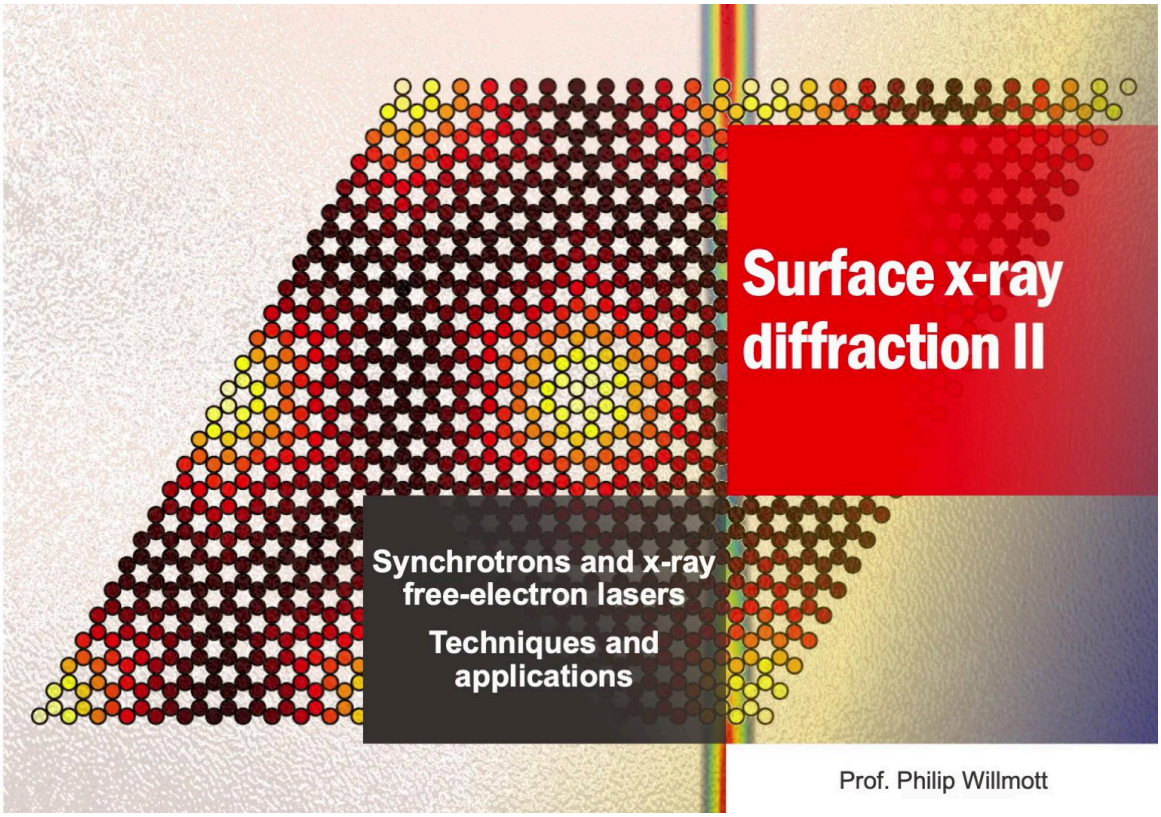
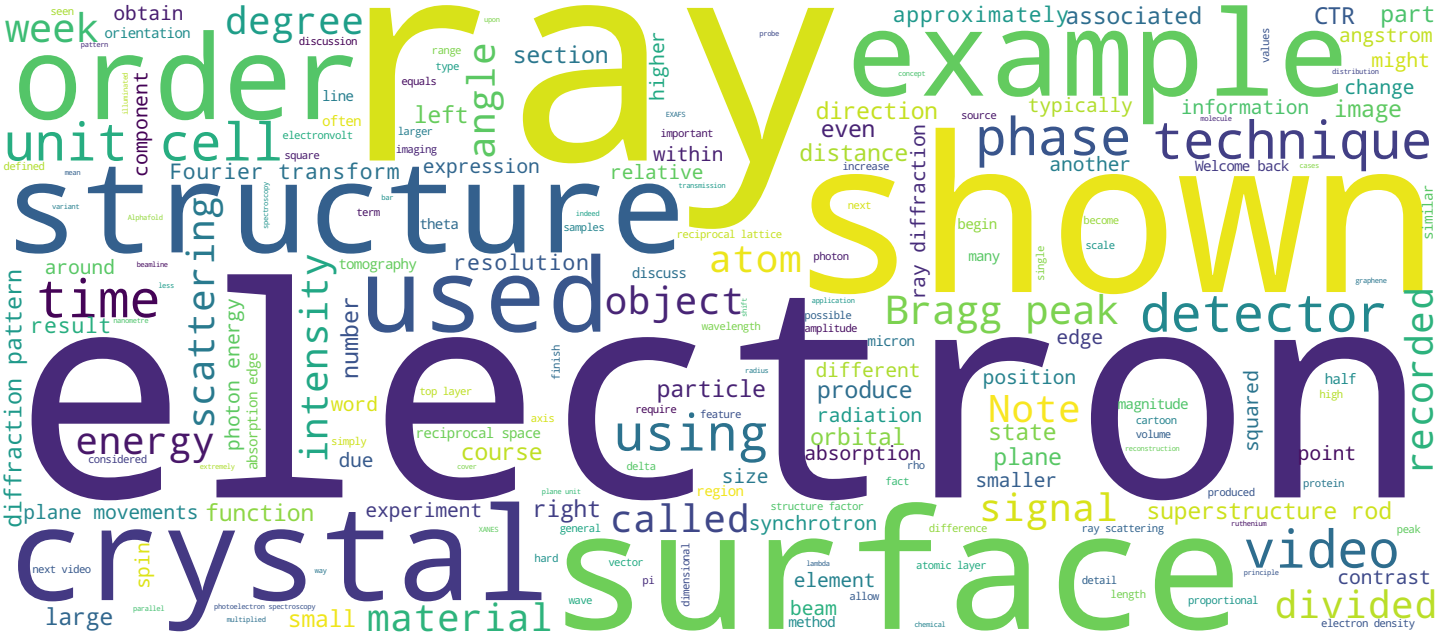
EPFL



