $\Delta \theta$ with an intensity effect of $\Delta II$ (dashed line). Taking the difference between these two peaks gives a typical difference curve as would be measured by a LIA, see Figure 5-21b.

According to elementary mathematics, each point on the rocking curve satisfies

$$\frac{\Delta I}{I} = \eta + \Delta \theta \left( \frac{\partial I}{\partial \theta} \right) \frac{1}{I},$$

where

$$\Delta I_i = I_i^+ - I_i^-$$

and
Figure 5-21: a: Plot of a typical rocking curve scan as would be obtained by means of an analyser scan (solid line) together with an electric-field-induced rocking curve with a $\Delta \theta$ and $\Delta I$ (dashed line), b: Plot of the difference curve as would be seen by the LIA.

\[ \eta = \frac{\Delta I}{I}. \]

$I_i$ represents the measured intensity at point $i$ on the rocking curve and $I_i^\circ$ is the measured intensity at point $i$ on the rocking curve corresponding to the positive/negative state of the electric field.

From the observed data points $I_i^\circ$ and $I_i$, a linear fit of $\Delta I/I_i$ versus $(\partial I/\partial \theta)/I_i$ can be applied, allowing the calculation of $\eta$ and $\Delta \theta$ as the abscissa at $(\partial I/\partial \theta)/I_i = 0$ and the slope, respectively. Note that, since the experiment uses a broad-energy X-ray band beam, all measured values of $I_i^\circ$ are in fact integrated values.

For the data analysis a background correction was applied to the measured rocking curves $I_i^\circ$ and $I_i$, i.e. the background was subtracted. In order to obtain values for $\partial I/\partial \theta$, the IDL internal derivation function Deriv was used, whereas Poly_fit was used to calculate a linear fit. Furthermore, in principle $\Delta \theta$ can be determined with the highest accuracy on the edges of the rocking curve whereas $\eta$ can be determined with the highest accuracy at the top of the rocking curve. However, the objective of this experiment was to test whether the $\eta$ can be obtained in a fast way so only the top part of the rocking curves were used.
A simulation for a two-step modulation experiment was performed on the Gaussian shaped rocking curve (solid line) of Figure 5-21a. In the same figure is shown a plot of a shifted rocking curve ($\Delta \theta = 3$ arb.u.) with an $\eta$ effect of 5.6% (dashed line). A line was fitted through the data points of $\Delta I/I$ versus $(\partial I/\partial \theta)/I$, as can be seen in Figure 5-22. The determined values of $\Delta \theta$ and $\eta$ are 3 arb.u. and 5.6%, respectively.

![Figure 5-22: Plot of $\Delta I/I$, versus $(\partial I/\partial \theta)/I$, (asterisks) and the linear fit (solid line).](image)

5.11 Experimental Station

The multi-layer experiment was performed at the Optics beam-line of the ESRF. The multi-layer was placed in the beam 39 m from the source. The generated broad-energy X-ray band beam, as set by the fixed parameters of the multi-layer, had a mean energy of 68.5 keV with an energy width of 1.4%. The set-up allowed focusing in the vertical plane, while the scattering by the sample was in the horizontal plane. The multi-layer to sample distance was 4.2 m. After the multi-layer and between the diffractometer and detector, slits were installed. The multi-layer remained unshielded. The electric field and gating system were similar to the one used in the bent-Laue method (see §5.6).

The experimental set-up of the multi-layer is shown in Figure 5-23.
5.11.1 Results and discussion

The multi-layer was used in electric field experiments on a AgGaS₂ crystal (Chapter 3). Both effects, \( \Delta \theta \) and \( \eta \), were determined for two different sets of reflections, the \((h,h,2h)\) and \((hh0)\), and their predicted linear behaviour versus the applied electric field was investigated. Furthermore, the piezoelectric constants for the [221] and [110] directions were determined.

Linear behaviour of \( \eta \) and \( \Delta \theta \) versus electric field

Various electric fields (0.3 \( \times \) 10⁶, 0.6 \( \times \) 10⁶ and 1.2 \( \times \) 10⁶ Vm⁻¹) were applied to the crystal in order to study the (linear) behaviour of \( \eta \) and \( \Delta \theta \) for the (448) reflection. The \( \eta \) and \( \Delta \theta \) values were determined from the rocking curve scans. Figure 5-24a shows the plot of \( \eta \) versus electric field, whereas Figure 5-24b shows the plot of \( \Delta \theta \) versus the electric field.

The theoretically expected linear behaviour is shown in Figure of 5-24a and 5-24b by the linear fit (solid line). When extrapolating to 0 Vm⁻¹, the value for \( \eta \) is about zero, whereas \( \Delta \theta \) deviates significantly from zero. This deviation may be caused by using only data from the top part of the rocking curve for the determination of \( \Delta \theta \) (§5.10).

