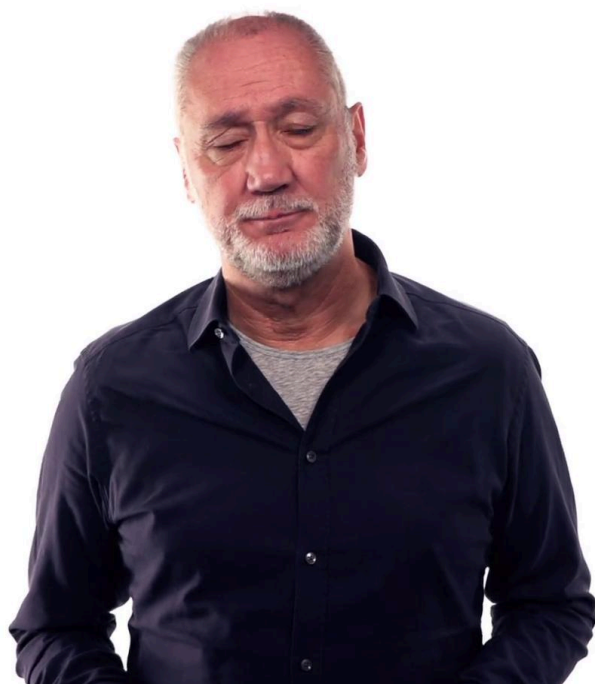


Contents and objectives of this video



- SXRDR basics
 - Goals of SXRDR
 - Surfaces and interfaces
 - CTRs
 - Recording SXRDR data

Welcome back to the third section of Week 2 of this second course on synchrotrons and X-ray free-electron lasers. In this, the first of two videos in this section, we'll discuss the basic principles behind surface X-ray diffraction and how this is used to investigate the structures of surfaces and interfaces. I will introduce you to the concept of crystal truncation rods, or CTRs, from two different approaches, the first being intuitively simple, the second being more representative of surface diffraction signal recorded at synchrotrons. We'll finish this first video with an overview of the practical issues of tracking and recording surface diffraction signal.

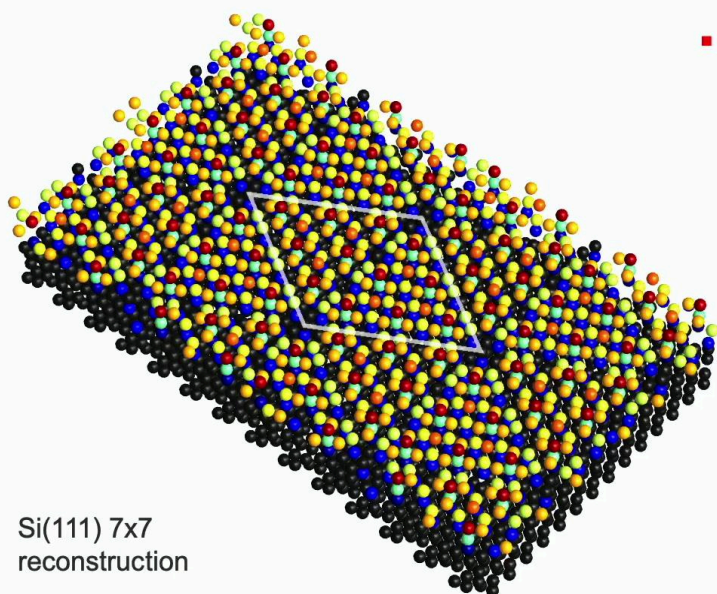
Notes

Summary



0m 05s

Goals of SXRD



- Study of crystalline surfaces *and* interfaces
 - Surfaces/interfaces different from bulk
 - “Dangling” bonds
 - Polar discontinuities
 - Surface energy minimization – relaxations and reconstructions
 - Interesting and unexpected new physical properties
 - See e.g. $\text{LaAlO}_3/\text{SrTiO}_3$ interface
S.A. Pauli *et al.*,
[DOI:10.1103/PhysRevLett.106.036101](https://doi.org/10.1103/PhysRevLett.106.036101)

What are the goals of surface X-ray diffraction? How do they differ, for example, from those of more conventional diffraction techniques? To answer these questions, we need to consider how an atom at a surface differs from atoms which are deep within the bulk of the same material. For example, the atoms of Silicon-111, that is silicon with a surface exposed on the crystallographic 111 plane, would, one might imagine, have a network of surface atoms in a corrugated hexagonal mesh as are highlighted here in these blue surface atoms. Now, in reality, however, dangling bonds that would otherwise be associated with atoms above now rearrange themselves to minimise the electrostatic energy which results in the famous 7 times 7 silicon-111 reconstruction. By 7 times 7, it's meant that 7 times 7 surface repeat motifs combine to produce a repetition length in these directions that is seven times larger, as highlighted by this diamond outline. Note that the rearrangement of atoms extends down to approximately three atomic layers. Indeed, it is these deviations from bulk structure that define a surface region. Such rearrangements of atomic positions aren't confined only to surfaces.

