Praktische Übungen für Fortgeschrittene

Teil II

– Röntgenbeugung –

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Charakterisierung der Struktur eines nanokristallinen Materials mittels Röntgenbeugung: Gitterparameter, Kristallitgröße und Verzerrung

1 Introduction

X-ray diffraction is a standard laboratory method for determining the structure of crystalline materials. The periodic arrangement of atoms in crystals leads to coherent scattering of photons (x-rays) that depends on the distance separating the atoms (lattice parameter), on the size of the crystalline regions in which the atoms are located (grain size), and on fluctuations in atomic position about the expected position in the crystal lattice (strain). In this experiment you will measure all three of these quantities for the nanocrystalline Pd sample prepared by inert-gas condensation.

In order to gain a basic understanding of the diffraction of x-rays by crystalline matter, it is helpful to consult one or both of the following references:

1. H. Ibach und H. Lüth, *Festkörperphysik: Eine Einführung in die Grundlagen*, Kapitel 2 & 3;

2. C. Kittel, *Einführung in die Festkörperphysik*, Kapitel 1 & 2.

In these books the standard notation for describing crystal structures is described, and the origin of coherent x-ray scattering from crystals in the form of Bragg peaks is explained. To test and develop your understanding of these points, we have provided a problem set that is to be completed *before* starting the x-ray diffraction experiment (see Sec. 7). The questions in the problem set provide the theoretical basis for the data analysis that you will perform on your diffraction measurements.

During the actual experiment we will have time to discuss several issues not covered in the two references provided above. Foremost among these is the production of x-rays by bombarding a target material with high-energy electrons; this occurs in the *x-ray tube*, whose position is indicated in the schematic diagram describing a typical *x-ray diffractometer* (Fig. 1). We will also discuss various means for measuring the intensity of x-rays diffracted by a given sample into the *detector*, and we will review the basic electronic components necessary for generating x-rays, detecting them and controlling the movement of the *goniometer*.

Finally, you will analyze the diffraction data recorded during the experiment. Your goal will be to learn as much as possible about the structure of the nanocrystalline sample. Questions that you will try to answer include: Is the nanocrystalline sample crystalline? What is its lattice parameter? How does the lattice parameter differ from that of the same material prepared in a coarse-grained state? What is the average grain size of the material? How much inhomogeneous strain is present in the sample? The following discussion should help you to understand the types of data analysis that must be performed in order to answer these questions.

2 Determining the lattice parameter

2.1 The Bragg equation

The angles at which coherent scattering should be expected from an array of atomic planes with interplanar spacing d' can be calculated from the *Bragg equation*. This equation is normally written

$$2d' \sin \theta = n\lambda, \tag{1}$$

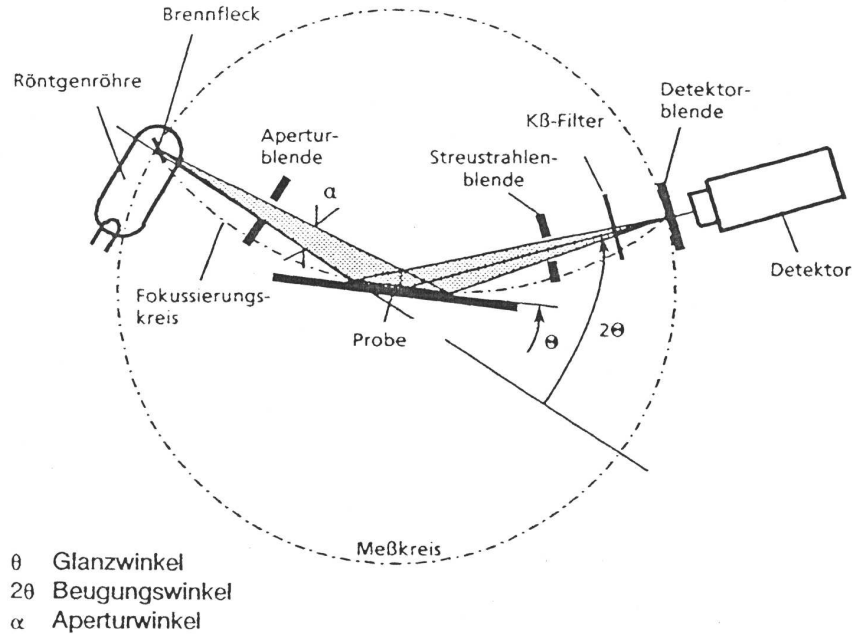θ   Glanzwinkel
2θ Beugungswinkel
α   Aperturwinkel

Figure 1: Schematic diagram of an x-ray diffractometer illustrating its main components.

where θ is half of the angle between the incident and diffracted beams, λ is the wavelength of the x-ray radiation, and n is the order of the diffraction peak. It is customary, however, to divide both sides of Eq. (1) by n and define an "effective planar spacing" $d \equiv d'/n$. Then the Bragg equation becomes

$$2d \sin \theta = \lambda. \tag{2}$$

In question 1(c) of the problem set, you will evaluate d for a simple cubic lattice and show that it is equal to $a/\sqrt{h^2 + k^2 + l^2}$ in this case. The quantity a is the side length of the unit cell of the simple cubic lattice; a is called the *lattice parameter*. The symbols h, k and l are the *Miller indices* for various atomic planes in the lattice. Suppose that a given Bragg peak arises by diffraction from the (111) planes of a simple cubic lattice. Then $d_{(111)} = a/\sqrt{3}$ and the Bragg equation will be satisfied when $\sin \theta_{(111)} = \lambda/2d_{(111)}$. Now let's consider the Bragg peak arising from the (222) planes. In this case $d_{(222)} = a/2\sqrt{3}$, which is just $d_{(111)}/2$. Therefore, the Bragg equation is satisfied when $\sin \theta_{(222)} = \lambda/2d_{(222)} = \lambda/d_{(111)}$. Let us compare these two expressions for the angles at which the (111) and (222) Bragg peaks are expected to occur:

$$2d_{(111)} \sin \theta_{(111)} = \lambda \quad (111) \tag{3}$$
$$2d_{(111)} \sin \theta_{(222)} = 2\lambda \quad (222). \tag{4}$$

