

Solid State Physics - IM2601

Laboration 1

Fredrik Forsberg¹, Jim Holmström¹, and Samuel Zackrisson¹

¹Engineering Physics, Royal Institute of Technology

¹{fforsber, jimho, samuelz}@kth.se

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1 Introduction

The standard method for characterization of any material's crystalline structure is X-ray diffraction, also known as XRD. By studying how the X-rays reflects from the crystalline material, one can get an understanding of the material's properties and structure.

In this laboratory we are faced with two main tasks. Firstly, to compute the wavelength (λ) of the X-rays, by measuring the diffraction behavior of NaCl and comparing it to our theoretically calculated values. Secondly, for four samples, labeled A, B, C and D, determine either the material in question or the orientation of the crystal plane of said material.

2 Experiment procedure

2.1 $\beta - 2\beta$ scan

We can describe the reflection of an X-ray beam by treating it as specular (mirrorlike) and assuming elastic scattering. Based on these premises Bragg's law holds [1].

$$2 \cdot d(hkl) \cdot \sin(\theta) = \lambda \quad (1)$$

$d(hkl)$ is the distance between parallel lattice planes of the configuration $(h, k, l) \in (2\mathbb{Z})^3$ characterizing the reciprocal lattice vector $\mathbf{G} = \frac{2\pi}{a}(h, k, l)$. a is here the lattice constant - a material parameter. $d(hkl)$ can be normalized and shown to be equal to $\frac{2\pi}{|\mathbf{G}|} = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$ [1]. In this laboratory we use a $\beta - 2\beta$ scan, also known as coupled

mode scan. The incident beam hits the sample at an angle β , which is the same as the angle of the reflected beam. This is done by rotating the sample to an angle β and subsequently moving the detector to an angle of 2β , as shown in figure 1.

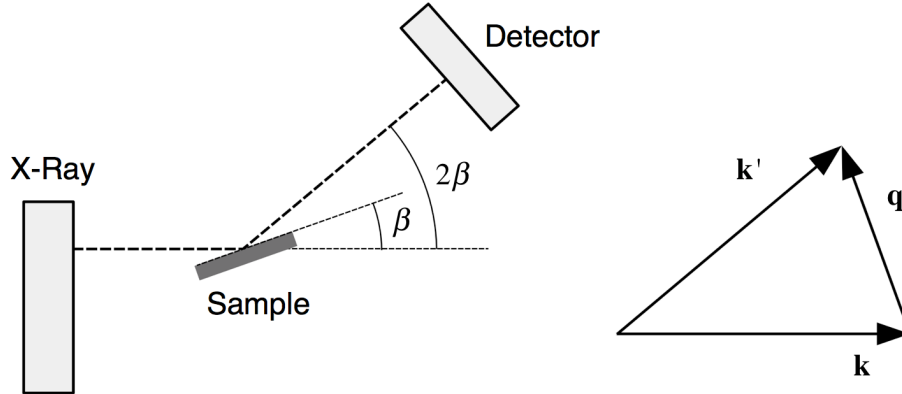


Figure 1: The $\beta - 2\beta$ scan setup and visualization of corresponding wave vector in reciprocal space

The scattering vector \mathbf{q} equals to the difference between the outgoing and incoming wavevectors, $\mathbf{k}' - \mathbf{k}$. By equation (20) in chapter 2 from Kittel [1] the scattering amplitude F is theoretically found to be

$$F = \sum_{\mathbf{G}} \int dV n_{\mathbf{G}} e^{i(\mathbf{G} - \mathbf{q}) \cdot \mathbf{r}} \quad (2)$$

When the scattering vector equals a particular reciprocal lattice vector, $\mathbf{q} = \mathbf{G}$, the intensity of the reflection will peak in the diffractogram if the structure factor allows it. This occurs since when \mathbf{q} differs significantly from \mathbf{G} , F will become negligibly small. In coupled mode the scattering vector will be normal to the crystal plane, and thus a multiple of the Miller index. The possible \mathbf{G} -vectors are integer multiples of the Miller index.

In bounded mode the scattering vector \mathbf{q} is altered only by the single angle β . The length of the scattering vector can be determined from figure 1 as $|\mathbf{q}| = 2|\mathbf{k}| \sin(\beta)$. This means in that \mathbf{q} is bounded by β which creates the limitation $2|\mathbf{k}| \sin(\beta_{min}) < |\mathbf{q}| < 2|\mathbf{k}| \sin(\beta_{max})$. A great limitation is furthermore that in coupled mode, only beams reflected off planes with normals parallel to the scattering vector might be measured by the detector. The covered space of the reciprocal space is therefore only a limited curve. If we didn't have coupled mode on, then we could have freely moved the detector for every angle β and therefore gained more information and another degree of freedom.