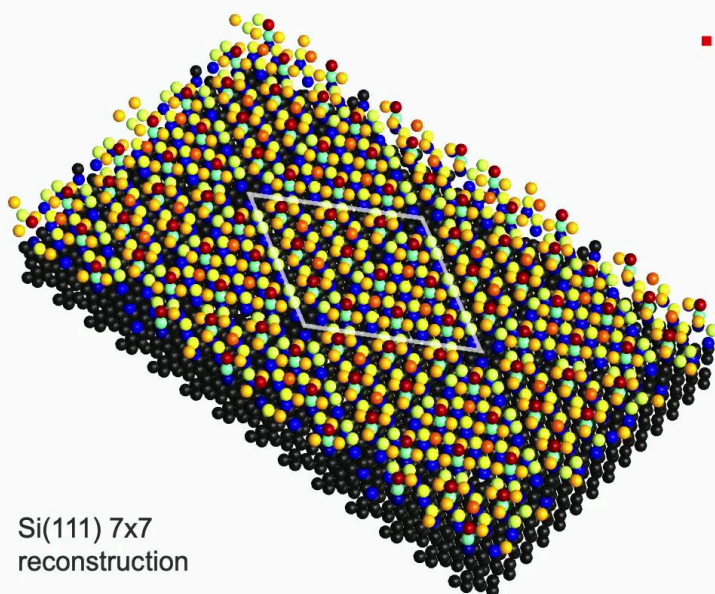
Notes

Summary



0m 48s

Goals of SXRD



- Study of crystalline surfaces *and* interfaces
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Also, the boundary between two materials, such as found in heteroepitaxial thin film growth, can exhibit rearrangements due to differences in bond strengths or polar discontinuities in which one side of the interface may consist of atoms in a certain anionic-cationic balance, and the other with a different configuration. This can lead to interesting and unexpected interfacial physical phenomena. such as a two-dimensional conducting layer forming at the interface between two insulating materials as described in the link provided here for lanthanum aluminate on strontium titanate. In this case, the lanthanum and aluminium are both 3 plus valent, whereas the strontium is 2 plus and the titanium 4 plus. This difference in their ionicity causes this two-dimensional electron gas to appear at the interface.

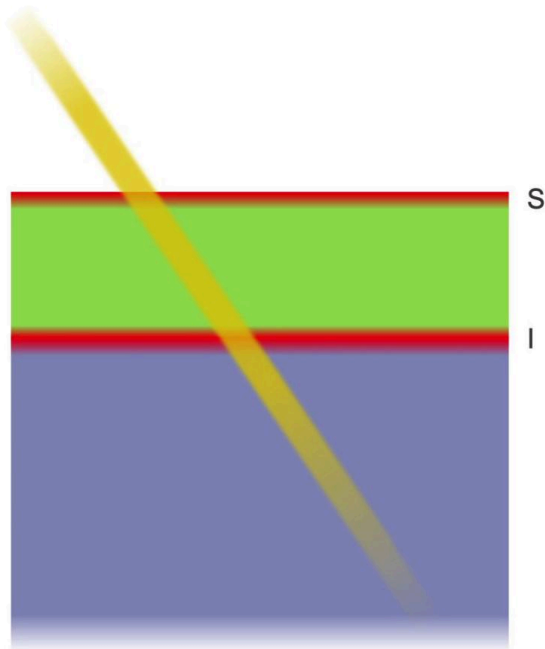
Notes

Summary



2m 21s

Signal from surfaces or interfaces



- How does one find out the structure of a surface or interface using scattering methods?
- Surfaces and interfaces different from bulk
- Very small scattering volume
 - $\sim 1 - 5$ ML, or $1 - 5$ nm depth
 - c.f. extinction length $\sim 10 \mu\text{m}$
- Go to positions in reciprocal space where bulk signal is weak...
- Let's discuss this in more detail

How does one go about finding the structure of a surface or interface region using X-ray scattering? One of the fundamental issues is the extremely small volume that is being probed. If, for example, we illuminate an area of 5 millimetres by 0.2 millimetres, in other words, 1 square millimetre of sample surface, which, by the by, is already on the liberal side, and expect changes in atomic positions due to the surface extending down to nanometres, let's say, then the total scattering volume from that surface region is only 2,000 cubic microns. The extinction depth of crystalline materials due to scattering, in other words, not absorption, is maybe 10 microns, some 5,000 times larger. So the general strategy is to go to positions in reciprocal space away from bulk Bragg peaks. Luckily, this is nearly all of reciprocal space, the Bragg peaks being in general very sharp and narrow. But where should we look exactly? Let's discuss this now.