Comparing Eqs. (3) and (4) with Eq. (1), we see that the (222) diffraction peak is just the second order (i.e., $n = 2$) of the (111) diffraction peak! In other words, the Miller indices automatically keep track of the various orders of diffraction in a systematic (although somewhat complicated) manner.

For most crystal structures, many (hkl) combinations will lead to *no* measurable intensity at the angle fulfilling the Bragg equation. The reason for this is that enough *destructive interference* occurs to cancel out the *constructive interference* from the atomic planes of interest. This destructive interference arises from atomic planes associated with the *basis* of the crystal structure rather than with the crystal structure's *lattice* type. We'll discuss a few examples during the laboratory session that should clarify this point, but even if you don't have a well-developed intuitive feel for the reasons behind these "missing" (hkl) values, you can calculate them for any crystal structure by working

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out the *structure factor*. In problem 2(a) you'll do this for palladium, which has the fcc structure with a four-atom basis, and find that, for instance, the (100) peak is excluded while the (200) is not! Intuitively, you might think that if the second-order peak is present, then the first-order peak must be, too. This is wrong, however, because in (100) Bragg orientation the atoms located on the (200) plane of the fcc unit cell diffract exactly 180° out of phase with the atoms located on the (100) plane, resulting in zero net diffracted intensity.[1]

2.2 Correcting for sample-positioning error

Once you have measured a Bragg peak with x-rays of known λ, you can determine d from the peak position θ using Eq. (2).[2] If you also know the lattice type and the (hkl) value, then you can calculate the lattice parameter a from the relationship between a and d. In general, if you do this for more than one Bragg peak (even for different orders of diffraction from the same atomic planes), you will calculate a slightly different lattice parameter a for each peak! There are several reasons for this, but the main one is the fact that the sample being measured can never be mounted in the x-ray diffractometer at exactly the correct position relative to the x-ray tube and detector: the sample is always a little bit too high or too low, when viewed from the side as in Fig. 1. This mounting error leads to a systematic variation in a because the misorientation of the sample causes small shifts in the angles θ of the Bragg peaks used to calculate a.

Fortunately, there are techniques available for correcting this systematic error. A simple calculation shows that a displacement $\tilde{d}$ of the sample normal to the plane defined by its surface causes a relative shift $\Delta a/a$ in the lattice parameter as given by the following equation:

$$\frac{\Delta a}{a} = -\frac{\tilde{d}}{r} \frac{\cos^2 \theta}{\sin \theta}, \tag{5}$$

where r is the radius of the diffractometer. (The displacement $\tilde{d}$ is positive when the sample lies *above* the correct position—that is, when the sample is too high in Fig. 1.) If we let the symbol a_0 represent the true lattice parameter of the sample and a represent the measured value, then $\Delta a/a = (a - a_0)/a_0$, which, when substituted into Eq. (5), implies

$$a = a_0 - \left(a_0 \frac{\tilde{d}}{r} \right) \frac{\cos^2 \theta}{\sin \theta}. \tag{6}$$

Thus, a plot of a against the function $\cos^2 \theta / \sin \theta$ should give a straight line (if sample displacement is the main source of error). The true lattice parameter a_0 is just the intercept of the straight line with the $\cos^2 \theta / \sin \theta = 0$ axis, as illustrated in Fig. 2.

3 Determining the average crystallite size

3.1 One-dimensional crystal

In question 3 of the problem set, you will calculate the dependence of Bragg-peak width on crystal size for the case of a one-dimensional crystal. You should find that the width of the peak is inversely proportional to the number of lattice points M contributing to the diffraction signal. Let's develop an expression relating M to the width of a Bragg peak measured as a function of 2θ. Referring

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[1] Complete destructive interference requires that the total scattering factor of atoms in the (200) plane equal that of the atoms in the (100) plane. This is true for the fcc lattice structure if all of the atomic sites are occupied by the same type of atom.

[2] X-ray diffraction measurements are usually plotted as a function of 2θ rather than of θ, so you'll have to divide the measured peak position by 2 before using Eq. (2).
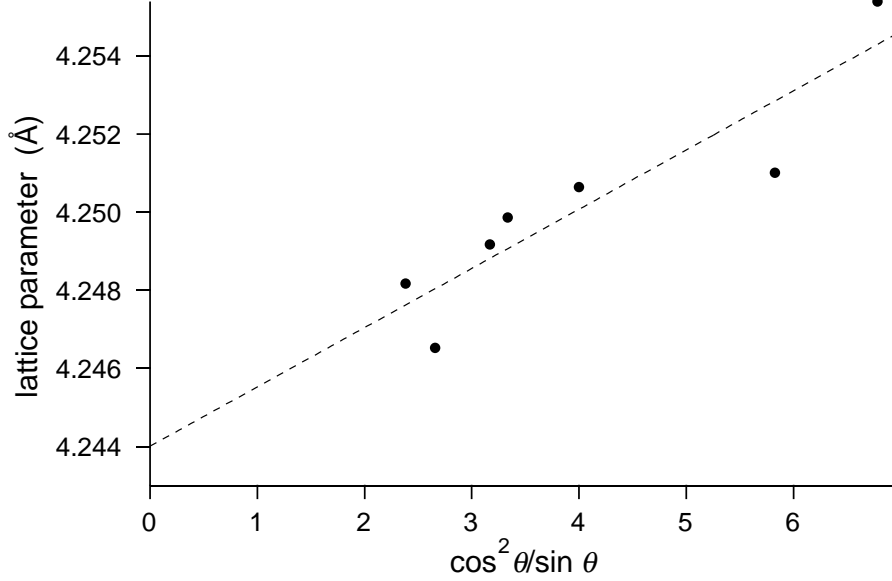
Figure 2: Plot of measured lattice parameter a against $\cos^2 \theta / \sin \theta$. The intercept of the straight line fit to the data points with the vertical axis gives the lattice parameter a_0 corrected for the influence of sample-positioning error.