École polytechnique fédérale de Lausanne



Search MOOC

Video

EPFL

Contents and objectives of this video

- Relaxations
- Reconstructions
- Examples

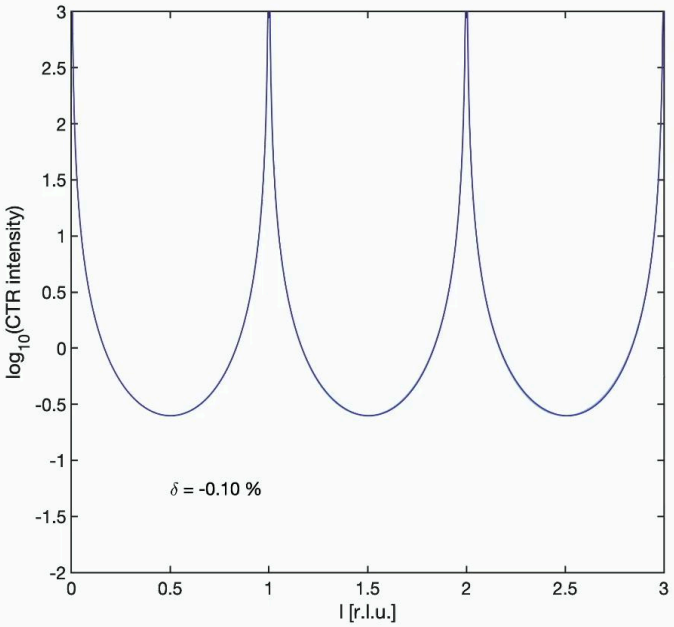
Welcome back to the second video of Section 3 of week two of this course, in which we're discussing surface X-ray diffraction. We will consider two ways in which surface and interface atoms can modify their configuration, namely relaxations, in which there are only out-of-plane shifts, but not in-plane movements, and reconstructions, in which there are typically both in-plane and out-of-plane movements, and for which the in-plane movements result in a new, larger periodicity of the structure in the surface plane compared to the bulk periodicity. In both cases, we will look at real examples from recent studies.