Notes

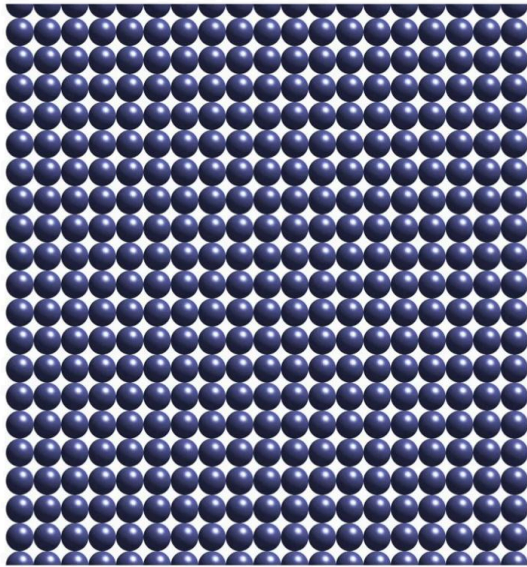
Summary



3m 20s

Crystal truncation rods – the signal that keeps on giving

■ The “LEED/RHEED” explanation



We begin with a conceptually relatively simple explanation of surface X-ray signal, which I like to call the LEED-RHEED signal, on account of these two electron diffraction techniques having only a very shallow penetration depth into bulk condensed matter. On the left is a cartoon of a bulk crystalline structure, while on the right is its diffraction pattern. If we increase the separation of the atoms in one direction, let's say vertically, the corresponding diffraction pattern will shrink in the same direction in an inversely proportional manner. For example, if the distance between atomic planes doubled, then the separation of the diffraction spots in that direction will halve. All right, so let's begin.

Notes

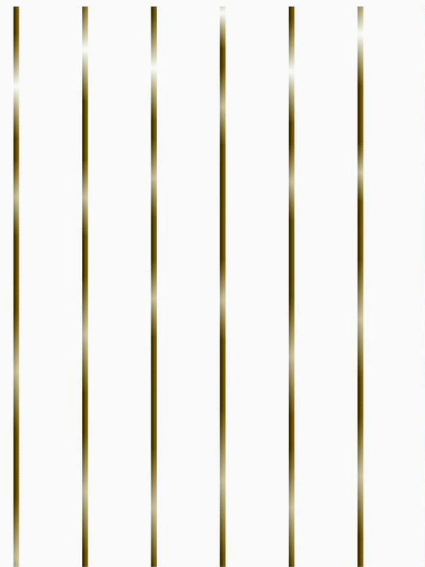
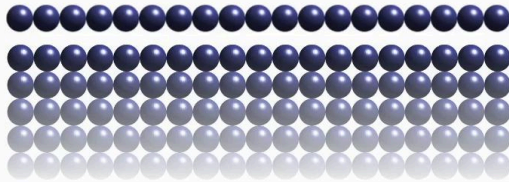
Summary



4m 25s

Crystal truncation rods – the signal that keeps on giving

- The “LEED/RHEED” explanation



Continuous signal, but modulated

As a separation in real space becomes much larger than the original value, the diffraction pattern in that direction becomes increasingly packed until when there is really only one atomic plane left, separated to all intents and purposes by an infinite distance from the planes above and below. The corresponding pattern in reciprocal space is continuous in that direction. This continuous signal perpendicular to the surface plane is called crystal truncation rods. A two-dimensional structure which has got periodicity in the plane will be continuous out of the plane in its diffraction pattern. In reality, the top layer of an exposed surface may differ in its separation from the subsequent layers, in which case, the CTRs are continuous, but may exhibit fluctuations in intensity that depend on the details of the vertical deviations of the top layers or layers from their bulk values.