to Fig. 3, we assume that the peak center is at $\mathbf{a} \cdot \Delta \mathbf{k} = 2\pi h$ and that the width of the peak can be estimated from the difference between $\mathbf{a} \cdot \Delta \mathbf{k} = 2\pi h + (\epsilon/2)$ and $2\pi h - (\epsilon/2)$. We must express these positions along the horizontal axis in terms of θ. From Fig. 4 we see that $|\Delta \mathbf{k}| = 2|\mathbf{k}| \sin \theta$. By definition of $\mathbf{k}$, $|\mathbf{k}| = 2\pi/\lambda$; also, the vectors $\mathbf{a}$ and $\Delta \mathbf{k}$ are parallel to each other, so the angle between them is zero. Thus, $\mathbf{a} \cdot \Delta \mathbf{k} = 4\pi a \sin \theta / \lambda$.

Now we can express the peak center by equating $2\pi h$ to $4\pi a \sin \theta / \lambda$—this is just the Bragg equation! Let's use the symbol θ_0 to denote the angle θ that satisfies this equation. There are two other angles, $\theta_0 + (\delta \theta_0/2)$ and $\theta_0 - (\delta \theta_0/2)$, at which $\mathbf{a} \cdot \Delta \mathbf{k}$ equals $2\pi h + (\epsilon/2)$ and $2\pi h - (\epsilon/2)$, respectively. Subtracting $2\pi h - (\epsilon/2)$ from $2\pi h + (\epsilon/2)$, we have:

$$
\begin{aligned}
\epsilon &= \frac{4\pi a}{\lambda} \left[\sin \left(\theta_0 + \frac{\delta \theta_0}{2} \right) - \sin \left(\theta_0 - \frac{\delta \theta_0}{2} \right) \right] \\
&= \frac{4\pi a}{\lambda} \left[\sin \theta_0 \cos \left(\frac{\delta \theta_0}{2} \right) + \cos \theta_0 \sin \left(\frac{\delta \theta_0}{2} \right) - \sin \theta_0 \cos \left(\frac{\delta \theta_0}{2} \right) + \cos \theta_0 \sin \left(\frac{\delta \theta_0}{2} \right) \right] \\
&\approx \frac{4\pi a}{\lambda} \delta \theta_0 \cos \theta_0, \quad (7)
\end{aligned}
$$

where we have used $\sin(\delta \theta_0/2) \approx \delta \theta_0/2$ for small $\delta \theta_0$. But in question 3(d) of the problem set, you show that $\epsilon = 2\pi/M$. Equating Eq. (7) to $2\pi/M$, we find

$$
Ma \approx \frac{\lambda}{\delta(2\theta_0) \cos \theta_0}. \quad (8)
$$

For a one-dimensional crystal, the length L is equal to $(M-1)a$. Since $M - 1 \approx M$ for large M, we can write Eq. (8) as

$$
L \approx \frac{\lambda}{\delta(2\theta_0) \cos \theta_0}. \quad (9)
$$

This equation relates the size L of a one-dimensional crystal to the width $\delta(2\theta_0)$ of an x-ray diffraction peak arising from that crystal. (Note that $\delta(2\theta_0)$ must be expressed in *radians* in order for the units to come out correctly!)
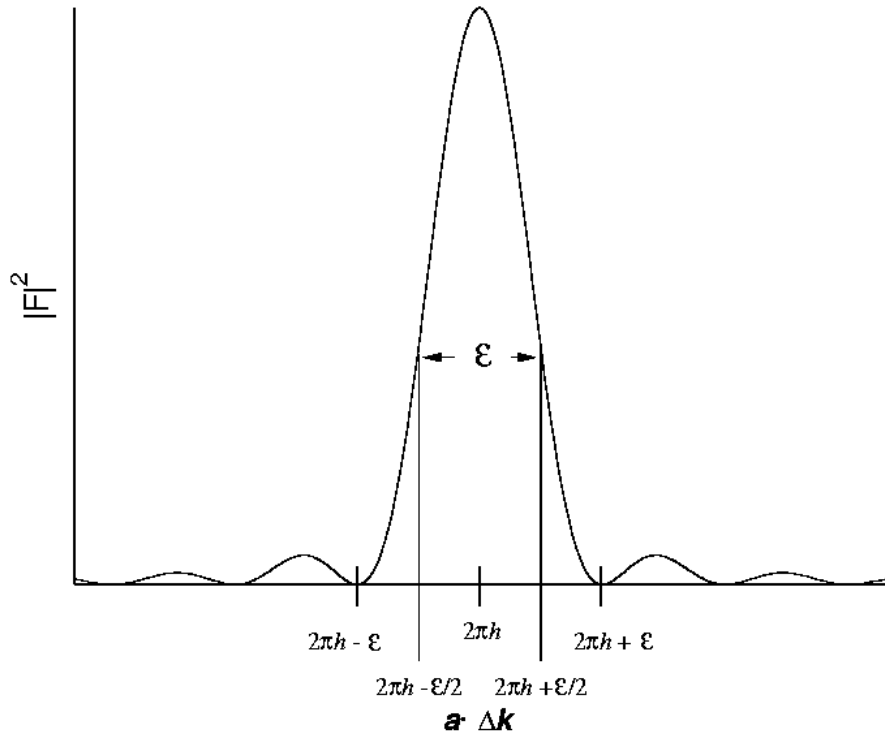
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Figure 3: Plot of Bragg peak calculated in question 3 of the problem set ($M = 10$). The peak width is estimated to be half of the distance 2ϵ between the first zero-crossings of peak intensity (at $2\pi h \pm \epsilon$) relative to the peak maximum.