Determination of piezoelectric constants

Scans were recorded for the \((h,h,2h)\) reflections, with \( h=4, 5, 6, 7 \), with an electric field of 2.6 \( \times \) 10⁶ Vm⁻¹. In Figure 5-25 the \( \Delta \theta \) obtained from Equation 5-6 is plotted versus tan\( \theta \) (line A). This plot shows that the fit is rather poor. The piezoelectric constant for the [221] direction was determined to be 6.9(5) \( \times \) 10⁻¹¹ CN⁻¹.

However, when rejecting the \( \Delta \theta \) value of the (448) reflection as being an outside acceptable values, the Barsch plot of the (5,5,10), (6,6,12) and (7,7,14) reflections is as shown in Figure 5-25 (line B). From this figure, the piezoelectric constant was determined of 4.8(1) \( \times \) 10⁻¹¹ CN⁻¹.
Figure 5-24: The linear behaviour of $\eta$ and $\Delta \theta$ versus electric field for the (448) reflection of AgGaS$_2$. a: Plot of $\eta$ versus electric field and b: Plot of $\Delta \theta$ versus electric field with their respective linear fit.

Figure 5-25: Barsch plot for the reflections (448), (5,5,10), (6,6,12) and (7,7,14). Line A (dashed) represents a least-squares fit through all data points, whereas line B (solid) is a fit through the (5,5,10), (6,6,12) and (7,7,14) data points.
Since this piezoelectric constant of the [221] is a linear combination of the piezoelectric tensor elements \(d_{14}\) and \(d_{36}\), i.e. \(2.0\times10^{-12} d_{14}+0.191 d_{36}\), a value of \(4.8(5)\times10^{-12} \text{CN}^{-1}\), calculated from the \(d_{14}\) and \(d_{36}\) values\(^{22}\) \(8.8(9)\times10^{-12}\) and \(7.6(1.8)\times10^{-12} \text{CN}^{-1}\), respectively), is expected. It is clear that the piezoelectric constant for the [221], determined from Figure 5-25 (line A), does not agree to the reported value of Graafsma et al. Unfortunately, these discrepancies still remain unclear.

To determine the piezoelectric constant of the [110] direction, i.e. \(d_{36}\), the (220), (440), (660) and (880) reflections were measured with an applied electric field of \(2.6\times10^{6} \text{V m}^{-1}\). Figure 5-26 shows the Barsch plot and the linear fit through the data points. The piezoelectric constant \(d_{36}\), based on line B of Figure 5-25, is \(8.9(9)\times10^{-12} \text{CN}^{-1}\), which agrees well with the value of \(8.8(9)\times10^{-12} \text{CN}^{-1}\) found by Graafsma et al.\(^{22}\)

![Barsch plot for the (220), (440), (660), and (880) reflections. The solid line represents a least-squares fit through the data points.](image)

**Fine structure**

A plot of the measured difference curve (solid line) of the (5,5,10) reflection with an electric field of \(2.6\times10^{6} \text{V m}^{-1}\) is shown in Figure 5-27. In the same figure a simulated difference curve is plotted (dashed line) using the \(\eta\) and \(\Delta \theta\) values of \(8(3)\times10^{-5}\) and \(2.3(1) \mu\text{rad}\), respectively, which were determined by least squares. Although the general shape of the simulated curve is in agreement with the measured difference curve, some structural irregularities can be observed which cannot be reproduced by the simulation. This kind of fine structure was visible in many other difference

100
curves of different reflections. Furthermore, the effect was reproducible for a set of scans of the same reflection.

![Graph of measured and simulated AI curve](image)

**Figure 5-27**: The measured and simulated \( \Delta I \) curve of the \((5,5,10)\) reflection of AgGaS\(_2\) with an electric field of \(2.6 \cdot 10^6\) Vm\(^{-1}\).

To comprehend this phenomenon a hypothesis was put forward that a fine structure may be present on the rocking curve. Figure 5-28a shows a simulated rocking curve with fine structure (solid line). This curve has been constructed by adding to a large Gaussian peak \( A \) two smaller Gaussian-shaped peaks (dotted lines) with their maxima being displaced equally to either side of the main maximum. The dashed line represents the rocking curve after application of an electric field, i.e. a change in Bragg angle and a change in integrated intensity. Figure 5-28b represents the difference curve (solid line) of the rocking curves with fine structure \((B \text{ and } C)\) of Figure 5-28a. Evidently, the fine structure of the rocking curve causes a fine structure in the difference curve of Figure 5-28b. In contrast, the dotted-line curve of Figure 5-28b would be the difference between the rocking curves without any fine structure.