Notes

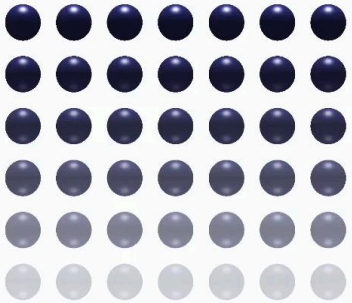
Summary

0m 05s

Relaxations and reconstructions



- Relaxations
  - Vertical (out-of-plane) movements only



$$I(l,\delta) = \left| A(Q) \left(\frac{1}{1 - e^{i2\pi l}} + e^{-i2\pi(1+\delta)l} \right) \right|^2$$

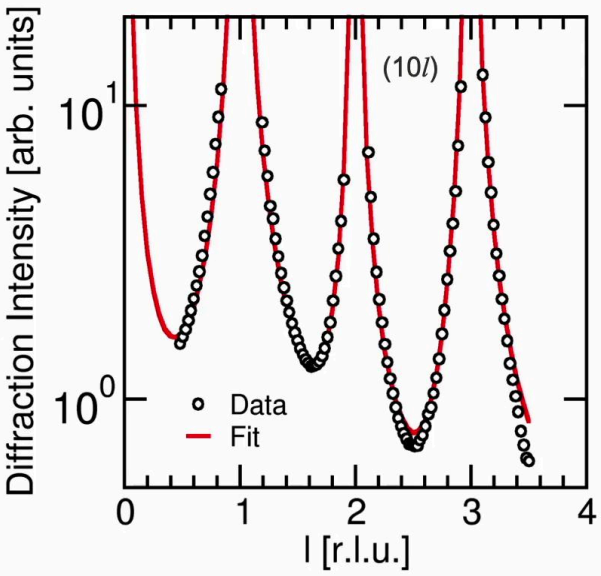
Relaxations describe vertical shifts of all components of one or more atomic layers. For each layer, the shifts are equal. Otherwise, the periodicity in the surface plane will increase, resulting in a so-called surface superstructure, which we will look at shortly. In the kinematical approximation, the intensity of a CTR of a crystal for which there is a wholesale shift delta of the top layer is given by the equation shown bottom right. The effect of relaxations is to skew the otherwise symmetric profile of the CTRs between Bragg peaks. In this animation, the impact of shifting the top layer alone by plus or minus 5% is shown. Note that in the real space cartoon of the shift of this top layer on the right, I have exaggerated the movements by a factor of 10, hence these limits of plus or minus 5% are actually shown as plus or minus 50%. Note that the signal intensity can change by up to two orders of magnitude in the weaker parts of the CTR, even for such apparently modest deviations.

Notes

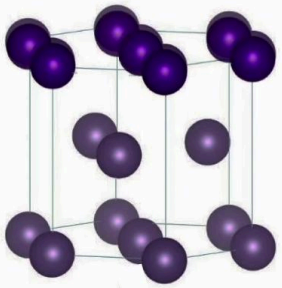
Summary

0m 45s

Relaxations and reconstructions



- Example: surface of Ru(0001)
  - Hexagonal close packed (hcp) u.c.
  - Bulk interatomic layer separation = 2.141 Å
  - Top layer: (2.080±0.003) Å
  - Contraction of 2.8%



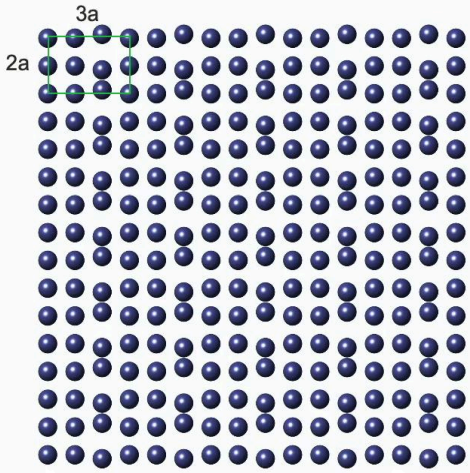
The surface of ruthenium(0001), a hexagonal, close-packed crystal, has bulk interlayer separations of 2.141 angstroms. CTRs of this crystal were recorded and fit to a shift of just the top atomic layer, which produced a best fit of 2.080 angstroms. In other words, a contraction of 2.8%. The 1 0 L rod is shown on the left.