3.2 Three-dimensional crystal

Surprisingly, diffraction from a three-dimensional crystal is qualitatively identical to diffraction from a one-dimensional crystal if we identify the diffracting *planes* in the 3D crystal with the diffracting *points* in the 1D crystal! We will discuss during the laboratory session why this is true, but you should try to find a good explanation ahead of time. In 1918, Scherrer published a more precise derivation of Eq. (9) than we have performed here and found that

$$D = \frac{1.2\lambda}{\delta(2\theta_0)\cos\theta_0},$$
(10)

where the constant 1.2 is exact only for spherical crystallites of diameter D. Equation (10) relates the Bragg-peak broadening $\delta(2\theta_0)$ (measured in radians!) from a single crystallite to the crystallite diameter D. In the case of our nanocrystalline materials, x-ray diffraction occurs simultaneously from a huge number of crystallites, each having a different size. In this case, the quantity D that one calculates using Eq. (10) is an *average* diameter. This average is somewhat different from the one ordinarily encountered in physical measurements: instead of averaging the crystallite sizes according to the number of crystallites of a given size, the x-ray diffraction process averages the crystallite sizes according to the *volume* of each crystallite. In other words, the bigger crystallites carry more weight in the averaging process than the smaller ones. Therefore, the average size D calculated from Eq. (10) is always an upper bound for the numerical average size $\langle D \rangle$.
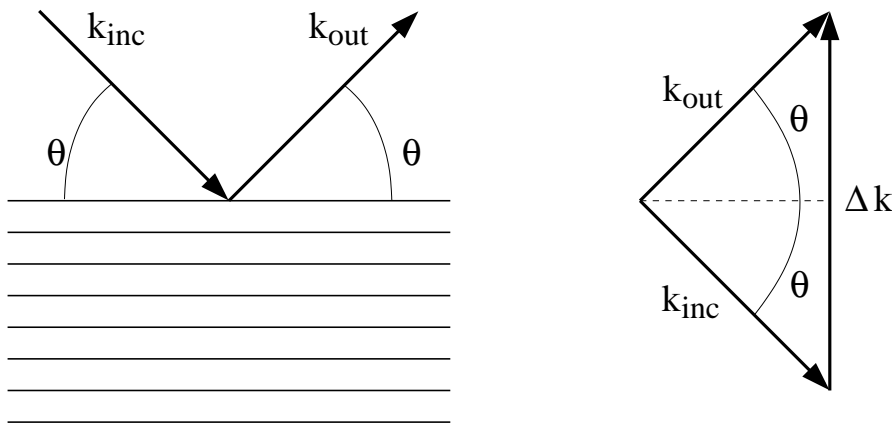
Figure 4: Vector plot identifying the relative orientation of the incident x-ray beam $\mathbf{k}_{\text{inc}}$, the diffracted x-ray beam $\mathbf{k}_{\text{out}}$ and the change $\Delta\mathbf{k} = \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{inc}}$ that occurs upon diffraction. Note that $|\mathbf{k}_{\text{inc}}|$ and $|\mathbf{k}_{\text{out}}|$ are both equal to $|\mathbf{k}| = 2\pi/\lambda$ because the scattering process is elastic (i.e., scattering occurs with no change in x-ray beam energy).

4   Measuring inhomogeneous strain

The schematic diagrams that you see in textbooks of crystal structures always imply that the interatomic spacing (i.e., the nearest-neighbor spacing) is a constant determined by the lattice parameter. That's not true! In fact, the spacing between adjacent atoms is *always changing* due to the atomic vibrations induced by thermal energy (phonons). Atoms vibrate about average positions that are, indeed, separated by a constant distance determined by the lattice parameter, but the *instantaneous* spacing between any two atoms varies with time due to the thermal motion of the atoms themselves. Even if it were possible to cool a crystal down to absolute zero Kelvin, these vibrations would be present thanks to quantum mechanics: just as with a harmonic oscillator, the lowest possible energy state is one in which there is still a finite amount of kinetic energy stored in atomic motion. (The vibrations at $T = 0$ K are called *zero-point motion.*) The influence of atomic vibrations on x-ray diffraction peaks can be measured through the dependence of peak intensity with diffracting angle; the mathematical factor describing this angular dependence is called the *Debye-Waller factor* and is too complicated for us to consider in this experiment.