In short, the locus of scattering vectors in reciprocal space is a line segment along the normal to the crystal plane cut.

A Leybold Didactic diffractometer (no. 554 811) was used in this laboratory. The measurements were all made in coupled mode (i.e $\beta - 2\beta$ scan). The default settings for the diffractometer were a voltage of 35 kV (maximal), a current of 1 mA (minimal) and a step angle of 0.1° (minimal). For the NaCl measurement, a time step of 1 s and incident angles from 2.5° to 30° were used. The other samples were measured with a time step of 4 s and incident angles from 2.5° to 35° . The measurement result of the reflected intensity (number of photons hitting the GM-counter per second) and its corresponding incident angle β was automatically recorded during the laboratory. The peaks were thereafter manually detected by searching for distinct local maxima. The first maximum, with a broader peak, come from the bremsstrahlung and do not concern this experiment, thus omitted.

2.2 Structure factors

The structure factor must be nonzero for a diffraction peak to appear. The structure factor $S_{\mathbf{G}}$ of crystal structures are calculated here using methods given in [1]. Here n is the number of atoms in the basic lattice, and atom j is at position \mathbf{r}_j with atomic form factor f_j . The atomic form factors are approximately equal to the atomic number.

$$S_{\mathbf{G}} = \sum_{j=1}^n f_j e^{-i(\mathbf{r}_j \cdot \mathbf{G})}$$

As $\mathbf{G} = \frac{2\pi}{a}(h, k, l)$ the structure factor of an fcc lattice with lattice constant a is

$$S_{\mathbf{G}}^{fcc} = f \cdot \left[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{l+h} \right]$$

The fcc structure factor is nonzero if and only if h , k and l are all even or all odd.

2.2.1 NaCl

The two atoms in the conventional cell of NaCl, one Na and one Cl, are each in an fcc structure. Putting an Na at the origin, the Cl structure will be displaced by $\frac{a}{2}\mathbf{e}_x$. The structure factor sums can then be expressed using the fcc structure factor above as

$$\begin{aligned} S_{\mathbf{G}}^{NaCl} &= \left(f_{Na} + f_{Cl} e^{2\pi i \cdot \frac{h}{2}} \right) \cdot \left[1 + (-1)^{h+k} + (-1)^{k+l} + (-1)^{l+h} \right] \\ &= \left(f_{Na} + f_{Cl} (-1)^h \right) \cdot S_{\mathbf{G}}^{fcc} \end{aligned}$$

Taking $f_{Na} = 11$ and $f_{Cl} = 17$ - the atomic numbers - the structure factor will only be 0 when the fcc part is $S_{\mathbf{G}}^{fcc} = 0$.

NaCl has lattice parameter 5.63 \AA .

2.2.2 Si

Silicon is monoatomic with two atoms in the conventional cell, at $(0, 0, 0)$ and at $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The structure factor becomes

$$S_{\mathbf{G}}^{Si} = f_{Si} \cdot \left(1 + e^{\pi i \frac{h+k+l}{2}}\right) \cdot S_{\mathbf{G}}^{fcc}$$

This structure factor is 0 whenever $S_{\mathbf{G}}^{fcc} = 0$. It also disappears when $h + k + l \equiv_4 2$, as this makes $\left(1 + e^{\pi i \frac{h+k+l}{2}}\right) = 0$.

Si has lattice parameter 5.43 Å.

2.2.3 InP and GaAs

The remaining two crystals in this lab both have a zincblende structure with two atomic factors, f_{α} and f_{β} . The α -atoms are in an fcc structure starting at the origin and the β -atoms are displaced by $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, again in a cubic fcc structure. The structure factor becomes

$$S_{\mathbf{G}}^{\alpha\beta} = \left(f_{\alpha} + f_{\beta} e^{\pi i \frac{h+k+l}{2}}\right) \cdot S_{\mathbf{G}}^{fcc}$$

The atomic form factors are $f_{Ga} = 31$, $f_{As} = 33$, $f_{In} = 49$ and $f_P = 15$. The structure factor for InP is only zero if and only if the fcc structure factor is zero, because the atomic form factors are very different. The structure factor for GaAs is also 0 in that case. However, the structure factor becomes small when $h + k + l \equiv_4 2$. The atomic form factors are near equal so GaAs is expected to have a small structure factor when $S_{\mathbf{G}}^{Si} = 0$.