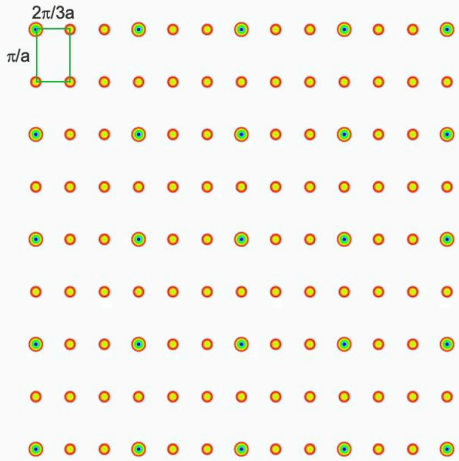
Notes

Summary

2m 04s

Relaxations and reconstructions





- Reconstructions
  - In-plane movements
  - Vertical (out-of-plane) movements also possible

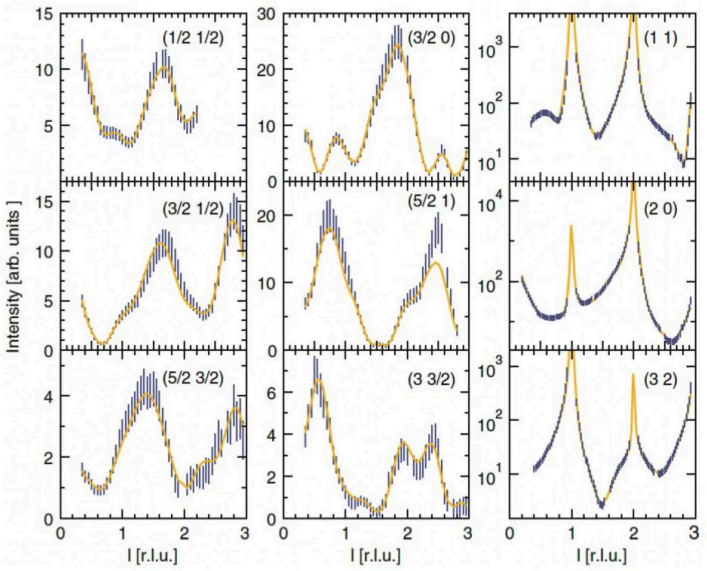
Reconstructions arise due to either unequal out-of-plane movements for a given atomic layer or in-plane movements. Both result in a new in-plane periodicity in the surface region. If we consider the cartoon on the left of a square bulk lattice, the in-plane unit cell dimensions, a, correspond to reciprocal space in-plane separations of Bragg peaks of 2 pi divided by a. If the surface atoms then rearrange because they're at the surface, new diffraction features will emerge. In this cartoon, the surface region assumes a new periodicity of 2a vertically and 3a horizontally, and in the diffraction pattern that is in reciprocal space, the new features called superstructure rods are three times closer in the horizontal direction and twice as small in the vertical direction.