However, atomic vibrations aren't the only cause of variations in interatomic spacing: the presence of inhomogeneous strain in a sample can cause them, too. Inhomogeneous strain is a variation in spacing between *atomic planes* rather than between the atoms themselves (Fig. 5). (Of course, if the plane spacing varies, then so will the spacing between atoms located in different planes). Such strain can be induced by subjecting a material to mechanical force, such as pressing, grinding, milling, stretching or cutting. In the case of the nanocrystalline sample prepared by inert-gas condensation, the crystallites that condensed in the gas phase were collected by convection onto a cold surface and then scraped into a press, where they were compacted at high pressure. It is this last step—cold compaction—that can introduce inhomogeneous strain into the nanocrystalline samples.

Why are we interested in inhomogeneous strain? In question 4 of the problem set, you show that a distribution of lattice parameters causes a broadening of Bragg peaks. The variation in interplanar spacing that we call inhomogeneous strain is equivalent to the presence of a distribution of lattice parameters! That is, a material containing strain has a *local* lattice parameter that varies about some average value a_0. The larger the relative variation $|\delta a_0/a_0|$, the larger the resulting Bragg-peak
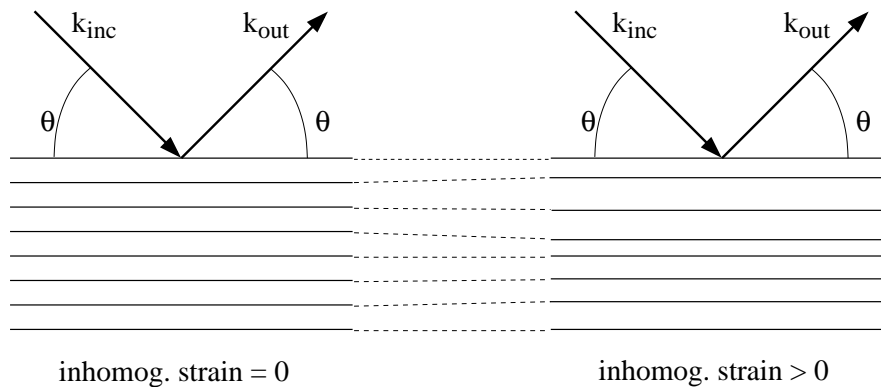
Figure 5: Schematic diagram illustrating the difference between a crystal without inhomogeneous strain (left) and a crystal with inhomogeneous strain (right). The local variation in interplanar spacing is equivalent to a distribution of lattice parameters (see question 4 of the problem set).

broadening $\delta(2\theta_0)$ will be. In question 4(a) you show that

$$\delta(2\theta_0) = 2\tan\theta_0 \left| \frac{\delta a_0}{a_0} \right|, \tag{11}$$

where $2\theta_0$ is the Bragg-peak position. Thus, from a measurement of the strain-induced peak broadening, one can calculate the amount of strain present in the sample. (Note that *strain* is defined to be the quantity $\frac{1}{2}|\delta a/a|$, which is usually written as e in the literature.)

5 Correcting for size-broadening and strain-broadening simultaneously

5.1 Instrumental broadening

In the above sections we have seen that there are at least two independent effects (crystallite size and inhomogeneous strain) that can cause Bragg peaks to broaden. In fact, there are many more than two such effects, but these are two of the three most important. The third one, which we have not yet discussed, is called *instrumental broadening*. This is the width of a Bragg peak that one would measure from a perfect single crystal of infinite size containing no inhomogeneous strain. According to theory, Bragg peaks should be delta functions in this case (consider the form of $|F|^2$ in question 3(b) of the problem set in the limit $M \to \infty$). In practice, Bragg peaks are *never* delta functions; instead, they have a finite (i.e., non-infinite) height and a nonzero width. There are many reasons for this: for instance, (i) the detector cannot measure the angular variation of intensity with infinite resolution, (ii) there always exists a slight dispersion $\Delta\lambda$ in the wavelength of x-rays used to irradiate the sample, and (iii) the x-rays are scattered at various depths from the sample rather than all from the top atomic plane. We'll discuss these factors during the laboratory session.

What's important for analyzing our nanocrystalline materials is to know how much of the peak broadening is due to size and strain and how much is due to instrumental sources. To determine the latter, we will measure the Bragg peaks from a LaB_6 reference sample known to have large grains (i.e., much larger than 100 nm) and almost no strain. Then any residual peak broadening must be due to instrumental sources. We will denote this amount of broadening as $\delta(2\theta_0)_{\text{inst}}$.

5.2 Total peak broadening

The total amount of Bragg-peak broadening is a combination of $\delta(2\theta_0)_{\mathrm{inst}}$ and the broadening due to crystallite size, $\delta(2\theta_0)_{\mathrm{size}}$, and that due to inhomogeneous strain, $\delta(2\theta_0)_{\mathrm{strain}}$. Unfortunately, we don't know exactly how these various effects combine with one another; mathematically, we know only that the three sources of broadening are *convoluted* together to yield the total broadening (convolution = *Faltung*). In order to make separation of the various effects possible, we must assume a mathematical form for each of the three types of broadening. For example, we may assume that each of the three results in a *Lorentzian* broadening of the Bragg peaks. A Lorentzian intensity curve is defined as