Notes

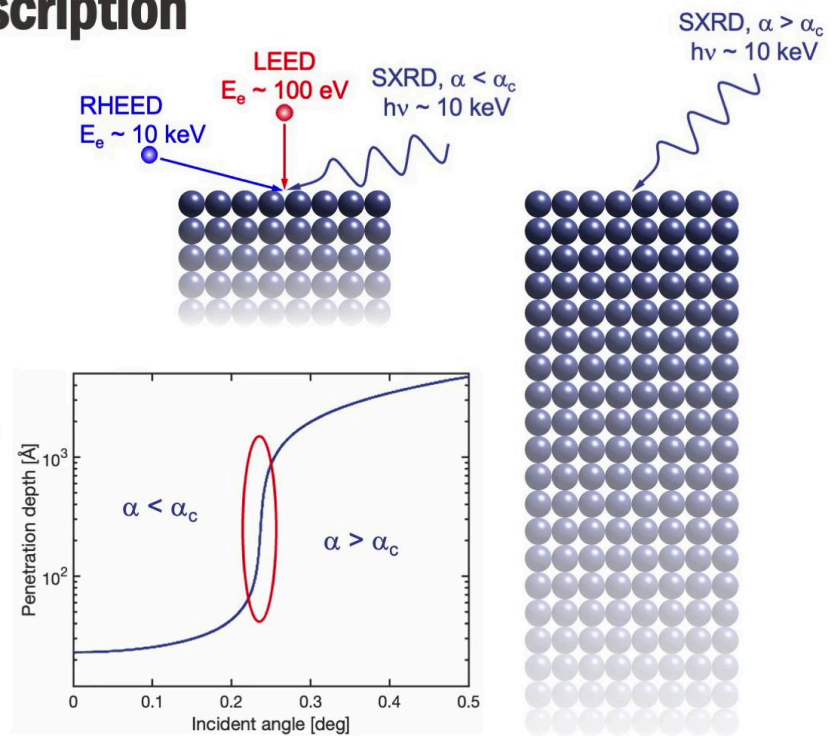
Summary



5m 15s

CTRs – a better description

- Why?
 - LEED, RHEED: surface sensitive (~ nm)
 - X-rays: bulk (~ 100 nm)
- X-rays
 - $n < 1$
 - Total external reflection
 - Evanescent standing wave below α_c
 - Enhanced surface sensitivity
 - BUT: normally $\alpha > \alpha_c$
- Why?
 - Buried interfaces
 - Experimental stability



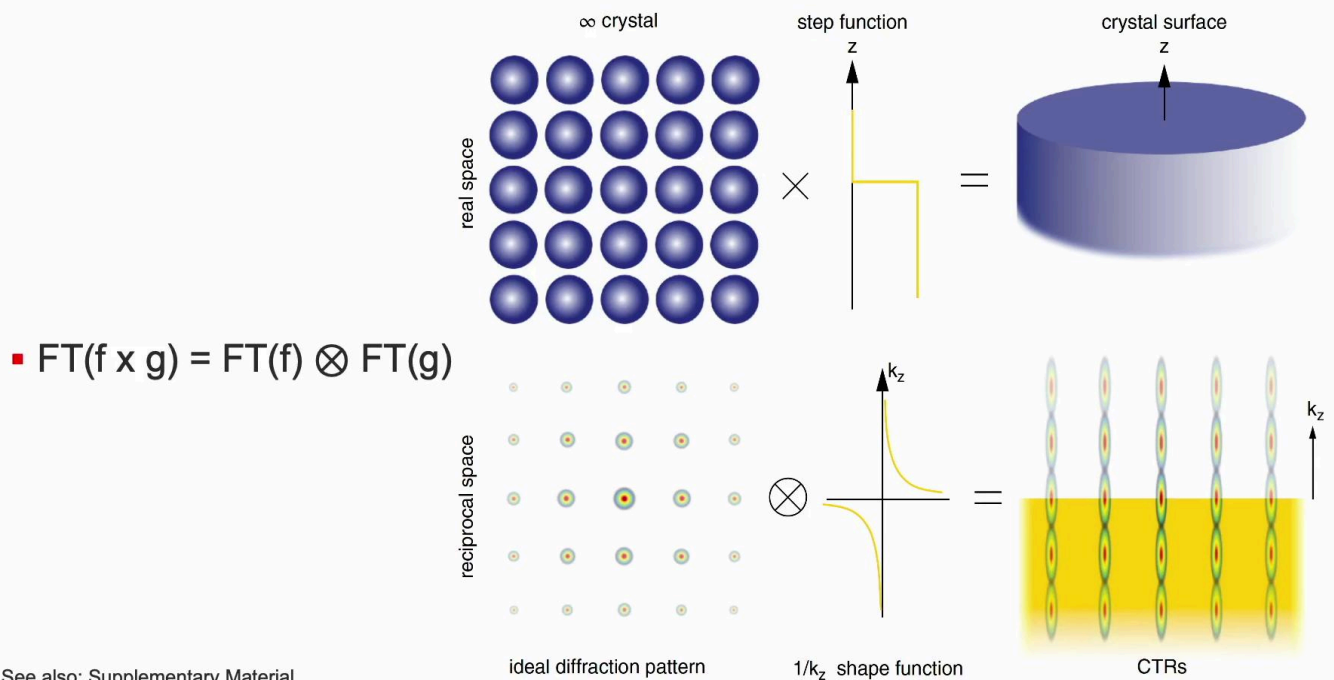
Okay, that was the explanation using the so-called LEED-RHEED approach. A better explanation is, first of all, not to assume that only the top-most one or two layers are probed. This clearly isn't a good model for buried interfaces. It is also problematic when applied to X-rays. One can indeed set the incident angle to be less than the critical angle α_c , and this does indeed confer enhanced surface sensitivity, but at the expense of bulk signal, which one wants to record for comparative purposes. Moreover, the highest surface sensitivity is exactly at α_c , but this changes extremely sharply with only the tiniest deviations from α_c , as one can see from the steep gradient in the curve of the penetration depth with incident angle, shown here. For the sake of experimental stability, therefore, it's highly unusual to set the incident angle on the sample to be very close to α_c . Instead, one usually sets an incident angle well above α_c .