Figure 5-29a shows the fine structure on the measured rocking curve (dotted line). From this figure, the fine structure is hardly visible in comparison to the simulation of Figure 5-28. In order to obtain the fine structure a Gaussian curve (solid line) was fitted through the observed data points (dotted line), as is depicted in Figure 5-29a, and the difference between the two curves was calculated which is shown in Figure 5-29b. From this plot it can be concluded that the fine structure on the measured difference curve of Figure 5-27 originates from a fine structure on the rocking curve.
Figure 5-28: a: Construction of a rocking curve with fine structure (solid line) and a displaced one (dashed line), by summation of a Gaussian-like curve with two smaller Gaussian-like curves (dotted lines), b: The difference curves of the two fine structured curves (solid line) and ideal curves (dashed-line).

Figure 5-29: a: Fine structure on the measured rocking curve (dotted line) of the (5,5,10) reflection of AgGaS$_2$ and the fitted gauss curve (solid line), b: The difference plot of the measured rocking curve and the fitted Gaussian curve shows the fine structure in detail.

The simulated fine structure found in Figure 5-29b was applied to the simulated difference curve of Figure 5-27. Combining a normal (Gaussian) rocking curve (Fig. 5-29a) with the determined small Gaussian curves (height, width and position determined from Fig. 5-29b) and the effect of the applied electric field ($\Delta \theta$ and $\eta$), results in a rocking curve with fine structure as is shown in Figure
5-30a. Although the obtained fit (solid line) resembles the general shape of the measured rocking curve (dotted line), no perfect overlap is achieved.

Figure 5-30: a: New simulated difference curve (solid line) containing a fine structure caused by addition of small Gaussian shaped peaks using the same determined $\eta$ and $\Delta \theta$ values of Figure 5-26b, b: Allowing a different $\Delta \theta$ for the small curves.

A second hypothesis has been investigated also, in which the fine structure has a different $\Delta \theta$ than the one of the main reflection. Figure 5-30b shows an improved agreement between the measured curve (dotted line) and the simulated curve (solid line) using different values $\Delta \theta$ for the fine structure and the main peak. Likewise, a fine structure was observed in the corresponding phase signal, as is shown in Figure 5-31 (solid line). For comparison, the fine structure on the difference curve (squares) is plotted in the same figure. As can be seen, both fine structures appear to be related to each other and a phase jump of 180°, where $\Delta l=0$ V, is clearly visible at $\theta=8.22^\circ$.

A possible source of the fine structure on the measured rocking curves may stem from imperfections within the crystal that somehow react differently to the electric-field, in speed as well as in change of Bragg angle, than the bulk of the crystal does. A similar effect was found by Stähler et al.\textsuperscript{[23]} in a stoichiometric LiNbO$_3$ sample, where surface layers under the Al electrodes differ in the $c$-axis by $6 \times 10^{-4} \Delta c/c$ from the bulk.
It should be noted that as long as the fine structure on the $\Delta l$ curve remains small, no problems in the determination of the $\eta$ and $\Delta \theta$ are to be expected. However, a large fine structure may be a source for systematic errors in the determination of $\eta$ and $\Delta \theta$.

![Figure 5-31: Fine structure on the phase signal (solid line) and projection of the fine structure (squares) on the difference curve.](image)

### 5.12 Conclusion

It has been shown that the combination of a white-beam source, such as a bending-magnet or wiggler, with a bent-Laue monochromator crystal and correct absorbers can give a broad-energy X-ray band-pass beam sufficiently flat for diffraction experiments on a crystal subjected to an external electric field. The general slope of the intensity distribution can be controlled easily by adjustment of the wiggler gap, vertical beam size and absorber thickness. Beam-line components, i.e. unpolished Be windows and C absorbers, will give a fine structure in the beam due to phase contrast. This fine structure can be reduced by using a reflection with a wider reflection curve (spatial averaging). The combination of this wide-band-pass beam with a high count-rate detector and a sensitive lock-in amplifier permits the measurements of changes in integrated intensity less than $0.001\%$ within seconds. The difference profiles obtained with the wide-band-pass beam also contained information on peak shift and peak deformation, although in a less direct way than for classical measurements, with a high degree of monochromaticity. The increase in measurement speed is two orders of magnitude, making a full structural study possible within a reasonable time. This opens the way to a wide range of new experiments, where small changes in diffracted intensity are induced by external perturbations, not limited to electric fields. The broad-energy X-ray band-pass monochromator could also be used for standard structure determinations, where one is merely
interested in integrated intensities. In this case, however, background subtraction needs special attention.

On the contrary, the multi-layer generates a broad-energy X-ray band without a flat region. Hence, no direct distinction can be made between $\Delta l$ and $\Delta \theta$ (and/or peak deformation), implying that both effects have to determined by analytical methods so that a (partial) profile scan is needed. The multi-layer method is less versatile in its application, i.e. only a few parameters can be adjusted (such as the Bragg angle) and the absence of a flat-topped profile makes it less suited for perturbation experiments.

For both methods the initial objective of measuring one single data point could not be met since phase contrast was observed in the bent-Laue method and no flat plateau could be generated by the multi-layer method.

References