$$I(2\theta) = \frac{C}{(2\theta - 2\theta_0)^2 + (\Gamma/2)^2}, \tag{12}$$

where C is a constant and Γ is the full-width at half maximum (FWHM) of a Bragg peak centered at $2\theta_0$ (Fig. 6). In this case, it's easy to show that the FWHM of the convolution of three Lorentzians
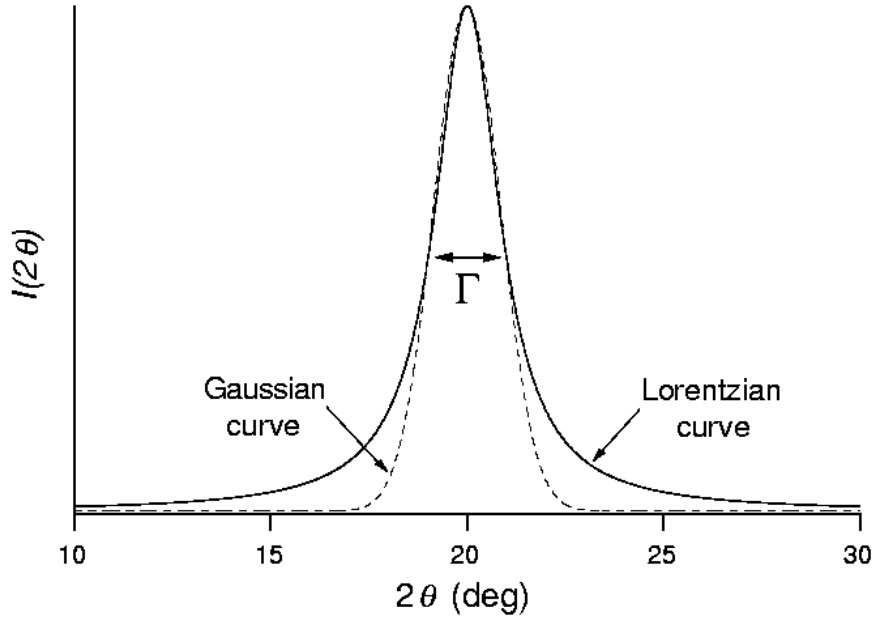

Figure 6: Plot of Lorentzian and Gaussian peak forms with FWHM equal to Γ. Note that the tails of the Gaussian peak fall off much more quickly than those of the Lorentzian, although the FWHM is identical in both cases; on the other hand, the peak of the Lorentzian is sharper than that of the Gaussian.

is just the sum of the FWHM's of each Lorentzian function:

$$\delta(2\theta_0)_{\mathrm{total}} = \delta(2\theta_0)_{\mathrm{inst}} + \delta(2\theta_0)_{\mathrm{size}} + \delta(2\theta_0)_{\mathrm{strain}} \qquad \text{(all Lorentzian)}, \tag{13}$$

where we assume that the $\delta(2\theta)$ quantities are intrinsically positive, of course. On the other hand, we might assume that each of the three sources of peak broadening is best described by a Gaussian function:

$$I(2\theta) = C \exp\left[-4\ln 2 \frac{(2\theta - 2\theta_0)^2}{\Gamma^2}\right], \tag{14}$$

where C is a constant and Γ is the FWHM (Fig. 6). From the properties of convolution integrals, one can show that the square of the FWHM of the convolution of three Gaussians is just the sum of the squares of the FWHM's of each Gaussian:

$$[\delta(2\theta_0)_{\mathrm{total}}]^2 = [\delta(2\theta_0)_{\mathrm{inst}}]^2 + [\delta(2\theta_0)_{\mathrm{size}}]^2 + [\delta(2\theta_0)_{\mathrm{strain}}]^2 \qquad \text{(all Gaussian)}. \tag{15}$$

5.3 Separating the various broadening contributions

We already know how large the instrumental-broadening term $\delta(2\theta_0)_{\text{inst}}$ is (we measure it directly from the large-grained Pd reference sample), and we can measure the total broadening $\delta(2\theta_0)_{\text{total}}$ for any Bragg peak from the nanocrystalline Pd sample. How do we figure out what $\delta(2\theta_0)_{\text{size}}$ and $\delta(2\theta_0)_{\text{strain}}$ are? To answer this question we will use a clever trick, but first we note that separating the size broadening from the strain broadening will be impossible from a measurement of just one Bragg peak. Why? Because from one measurement of $\delta(2\theta_0)_{\text{total}}$ we cannot possibly decide how much of the total broadening results from crystallite size and how much from inhomogeneous strain—the problem is underdetermined. Would it help to measure more than one Bragg peak? Yes! Then we will have two or more measurements of $\delta(2\theta_0)_{\text{total}}$, which should be enough to enable calculation of both $\delta(2\theta_0)_{\text{size}}$ and $\delta(2\theta_0)_{\text{strain}}$. Let's see how this works.

In question 4(b) of the problem set you show that the change of variable $s = 2(\sin\theta)/\lambda$ enables us to express the strain broadening [Eq. (11)] in the following form:

$$(\delta s_0)_{\text{strain}} = s_0 \left| \frac{\delta a_0}{a_0} \right|, \tag{16}$$

where a_0 is the lattice parameter and $|\delta a_0/a_0|$ is the relative change in lattice parameter due to inhomogeneous strain; note that the peak broadening due to strain is now expressed in terms of s rather than in terms of 2θ. We can perform the same change of variable with the size broadening. Recall from Eq. (10) that

$$[\delta(2\theta_0)]_{\text{size}} = \frac{1.2\lambda}{D\cos\theta_0}. \tag{17}$$

Making the change of variable $s = 2(\sin\theta)/\lambda$, we find

$$
\begin{aligned}
(\delta s_0)_{\text{size}} &= \frac{\cos\theta_0}{\lambda}[\delta(2\theta_0)]_{\text{size}} \\
&= \frac{\cos\theta_0}{\lambda} \cdot \frac{1.2\lambda}{D\cos\theta_0} \\
&= \frac{1.2}{D}.
\end{aligned} \tag{18}
$$

When we compare Eqs. (16) and (18), we see immediately that, while $(\delta s_0)_{\text{strain}}$ depends on s_0, $(\delta s_0)_{\text{size}}$ is a constant! This is the fact that allows us to separate the broadening due to strain from that due to size—at low angles (i.e., low s_0) Bragg peaks will have a small amount of strain broadening (because s_0 is small), whereas at large angles Bragg peaks will have a large amount of strain broadening; the size broadening, on the other hand, will be constant with respect to angle because $(\delta s_0)_{\text{size}}$ does not depend on s_0.