Notes

Summary



CTRs explained via the convolution theory



See also: Supplementary Material
"Fourier transforms and convolutions made simple"

A better way to describe CTRs, at least for X-rays and synchrotrons uses the convolution theorem. This states that the Fourier transform of the product of two functions f and g is equal to the Fourier transform of one convoluted with the Fourier transform of the other. Now, we can mathematically express a semi-infinite crystalline object, in other words, one that extends to minus infinity, but is terminated at z equals 0, thus producing a crystal surface as simply an infinitely large crystal in all directions multiplied by a step function equal to unity for z is less than or equal to 0 and is equal to 0 for z is greater than 0. Using our expression for the convolution theorem, we take the FT, Fourier transform, of our crystal, in other words, a perfect diffraction pattern, and convolute this with the Fourier transform of the step function, which is a curve which is proportional to $1/k_z$. This action of convolution smears out the diffraction pattern in the out-of-plane direction k_z in reciprocal space, resulting in a continuous signal again, our crystal truncation rods. The signal is intense where we expect it to be at the positions of the bulk Bragg peaks, but crucially, continues to exhibit some intensity in between.

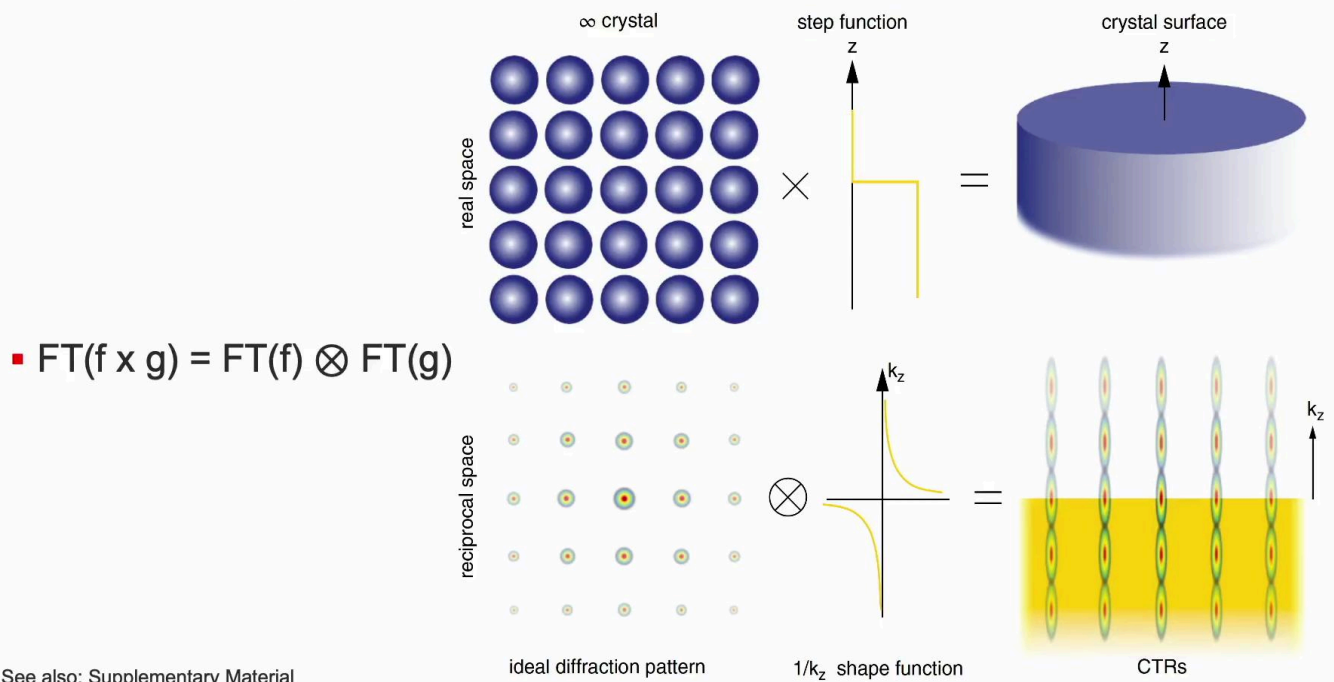
Notes

Summary



7m 32s

CTRs explained via the convolution theory



CTRs are labeled hkl , for example, $12l$. In other words, the two in-plane values h and k are well defined, while the 3rd Miller index is, in fact, kept general as l to indicate continuous signal intensity in that direction.

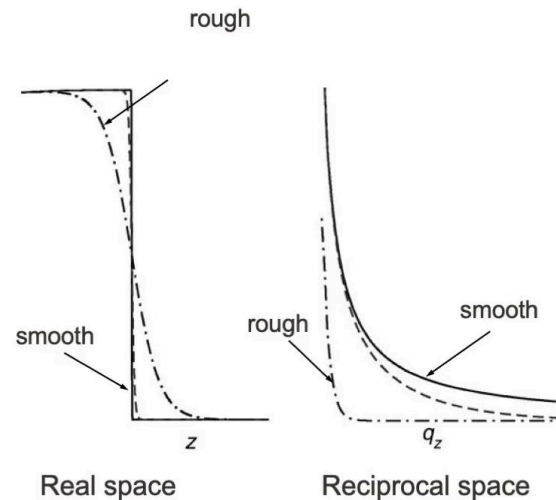
Notes

Summary



Why don't we see CTRs all the time?

- Why do you not always see CTRs?
 - After all, every crystal has a surface...
- But how flat is that surface?
 - Atomically flat – “shape function” quite broad in k-space
 - Rough, nobbly surface (on atomic scale)
