X-ray dynamic diffraction of crystalline multilayers and superlattices

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Abstract

Contents

1 Introduction

The discovery of X-ray diffraction in crystals by Laue, Fridrich and Knipping in 1912 served as the starting point for the development of scientific research along a number of important lines. One of the first and best-known lines of investigation, which advanced rapidly as a result of the discovery, was X-ray analysis of the atomic structure of crystals. The huge amount of experimental data on X-ray structural studies accumulated over more than half century was one of the most important preconditions for developing solid-state physics and chemistry, on the one hand, and the production, processing, and utilization of many materials of contemporary technology, on the other.

Inspired by the result of Fridrich's and Knipping's experiment, Laue devised the simplest theory of three-dimensional diffraction and interference. It was referred to as geometrical or kinematical theory. A characteristics feature of kinematical theory is that it takes into account only the interactions of each atom with the primary, or refracted, wave in a crystal. It neglects the interaction of an atom with the wave field induced in the crystal by the collettive scattering of all the other atoms. In other words it ignores the interaction of the diffracted waves with the refracted one. The kinematical theory is a good first approximation, when applied to highly imperfect crystals consisting of very small mosaic blocks. For the highly perfect type of crystal however, it is necessary to use the more rigorous dynamical theory, and grossly incorrect results would be obtained by using the kinematical approximation.

2 Dynamical theory of diffraction

As the incident wave propagates down into a perfect crystal its amplitude diminishes, as a small fraction is reflected into the exit beam as it passes through each atomic plane. In addition there is a chance that the reflected beam will be re-scattered into the direction of the incident beam before it has left the crystal. The theory which has been developed to allow for these multiple scattering effects is known as dynamical diffraction theory.
In the method first developed by C. G. Darwin in 1914, the crystal is treated as an infinite stack of atomic planes, each of which gives rise to a weak reflected wave which may subsequently be re-scattered into the direction of the incident beam.

2.1 One atomic layer: reflection and transmission

We consider first the reflection from a single layer of unit cells in the Bragg case. Let the incident beam be σ-polarized (i.e. the electric field is parallel to the layer) and have a wavelength λ. We can calculate the amplitude of the reflected and transmitted beams by considering the radiation scattered from an element of area $d\epsilon d\eta$ and integrating over the layer. We obtain the following expression for the instantaneous value of the electric field at point P (figure 1)

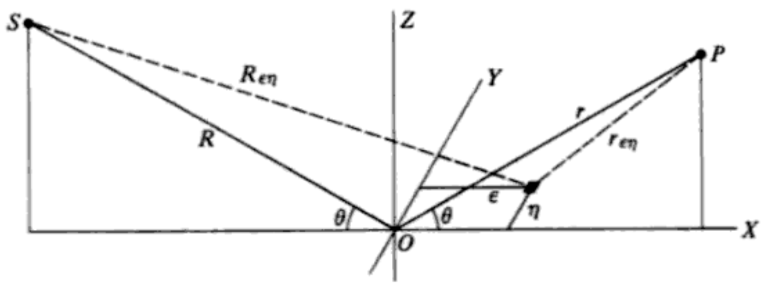


Figure 1

$$E_P = -ig_{\mathbf{H}} E_O e^{(2\pi i/\lambda)[(R+r)-ct]}. \tag{1}$$

We introduced the abbreviation

$$g_{\mathbf{H}} = r_e \frac{\lambda F_{\mathbf{H}} d}{V \sin\theta_B} \tag{2}$$

where $r_e = \frac{e^2}{mc^2} = 2.818 \cdot 10^{-5} \mathring{A}$ is the classical electron radius, $F_{\mathbf{H}}$ is the structure factor for the reciprocal lattice vector $\mathbf{H}$, d is the spacing of the reflecting planes, V is the volume of the unit cell and θ_B is the Bragg angle.