The lattice parameters of InP and GaAs are 5.87 Å and 5.65 Å.

3 Measurements results

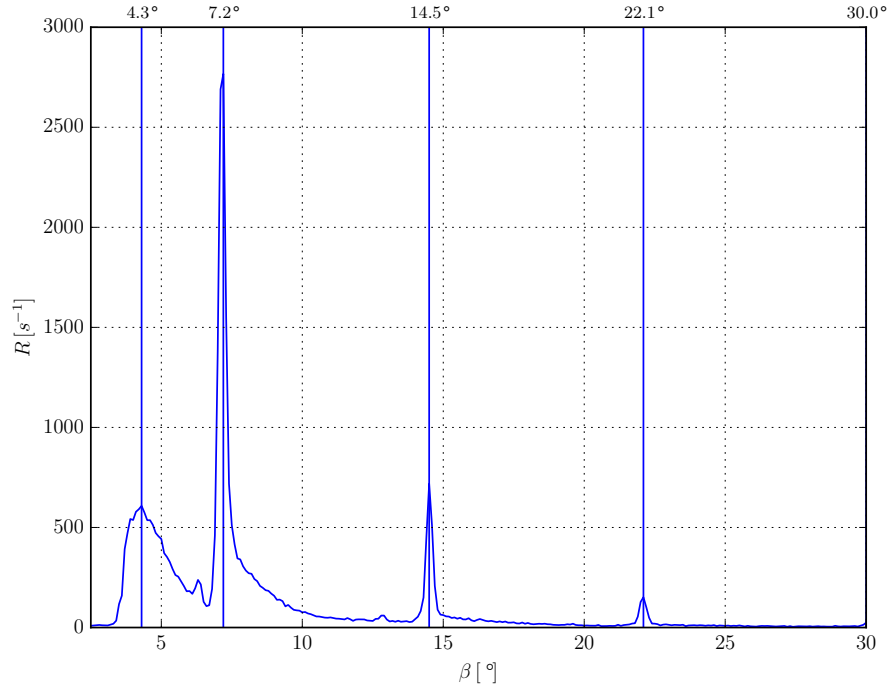


Figure 2: Diffractogram with $\beta - 2\beta$ scan of sample NaCl with automatically extracted peaks (not all are considered diffraction peaks) and their corresponding values.

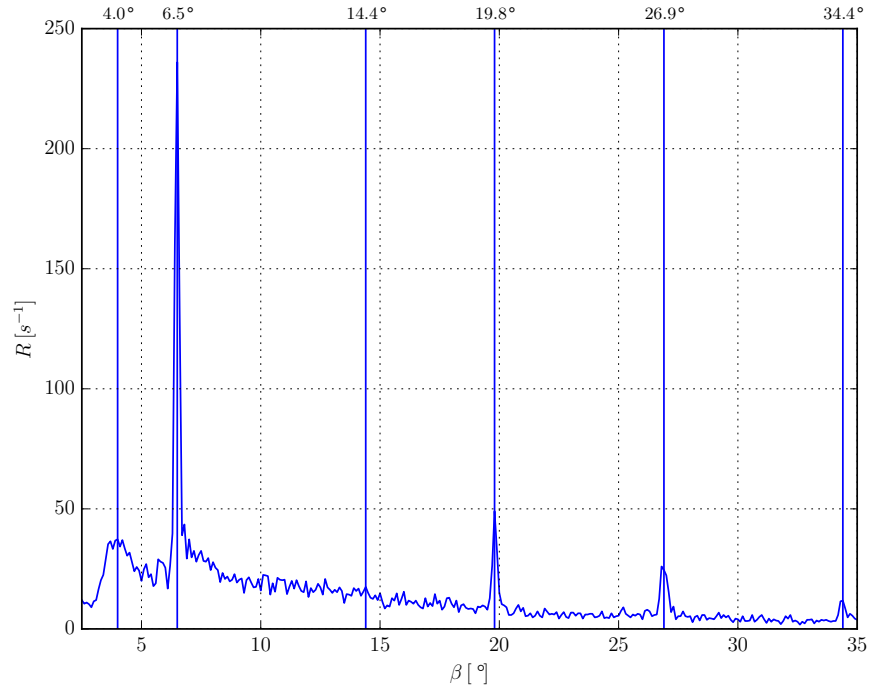


Figure 3: Diffractogram with $\beta-2\beta$ scan of sample A with automatically extracted peaks (not all are considered diffraction peaks) and their corresponding values.