 - Real-space: large depth variations
 - k-space: “shape function” very narrow
- Nanocrystals have CTRs with modulations that reveal their size



You might therefore reasonably ask, "Why the heck don't I always see CTRs as all samples are bound by surfaces?" However, the width of the Fourier transform of the step function is inversely proportional to the progress out of plane in real space from being a bulk crystal to being nothing, which is just a fancy way of saying how rough the surface is, how quickly does it go from being bulk to being rough and knobbly to actually not being there anymore. A rough surface needs some monolayers between the deepest valleys of the rough surface to the highest peaks, and its corresponding FT is very narrow compared to a surface which is atomically flat. Convoluting the ideal bulk diffraction pattern with a sharp 1 upon kz function means that the region between Bragg peaks soon becomes extremely weak, and no signal can be detected. The take-home message here is that if you try to do surface X-ray diffraction experiments on samples with surface or interface roughnesses much more than a couple of monolayers within the coherence volume of the radiation being used, you are most likely going to be disappointed.

Notes

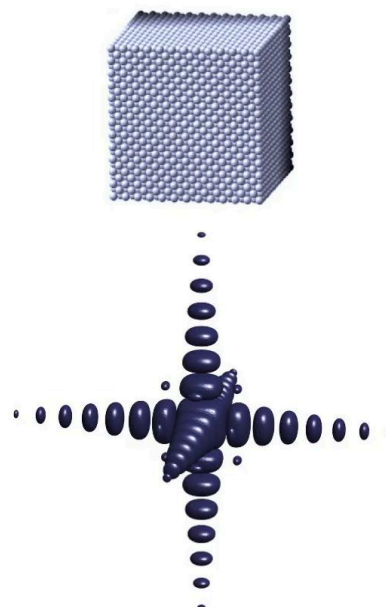
Summary



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See e.g. A. Pryor Jr. *et al.*, Scientific Reports DOI:10.1038/s41598-018-26182-1



Interestingly enough, however, nanocrystals with dimensions perhaps only one or two orders of magnitude larger than the X-ray wavelength can often have perfect crystalline surface facets, leading to CTRs extending in all directions perpendicular to those facets. Modulations in their intensity are caused by interference from opposite faces and will thus reflect the physical size of these nanoparticles. We will discuss this again in the sixth week when we look at coherent X-ray diffractive imaging, otherwise known as lensless imaging.