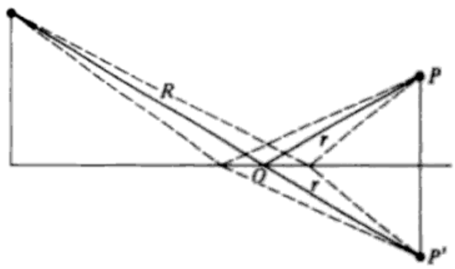


Figure 2

Similarly, the electric field in the beam which has passed through a layer of unit cells is expressed by

$$E_{P'} = (1 - ig_0) E_O e^{(2\pi i/\lambda)[(R+r)-ct]} \tag{3}$$

where

$$g_0 = r_e \frac{\lambda F_0 d}{V \sin\theta_B}. \tag{4}$$

Since V is of order d^3, $g_{\mathbf{H}}$ and g_0 are of order $r_0/d \simeq 10^{-5} \ll 1$.

2.2 Diffraction from a set of atomic planes

We now turn our attention to the problem of how to calculate the scattering from an infinite stack of atomic planes, where each one reflects and transmits the incident wave according to the equations given in section 2.1. The planes are labelled by the index r, with the surface plane defined by $r = 0$. The objective is to calculate the amplitude reflectivity, which is the ratio of the total reflected wavefield S_0 to that of the incident field T_0.
Both outside and within the crystal there are two wavefields: the T field propagating in the direction of the incident beam , and the S field in the direction of the reflected beam (figure 3).

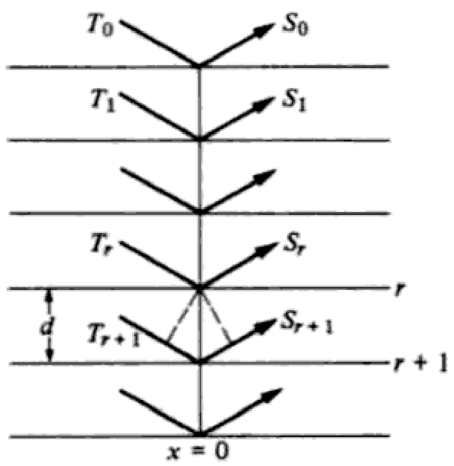


Figure 3

The derivation of Bragg's law relies on the fact that the reflected wave from layer $r + 1$ is in phase with the one from layer r if the pathlength differs by an integer number of wavelengths.

$$2 \sin \theta_B = m\lambda \tag{5}$$

As we are interested in deriving the (small) bandwidth of the reflecting region, the phase is restricted to small deviations about $m\pi$, and the phase is given by

$$\phi = m\pi + \Delta \tag{6}$$

where Δ is a small parameter. In our development of Darwin's theory Δ will be used as the independent variable.
Let the T field just above layer r on the z axis be denoted T_r, and similarly for S_r. On being transmitted through the rth layer, the S field just above layer $r + 1$ changes its phase according to equation 3, so that S_r can be written as $(1 - ig_0)S_{r+1}e^{i\phi}$. To obtain

the total field, we must also add the part due to the reflection of the wave T_r. In total then we have

$$S_r = -ig_{\mathbf{H}}T_r + (1 - ig_0)S_{r+1}e^{i\phi} \tag{7}$$

Next consider the T field just below the rth layer. The phase is shifted by ϕ. This field is composed of contributions from the field T_r after it has been transmitted through the rth layer, and from the wave $S_{r+1}e^{i\phi}$ after it has been reflected from the bottom of the rth layer. This leads to the second difference equation

$$T_{r+1}e^{-i\phi} = (1 - ig_0)T_r - ig_{\bar{\mathbf{H}}}S_{r+1}e^{i\phi} \tag{8}$$