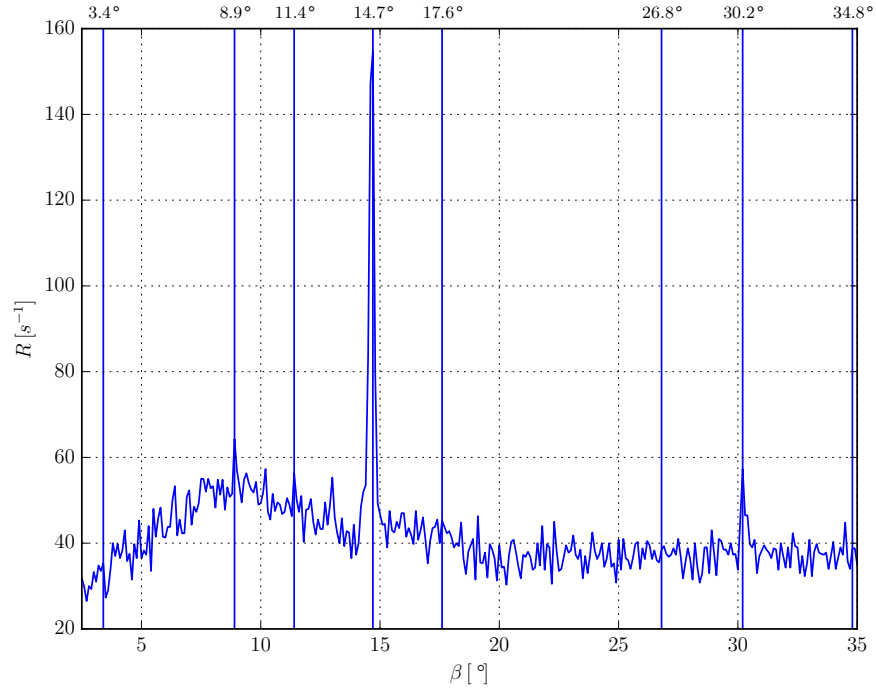


Figure 4: Diffractogram with $\beta-2\beta$ scan of sample B with automatically extracted peaks (not all are considered diffraction peaks) and their corresponding values.

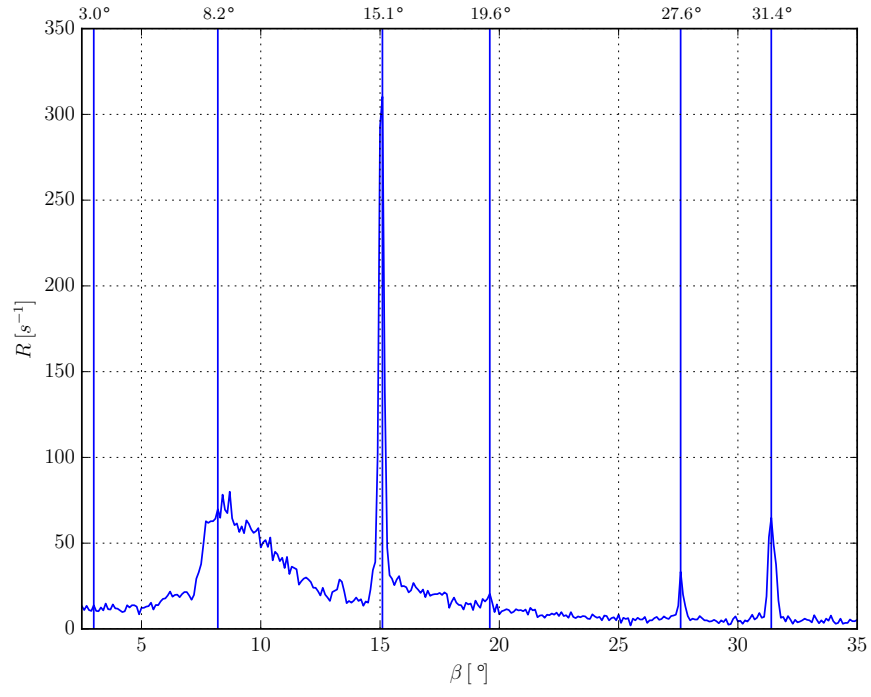


Figure 5: Diffractogram with $\beta-2\beta$ scan of sample C with automatically extracted peaks (not all are considered diffraction peaks) and their corresponding values.