To perform the actual size/strain separation, we proceed as follows. First, we will assume that the total broadening should be corrected for instrumental broadening simply by subtracting $(\delta s_0)_{\text{inst}}$ from $(\delta s_0)_{\text{total}}$; this will yield a corrected total broadening that we'll call $(\delta s_0)_{\text{corr}}$. Then we can assume that both strain and size broadening are Lorentzian: in this case we substitute Eqs. (16) and (18) into Eq. (13) to get

$$(\delta s_0)_{\text{corr}} = \frac{1.2}{D} + 2es_0 \qquad \text{(Lorentzian size and strain)}, \tag{19}$$

where we have followed the common practice of writing the strain $\frac{1}{2}|\delta a_0/a_0|$ as e. This is the equation of a straight line! Therefore, if we plot $(\delta s_0)_{\text{corr}}$ against s_0 for each Bragg peak measured, we should find that the points lie roughly along a straight line [Fig. 7(a)]. Fitting such a line to the points allows us to evaluate e from the slope of the line and D from the inverse of its intercept.
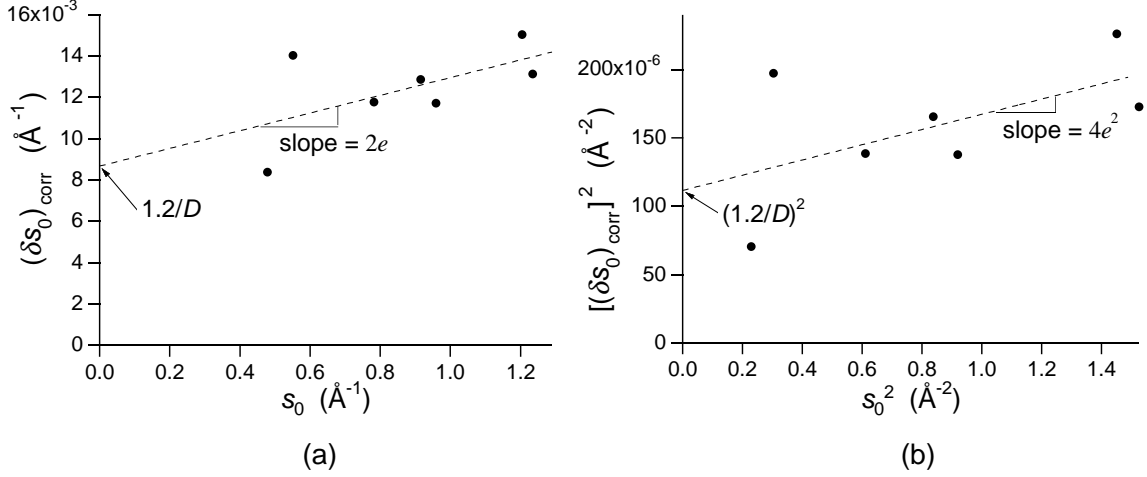
Figure 7: (a) Plot of $(\delta s_0)_{\mathrm{corr}}$ against s_0 for the Bragg peaks of a nanocrystalline material; (b) plot of $[(\delta s_0)_{\mathrm{corr}}]^2$ against s_0^2 for the Bragg peaks plotted in (a). The straight-line fits enable evaluation of the average crystallite size D and the inhomogeneous strain e, according to Eqs. (19) and (20).

Similarly, we can perform the same analysis under the assumption that the size and strain broadening are both Gaussian. In this case, substitution of Eqs. (16) and (18) into Eq. (15) yields

$$[(\delta s_0)_{\mathrm{corr}}]^2 = \left(\frac{1.2}{D}\right)^2 + (2es_0)^2 \qquad \text{(Gaussian size and strain).} \tag{20}$$

Again, this is the equation of a straight line, though as a function of s_0^2 rather than of s_0. If we plot $[(\delta s_0)_{\mathrm{corr}}]^2$ against s_0^2 for each Bragg peak measured, then we should find that the points lie roughly along a straight line [Fig. 7(b)]. As in the Lorentzian case, the slope gives e and the intercept gives D. During the laboratory session we will discuss which of these two analysis techniques is more reliable and trustworthy for determining D and e.

6 Data evaluation

In this experiment you will measure the Bragg peaks of a coarse-grained LaB_6 reference sample, a nanocrystalline $Pd_{90}Au_{10}$ sample and a nanocrystalline and coarse-grained CeO_2 sample. The data evaluation that you are expected to carry out consists of the following tasks:

1. Determine instrumental broadening using the LaB_6 reference sample and fitting the FWHM-values with the Caglioti function : FWHM=sqrt(A+B*tan(theta)+C*(tan(theta))^2)

2. Determine the lattice parameter of the nanocrystalline $Pd_{90}Au_{10}$ sample and the CeO_2 samples using the correction technique for sample-positioning error.

3. Estimate the average crystallite size D and the inhomogeneous strain e in the nanocrystalline samples under the assumption that both size and strain broadening are Lorentzian. Give the value for D in nanometers and the value for e in percent (%).

4. Estimate the average crystallite size D and the inhomogeneous strain e in the nanocrystalline samples under the assumption that both size and strain broadening are Gaussian. Give the value for D in nanometers and the value for e in percent (%).