A suitable trial solution for 7 and 8 including a phase shift and attenuation has the form

$$T_{r+1} = e^{-\chi}e^{im\pi}T_r \tag{9}$$

$$S_{r+1} = e^{-\chi}e^{im\pi}S_r \tag{10}$$

where χ is a general complex. We can now insert our trial solution into the equations. Noting that $e^{-i\phi} = e^{-im\pi}e^{-i\Delta}$ and expanding all the small parameters to second-order terms yields

$$\chi^2 = g_{\mathbf{H}}g_{\bar{\mathbf{H}}} - (\Delta - g_0)^2 \tag{11}$$

which has the solution

$$i\chi = \pm\sqrt{(\Delta - g_0)^2 - g_{\mathbf{H}}g_{\bar{\mathbf{H}}}}. \tag{12}$$

We can now calculate the amplitude reflectivity by inserting our solutions into equation 7. Let g be equal to $\sqrt{g_{\mathbf{H}}g_{\bar{\mathbf{H}}}}$. We obtain

$$X_R = \frac{S_0}{T_0} \simeq \frac{g}{i\chi + (\Delta - g_0)} \tag{13}$$

In order to obtain explicit formulae for the Darwin reflectivity curve the variable η is introduced and defined by

$$\eta = \frac{\Delta - g_0}{g}. \tag{14}$$

From equation 13 the amplitude reflectivity curve in terms of η is

$$X_R = \frac{S_0}{T_0} = \begin{cases} \eta - \sqrt{\eta^2 - 1} & \text{for } \eta \geq 1 \\ \eta - i\sqrt{1 - \eta^2} & \text{for } |\eta| \leq 1 \\ \eta + \sqrt{\eta^2 - 1} & \text{for } \eta \leq -1 \end{cases} \tag{15}$$

2.3 General case: substrate

In general the surface of the crystal will not be parallel to the atomic planes which reflect the incident beam, as shown in picture X. This implies a compression of the width of the exit beam. The asymmetry parameter b is defined as

$$b = \frac{\gamma_0}{\gamma_{\mathbf{H}}} \tag{16}$$

where γ_0 is the cosine of the angle between the incident beam and the surface normal and γ_H is the cosine of the angle between the diffracted beam and the surface normal (in the Bragg case b is always negative).
Equation 15 is still valid in the asymmetric case if we include the asymmetric parameter in the variable η as follows

$$\eta = \frac{-b\Delta - g_0(1-b)/2}{|b|^{1/2}g} \tag{17}$$

From equations 5 and 6 and using the fact that Δ is small we obtain

$$\Delta = \frac{2\cos\theta_B \pi d}{\lambda}(\theta - \theta_B) \tag{18}$$

Substitution of the expressions 2, 4 and 18 into equation 17 leads to a new expression for η

$$\eta = \frac{-b(\theta-\theta_B)\sin 2\theta_B - \frac{1}{2}\Gamma F_0(1-b)}{|b|^{1/2}C\Gamma(F_{\mathbf{H}}F_{\bar{\mathbf{H}}})}. \tag{19}$$

2.4 General case: epitaxial layer

In a similar way it is also possible to use dynamical theory to calculate the reflected and transmitted amplitude ratios (X_R and X_T) for layers of arbitrary thickness t. For convenience we introduce the parameters

$$T = \pi\Gamma(F_{\mathbf{H}}F_{\bar{\mathbf{H}}})^{1/2}\frac{t}{\lambda|\gamma_0\gamma_{\mathbf{H}}|^{1/2}} \tag{20}$$

$$\alpha = T(\eta^2-1)^{1/2} \tag{21}$$

$$Q = (\eta^2-1)^{1/2}\cos\alpha + i\eta\sin\alpha. \tag{22}$$

where η is the variable we defined in equation 19.
The equations for X_R and X_T reduce to

$$X_R = \frac{i\sin\alpha}{Q} \tag{23}$$

$$X_T = \frac{(\eta^2-1)^{1/2}}{Q}. \tag{24}$$

2.5 Recursion formulae

When an epitaxial layer with reflected and transmitted amplitude ratios X_R^1 and X_T^1 is added to a substrate with ratios X_R^0, X_T^0, the new amplitude ratios X_t, W for the crystal can be derived in a recursive way as follows