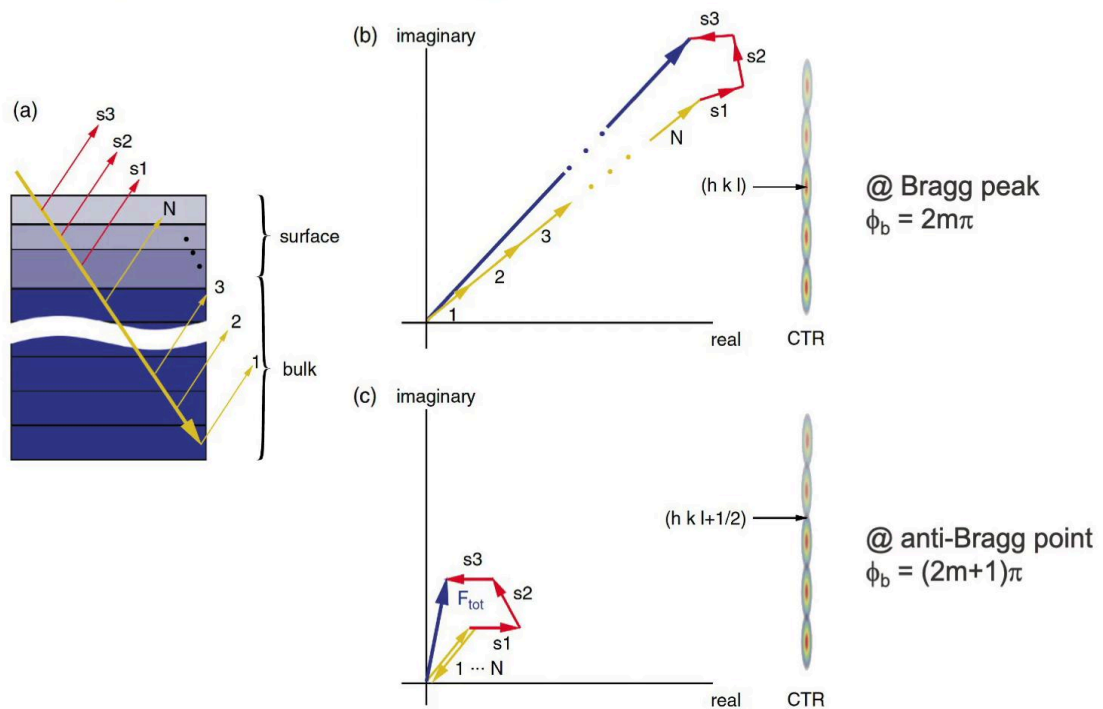
Notes

Summary



10m 44s

Intensity variations along CTRs



The higher sensitivity of CTRs to surface structure occurs at or near the so-called anti-Bragg points directly in between Bragg peaks. Here, the phase of structure factors of successive layers of bulk unit cells is an odd integer number of π , in contrast to the Bragg peaks where the structure factors all add up in phase. At the anti-Bragg point, bulk signal constantly cancels itself out from each layer. The surface region, however, will most likely have a different phase for each layer, given the here as red structure factors $s1$, $s2$, and $s3$. Their relative contribution is therefore much larger than close to the Bragg peak, and will thus have a much more significant impact on the relative intensity. We will look at this more quantitatively in the second video of this section.