7 Problem set

In diesem Versuch werden Sie die Struktur einer nanokristallinen Pd-Probe mittels Röntgenbeugung charakterisieren. Es ist notwendig, die folgenden Aufgaben schon *vor* der ersten Röntgenbeugungsmessung gelöst zu haben, um die Prinzipien der während des Versuchs durchzuführenden Messungen und Auswertungen verstehen zu können.

1. **Abstand zwischen den Ebenen.** (s. Kittel, Kap. 2, Nr. 1) Betrachten Sie eine Ebene hkl in einem Kristallgitter.

   (a) Zeigen Sie, daß der reziproke Gittervektor $\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ senkrecht auf dieser Ebene steht.

   (b) Beweisen Sie, daß der Abstand zwischen zwei aufeinanderfolgenden parallelen Ebenen des Gitters gleich $d(hkl) = 2\pi/|\mathbf{G}|$ ist.

   (c) Zeigen Sie für ein einfach kubisches Gitter, daß gilt

   $$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$

   wobei a der Gitterparameter ist.

2. Das Material, das Sie messen werden, ist u.a. eine Pd$_{90}$Au$_{10}$-Legierung. Pd ist kubischflächenzentriert (fcc) und hat einen Gitterparameter a von ungefähr 3.89 Å.

   (a) Berechnen Sie *explizit* (d.h. nicht einfach das Ergebnis aus Kittel kopieren) den Strukturfaktor für Palladium. Nehmen Sie dafür an, daß der Atomformfaktor von Palladium f ist. Welches sind die hkl-Werte der ersten acht erlaubten Bragg-Reflexe?

   (b) Benutzen Sie das Ergebnis von Aufgabe 1(c) in Kombination mit der Bragg-Gleichung, um die zu erwartenden Positionen der ersten acht erlaubten Bragg-Reflexe von Pd zu berechnen. Nehmen Sie an, daß das Material mittels Kupfer-Strahlung ($\lambda = 1.54056$ Å) gemessen wird. Vergessen Sie nicht, die Positionen als Winkel 2θ anzugeben.

3. **Beugung eines eindimensionalen Kristalls** (s. Kittel, Kap. 2, Nr. 3) Wir nehmen an, daß in einem linearen Kristall auf jedem Gitterpunkt $\rho_m = m\mathbf{a}$ (m ist eine ganze Zahl) ein identisches, punktförmiges Streuzentrum sitzt. Die Gesamtamplitude der Streustrahlung ist proportional zu $F = \sum \exp[-im(\mathbf{a} \cdot \Delta\mathbf{k})]$.

   (a) Zeigen Sie, daß die Summe über M Gitterpunkte den Wert

   $$F = \frac{1 - \exp[-iM(\mathbf{a} \cdot \Delta\mathbf{k})]}{1 - \exp[-i(\mathbf{a} \cdot \Delta\mathbf{k})]}$$

   hat, unter Verwendung des Ergebnisses

   $$\sum_{m=0}^{M-1} x^m = \frac{1 - x^M}{1 - x}.$$

   (b) Die gestreute Intensität ist proportional zu $|F|^2$. Zeigen Sie, daß gilt

   $$|F|^2 = F^*F = \frac{\sin^2 \frac{1}{2} M(\mathbf{a} \cdot \Delta\mathbf{k})}{\sin^2 \frac{1}{2}(\mathbf{a} \cdot \Delta\mathbf{k})}.$$

   (c) Wir wissen, daß für $\mathbf{a} \cdot \Delta\mathbf{k} = 2\pi h$ (h ist eine ganze Zahl) ein Beugungsmaximum erscheint. Was ergibt sich für $|F|^2$, wenn $\mathbf{a} \cdot \Delta\mathbf{k} = 2\pi h$ ist?

(d) Wir ändern $\Delta\mathbf{k}$ geringfügig und definieren eine Quantität ϵ so, daß, wenn $\mathbf{a}\cdot\Delta\mathbf{k} = 2\pi h + \epsilon$ in $\sin\frac{1}{2}M(\mathbf{a}\cdot\Delta\mathbf{k})$ eingesetzt wird, die Funktion $|F|^2$ ihren ersten Nullwert hat. Zeigen Sie, daß gilt $\epsilon = 2\pi/M$ – das heißt, daß die Breite des Beugungsmaximums proportional zu $1/M$ ist und dadurch für große Werte von M extrem schmal werden kann.

(e) Nehmen wir an, daß $\mathbf{a}\cdot\Delta\mathbf{k} = 4\pi a\sin\theta/\lambda$. Zeichnen Sie das erste Beugungsmaximum ($h = 1$) für $M = 10$, 100 und 1000 unter der Annahme, daß $\lambda = 0.7093$ Å und $a = 3.89$ Å.

4. **Verteilung von Gitterparametern.** Nehmen Sie an, daß ein bestimmtes Material eine relativ schmale Verteilung von Gitterparametern δa um den mittleren Wert a hat. Diese Verteilung führt zu einer Verbreiterung $\delta(2\theta)$ von Bragg-Reflexen.

(a) Mit Hilfe der Bragg-Gleichung zeigen Sie, daß gilt

$$|\delta(2\theta)| = 2\tan\theta\left|\frac{\delta a}{a}\right|,$$

wobei 2θ die Lage eines Bragg-Reflexes ist.

(b) Diese Gleichung für $|\delta(2\theta)|$ nimmt eine einfachere Form an, wenn θ durch einen neuen Parameter $s = 2(\sin\theta)/\lambda$ ersetzt wird. Zeigen Sie in diesem Fall, daß gilt

$$|\delta s| = s\left|\frac{\delta a}{a}\right|.$$