$$X_t = X_T^1 Y + X_R^1 \tag{25}$$

$$Z = X_R^1 Y + X_T^1 \tag{26}$$

$$Y = X_R^0 Z \tag{27}$$

$$W = X_T^0 Z. \tag{28}$$

After substitution, we obtain the reflected and transmitted amplitude ratios for the sample

$$X_t = \frac{X_R^1 - X_R^0({X_R^1}^2 - {X_T^1}^2)}{1 - X_R^0 X_R^1} \tag{29}$$

$$W = \frac{X_T^0 X_T^1}{1 - X_R^0 X_R^1}. \tag{30}$$

3 Implementation

In order to simulate the rocking curves of strained crystals, multilayers and superlattices in the dynamical theory, a Python program has been developed. The program *dynXRD* is applicable to any coplanar and non-coplanar Bragg-case geometry (see section 3.2) and to crystals with any number of different layers. Layers with arbitrary strain profile are also implemented (see section 3.3). At the moment perpendicular (σ) polarization is the only one enabled, but parallel (π) and mixed polarizations may be included in the future. The program requires *pyasf* () for the definition of the crystal structure and for the calculation of the structure factors.

3.1 Structure

The program calculates the reflected and transmitted amplitude ratios for an instance object of the class *Sample*. A *Sample* object is nothing but a sequence of other objects of the class *Epitaxial_Layer*.
For each *Epitaxial_Layer* the following attributes have to be given:

- **structure** of the crystal, which is taken from a *.cif* file
- **thickness** of the layer in Angstrom
- **R** matrix, i.e. a rotation matrix containing information about the orientation of the unit cell with respect to the surface of the sample
- **Miller** indices of the considered Bragg reflection.

A special type of *Epitaxial_Layer* is defined by the class *Substrate*. The thickness of a *Substrate* is set to be infinity and the transmitted amplitude is zero. A *Sample* is then made of a *Substrate* object and a list of *Epitaxial_Layer* objects.
Once the Miller indices (with respect to the substrate) are given by the user through the method *Sample.set_Miller*, the program calculates the $\mathbf{q}$ vector in the sample system by using rotation matrices. The Miller indices with respect to a layer are then obtained as the integers which best approximate the coordinates of the $\mathbf{q}$ vector in the reciprocal lattice system of the crystal. As a result we get the reciprocal space vector which corresponds to the Bragg case for the layer. The expressions for the angles between the incident beam and these vectors are then calculated with the method *Sample.calc_theta_layer*. After evaluation of these expressions we get the angle θ to insert in equation 19.

3.2 Geometrical parameters

The geometry of each crystal layer is needed in order to calculate the change in the angle θ and the quantities γ_0 and $\gamma_{\mathbf{H}}$ that we used to define the asymmetry parameter b (equation 16).
Let $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ be the lattice vector and $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ the reciprocal lattice vectors. Let $\hat{x}$, $\hat{y}$ and $\hat{z}$ be the unit vectors of the sample system, such that the normal to the sample surface is parallel to $\hat{z}$ and that $\hat{x}$ lies on the scattering plane. The geometry of the crystal layers can be specified in 2 different ways. With the method *Epitaxial_Layer.calc_orientation* the user can set the coordinates in the reciprocal lattice system of two vectors $\mathbf{v}_\perp$ and $\mathbf{v}_\parallel$ which are respectively parallel to $\hat{z}$ and $\hat{x}$. The two vectors given should be perpendicular by definition. If this is not the case an error message is printed. To prevent this, the method *Epitaxial_Layer.calc_orientation_from_angle* was developed: the user can give as input an angle ψ, which is the angle between $\mathbf{v}_\parallel$ and a reference vector $\mathbf{p}$. The vector $\mathbf{p}$ is defined as the vector perpendicular to $\mathbf{b}^*$ and $\mathbf{v}_\perp$:

$$\mathbf{p} = \mathbf{b}^* \times \mathbf{v}_\perp. \tag{31}$$

If $\mathbf{b}^*$ and $\mathbf{v}_\perp$ are parallel then $\mathbf{p}$ is defined as

$$\mathbf{p} = \mathbf{v}_\perp \times \mathbf{c}^* \tag{32}$$

Specification of $\mathbf{v}_\parallel$ is no longer required since it can be calculated from ψ. Now $\mathbf{v}_\parallel$ is automatically perpendicular to $\mathbf{v}_\perp$ and no errors occur.
The vector $\mathbf{v}_\perp$ and $\mathbf{v}_\parallel$ specify the geometry of the reflection. If $\mathbf{v}_\perp$ and $\mathbf{H}$ are parallel - i.e. if the asymmetry factor b is equal to -1 - the reflection is *symmetric*. If this condition is not fulfilled the reflection is said to be *asymmetric*. We call the geometry *coplanar* where the incident wave vector $\mathbf{k_0}$, the reciprocal lattice vector $\mathbf{H}$, and the surface normal $\mathbf{n}$ lie in the same plane or equivalently when $\mathbf{v}_\parallel$, $\mathbf{v}_\perp$ and $\mathbf{H}$ are coplanar.

3.3 Strained crystals

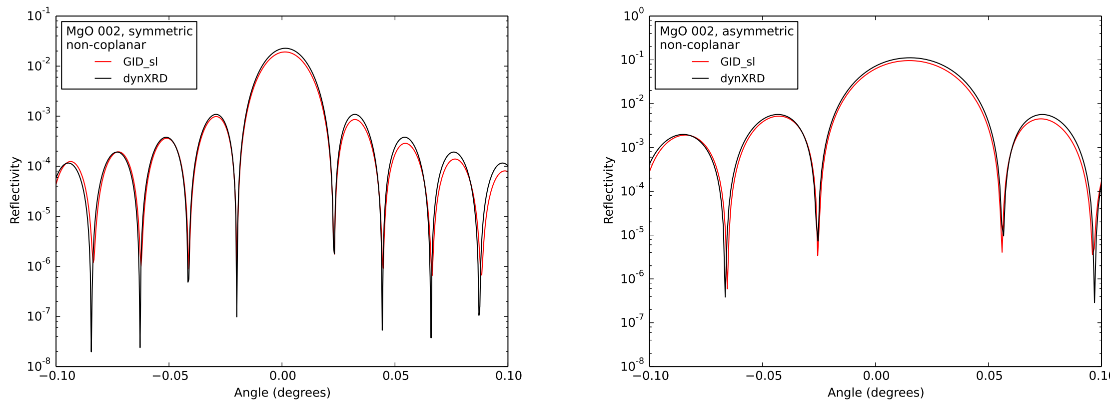
The recursion formulae (29) and (30) can be used for samples made of different epitaxial layers, but also hold for a single crystal with a given strain profile. The strained crystal is treated as a stack of layers with constant strain. To do so a new class of *Epitaxial_Layer* was defined. An instance of a *Strained_Layer* requires two arrays of the same length: an array containing the depths (distances from the substrate surface) and an array containing the strain of a lattice parameter (for example $\frac{\Delta a}{a}$) at different depths.
The amplitudes of the reflected and transmitted beams are calculated for each sublayer with constant strain by substituting the value of the modified lattice parameter in the expressions and using equations 23 and 24. The total amplitudes of the layer are then obtained by iterating the formulas 29 and 30 through all sublayers.