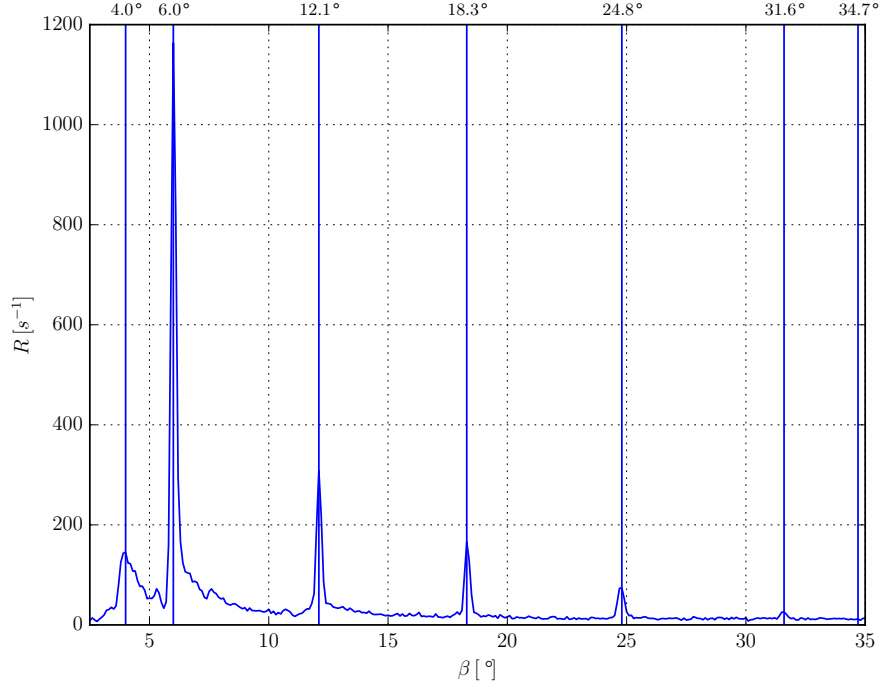


Figure 6: Diffractogram with $\beta-2\beta$ scan of sample D with automatically extracted peaks (not all are considered diffraction peaks) and their corresponding values.

| | NaCl | A | B | C | D |
|-----------|-------|-------|-------|-------|-------|
| β_1 | 7.2° | 6.5° | 14.7° | 15.1° | 6.0° |
| β_2 | 14.5° | 19.8° | 30.2° | 27.6° | 12.1° |
| β_3 | 22.1° | 26.9° | - | 31.4° | 18.3° |
| β_4 | - | 34.4° | - | - | 24.8° |

4 Discussion of the results

4.1 Finding the X-ray wavelength from the NaCl diffraction pattern

The crystal surface is cut parallel to the 100 lattice plane. In coupled mode the hkl -vectors will be integer multiples of this Miller index. $\mathbf{G} = \frac{2\pi}{a}(m, 0, 0)$ where m is an integer. The structure factor for NaCl is nonzero when h, k, l are all even or all odd. This happens when m is even. From (1) our diffraction maxima occurs when

$$\frac{2a}{n} \sin\theta = \lambda$$

where $a = 5.63 \text{ \AA}$.

As the (the X-ray wavelength) is constant an increasing angle comes with increasing m . The first maximum occurs for $m = 2$, the second for $m = 4$ et cetera. Calculating λ by inserting the measured peak angles give the following values for the X-ray wavelength.

| Angle | | m | λ |
|-----------|--------------|-------------------|---------------------|
| β_1 | 7.2° | 2 | 0.7056 \AA |
| β_2 | 14.5° | 4 | 0.7048 |
| β_3 | 22.1° | 6 | 0.7060 |
| | | $\hat{\lambda}$: | 0.7055 |

Given the X-ray wavelength, equation (1) can be used to find the expected angles for different materials and crystal cuts.

4.2 Determining the materials of sample A and D

As the crystal samples A and D are cut with Miller index 111, the integer triple $(h, k, l) = m \cdot (1, 1, 1)$ for integers m .