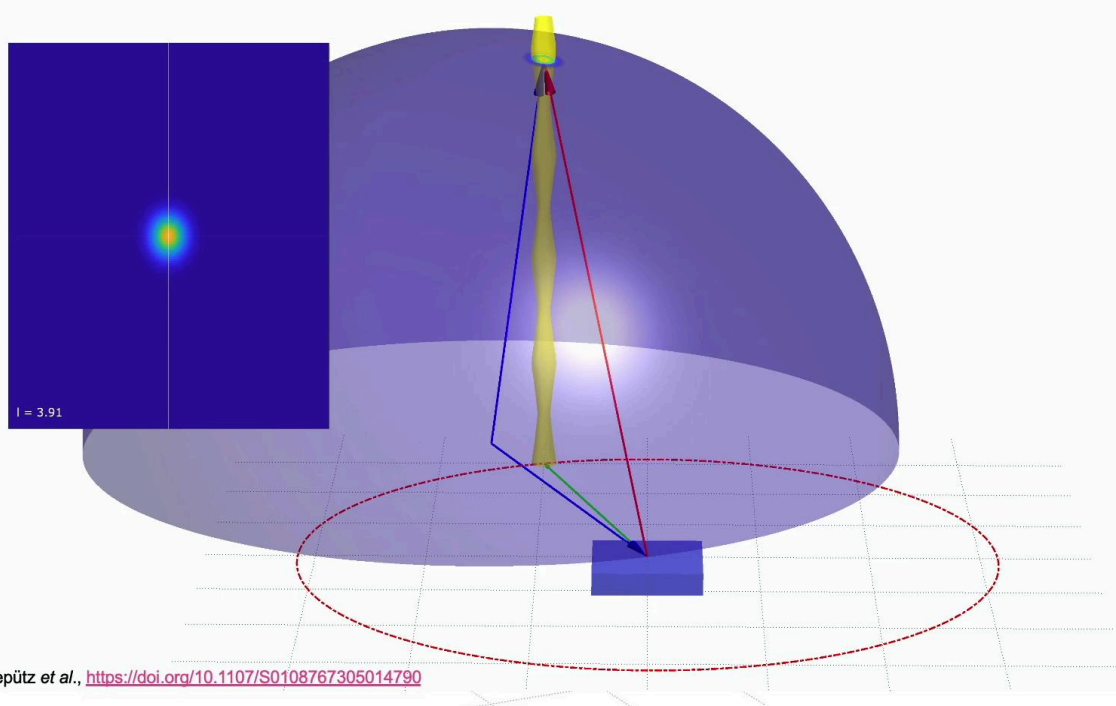
Notes

Summary



11m 22s

Recording SXR data



C.M. Schlepütz *et al.*, <https://doi.org/10.1107/S0108767305014790>

There are several configurations that are possible to record CTRs. This is just one commonly used setup in which the incident radiation hits the sample surface at a constant glancing angle, while a concerted rotation of the sample around its normal and two rotation angles of the detector, both azimuthally and in the polar coordinate, allows one to follow the CTR signal using the selected Bragg peak method. The detector is placed on the axis defined by k_{out} , and will record that part of the CTR where it intersects with the Ewald sphere. In the past, one would use a point detector and perform a rocking curve to obtain the intensity at any given point along the CTR. With the advent of fast photon-counting detectors, the entire intercept between CTR and Ewald sphere can be recorded in a single frame. The first ever use of the now legendary PILATUS detector was reported in 2005 on surface X-ray diffraction experiments carried out at the surface diffraction station of the Material Science beamline at the Swiss Light Source, detailed in the citation given here.

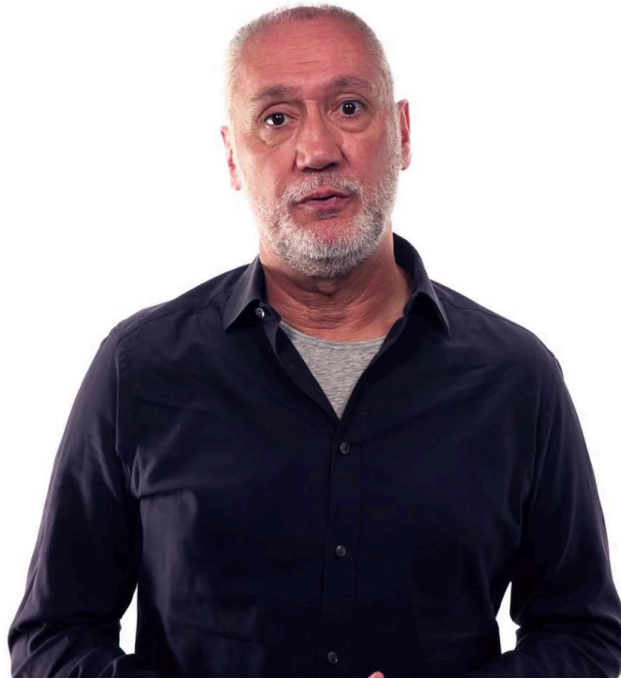
Notes

Summary



12m 21s

In the next video...



In the next video, we'll consider particular ways in which surfaces and interfaces can change their structure in so-called relaxations and reconstructions, and we will show real examples of these.

Notes

Summary

13m 36s