4 Results

The program *dynXRD* was first tested by comparing the results with the program *GID_sl* created by Sergey Stepanov (`http://x-server.gmca.aps.anl.gov/GID_sl.html`). Some examples are reported in sections 4.1 and 4.2. Results for strained layers also match with the rocking curves calculated by Bartels, Hornstra and Lobeek [1] (figure 7). In section 4.3 simulation and experimental data are compared in order to get information about the strain profile of the sample.

4.1 Rocking curves of crystalline multilayers

Figure 4 shows the simulated rocking curves of a MgO (cubic unit cell) layer of thickness 100 nm for a 002 reflection with energy 10 keV and different geometries.

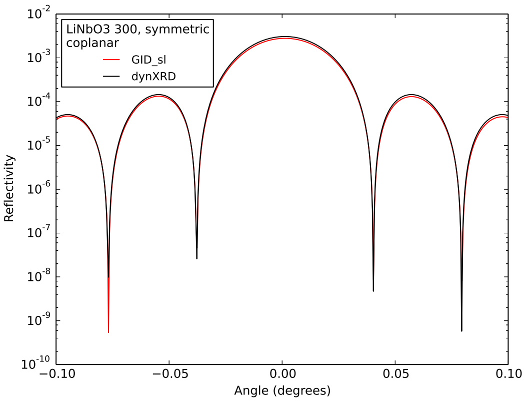


(a) Symmetric case: $v_{\parallel} = (1, -1, 0)$, $v_{\perp} = (1, 1, 1)$.

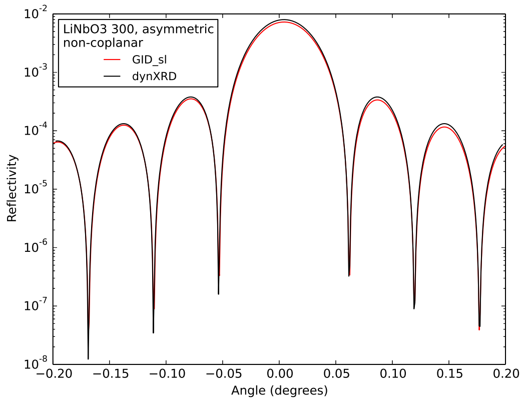
(b) Asymmetric case: $v_{\parallel} = (3, -2, -1)$, $v_{\perp} = (1, 1, 1)$.

Figure 4: 002 reflection for a MgO layer of thickness 100 nm in non-coplanar geometry.

The plots in figure 5 show the reflectivity of a $LiNbO_3$ (trigonal unit cell) layer of thickness 100 nm for a 300 reflection with energy 10 keV.

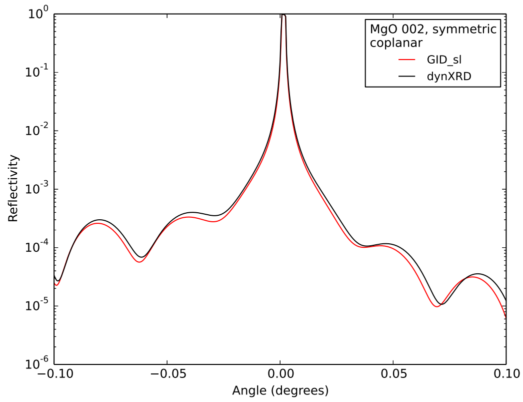


(a) Symmetric, coplanar case: $v_{\parallel} = (0, 0, 1)$, $v_{\perp} = (1, 0, 0)$.

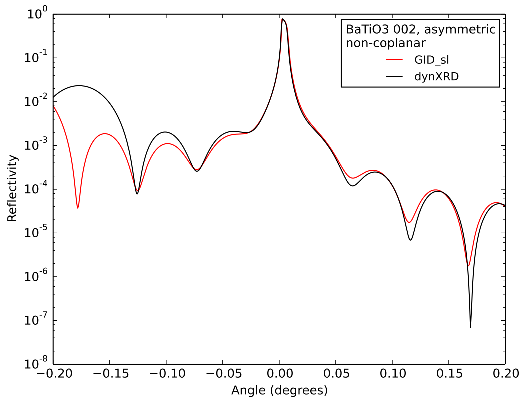


(b) Asymmetric, non-coplanar case: $v_{\parallel} = (-1, 1, 4)$, $v_{\perp} = (1, 1, 0)$.