With λ in equation (1) known, the equation can be rearranged to find expected angles for the a crystal.

$$\begin{aligned}\theta &= \sin^{-1} \left(\frac{\lambda}{2a} \sqrt{h^2 + k^2 + l^2} \right) \\ &= \sin^{-1} \left(\frac{\sqrt{3}\lambda}{2a} \cdot m \right)\end{aligned}\tag{3}$$

Which of these angles give peaks depend on the structure factor of the sample. For InP the structure factor is always nonzero along this plane - h, k, l always have the same parity. The structure factor of Si disappears when $h + k + l \equiv_4 2$, which happens for $m = 2, 6, 10, \dots$. GaAs is expected to have no or small peaks for this case, as the structure factor becomes very small due to the atomic form factors. The expected angles for our hypothetical sample materials are compared to the experimental measurements in the table below.

| Sample A | | Sample D | | InP | | Si | | GaAs | |
|-----------|--------------|-----------|--------------|-----|---------------|-----|---------------|------|---------------|
| θ | | θ | | m | θ | m | θ | m | θ |
| β_1 | 6.5° | β_1 | 6.0° | 1 | 5.975° | 1 | 6.461° | 1 | 6.208° |
| β_2 | 19.8° | β_2 | 12.1° | 2 | 12.02° | 3 | 19.73° | (2) | 12.49° |
| β_3 | 26.9° | β_3 | 18.3° | 3 | 18.20° | 4 | 26.74° | 3 | 18.93° |
| β_4 | 34.4° | β_4 | 24.8° | 4 | 24.60° | 5 | 34.24° | 4 | 25.63° |
| - | - | - | - | 5 | 31.36° | 7 | 51.97° | 5 | 32.73° |

The $m = 1, 3, 4, 5$ peaks of Si fit very neatly with the experimental data for sample A, while the InP peaks fit poorly. Nothing is visible in the sample A data near InP's $m = 2$ -peak. Sample A is clearly Si.

Sample B fits with InP and GaAs, but better with InP. The peak at β_2 would be diminished if it was a GaAs sample, as the structure factor would be very low.

4.3 Determining the crystal planes of samples B and C

Given the material and the wavelength, one can investigate along which plane a crystal was cut. These diamond/zincblende crystals must be cut along planes with Miller indices 100, 110 or 111, of which the hkl -triples then are multiples. For example, the 110-plane gives $\sqrt{h^2 + k^2 + l^2} = \sqrt{2}, \sqrt{4}, \sqrt{6}$ et cetera.

The first angles for which the structure factor is nonzero are plotted below for each crystal. Theoretical GaAs peaks for which the structure factor is almost 0 are within parentheses.

| GaAs | | | | | | | |
|-----------|-------|-----|----------|-----|----------|-----|----------|
| Sample B | | 100 | | 110 | | 111 | |
| θ | | m | θ | m | θ | m | θ |
| β_1 | 14.7° | (2) | 7.173° | 2 | 10.17° | 1 | 6.208° |
| β_2 | 30.2° | 4 | 14.46° | 4 | 20.68° | (2) | 12.49° |
| - | - | (6) | 22.00° | 6 | 32.00° | 3 | 18.93° |
| - | - | 8 | 29.96° | 8 | 44.94° | 4 | 25.63° |

| Si | | | | | | | |
|-----------|-------|-----|----------|-----|----------|-----|----------|
| Sample C | | 100 | | 110 | | 111 | |
| θ | | m | θ | m | θ | m | θ |
| β_1 | 15.1° | 4 | 15.06° | 2 | 10.59° | 1 | 6.461° |
| β_2 | 27.6° | 8 | 31.31° | 4 | 21.56° | 3 | 19.73° |
| β_3 | 31.4° | 12 | 51.22° | 6 | 33.45° | 4 | 26.75° |
| - | - | 16 | - | 8 | 47.31° | 5 | 34.24° |

The obvious best fit for GaAs is the 100-plane. The possible low-intensity peaks for $m = 2, m = 4$ are, if they're even there, lost in the measurement noise.

Sample D fits best with 100 as well. The unexplained, small peak β_2 corresponds well with $m = 6$, where the theoretical structure factor is zero. $m = 6$ is at least diminished, as the peaks do not follow the monotone-decreasing pattern of other plots.

5 Conclusion

It is a fairly straightforward procedure to determine which sample is which given the very limiting restraints on the problem. Had the crystal materials not been limited it would have been a much harder problem. Even as it is, it is not trivial. The mystery peak β_2

could be due to the mentioned diminished (theoretically zero) structure factor, or just from random noise.

$\beta - 2\beta$ is a simple yet powerful method for examining the structure of crystal samples.

References

- [1] Charles Kittel, *Introduction to Solid State Physics 8th Edition*, 2005.