Figure 5: 300 reflection for a LiNbO$_3$ layer of thickness 100 nm.



(a)



(b)

Figure 6

It can be noted that simulations made with *GID_sl* and *dynXRD* give analogous results in all cases even though the methods used by the programs are different.

4.2 Diffraction profiles of strained crystals

Simulations of strained crystals are shown in figure 6.

4.3 Comparison with experimental data

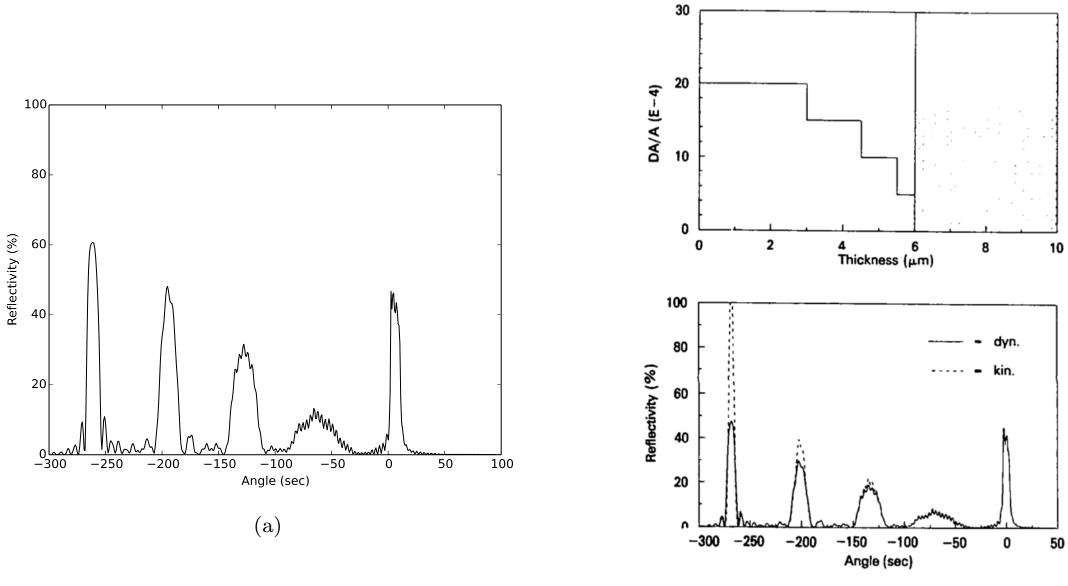


Figure 7

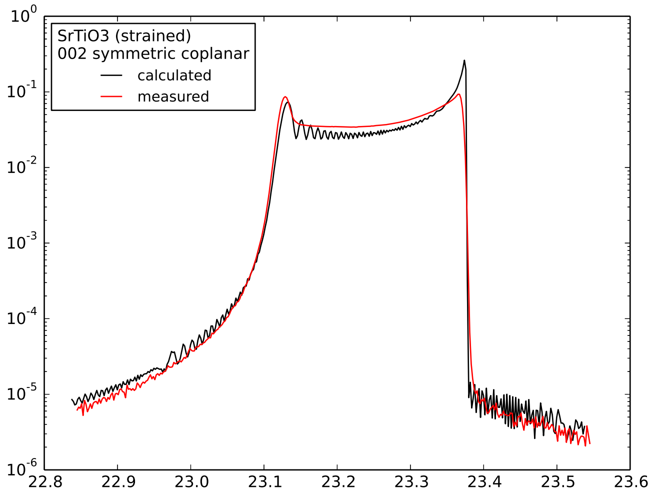


Figure 8

References

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