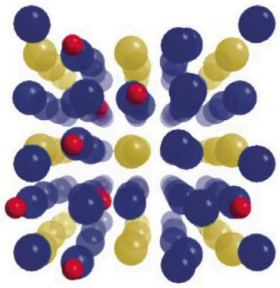
Notes

Summary

2m 35s

Superstructure rods





$SrTiO_3$ 2x2 surface
Ti: red, O: blue, Sr: yellow

- Sometimes called fractional-order rods
- Different in-plane periodicity than bulk structure
- No bulk contribution ⇒ no intense Bragg peaks
  - Intensities similar to minima of CTRs
- Intensity fluctuations much more modest than in CTRs
- Provide information exclusively about superstructure and not bulk

See R. Herger *et al.*, https://doi.org/10.1103/PhysRevLett.98.076102

Superstructure rods are therefore signatures of reconstructions involving unequal, out-of-plane and/or in-plane movements of near-surface atoms. Real data, these are the blue data points with error bars on the left, from surface diffraction experiments performed on titanium oxide, terminated strontium titanate, are shown here. The left and middle columns show different superstructure rods with half integer h and k values, indicative of a two-by-two reconstruction. The right-hand column shows three CTRs. Note that the minimum intensities of the CTRs are very similar to the typical intensities of the superstructure rods. The best fit model, given also by the yellow curves in the CTRs and superstructure rod plots, is shown on the right.

Notes

Summary

3m 34s

Example – graphene on ruthenium

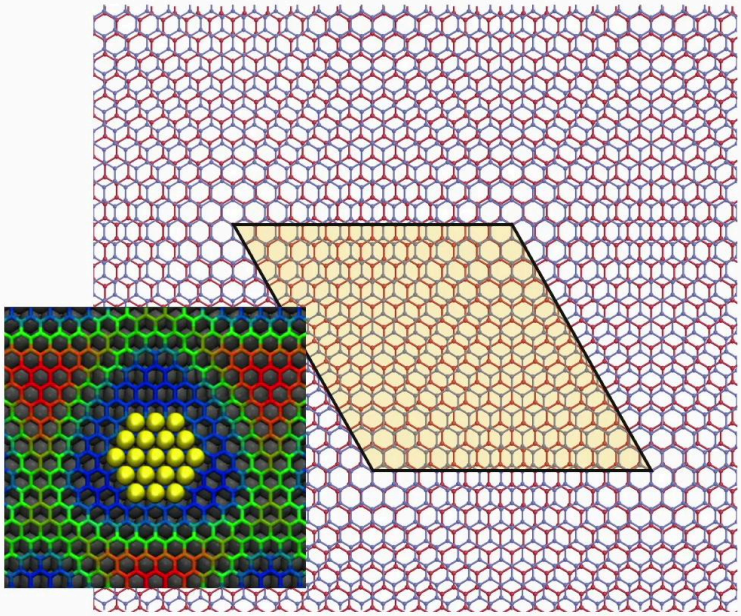
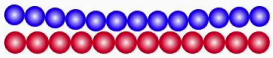


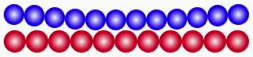
Image of nanoparticle on graphene from M. D. Jiménez-Sánchez *et al.*, Carbon
https://doi.org/10.1016/j.carbon.2020.11.086

- Graphene on ruthenium(0001)
  - Corrugated moiré pattern
  - Literature 2007
    - 13x13 on 12x12?

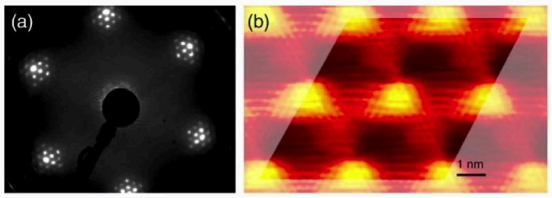


or

- 12x12 on 11x11?



- LEED and STM analysis ambiguous



See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

Okay, we're going to end this video with an entertaining example that really surprised me and my group when we discovered it. Since its discovery in 2004, graphene has been the subject of many diverse studies. One interesting application of graphene has been its structure when deposited on metal surfaces, which also have hexagonal surface symmetry, but different in-plane unit cell sizes. This produces a Moiré effect, as can be seen here, and a surface in-plane unit cell that is substantially larger than the individual metal or graphene unit cells. Clearly, the chemical bonding between graphene and the metal surface will vary considerably within this surface unit cell, and it was hoped that this might lead to a hexagonal bunching or buckling of the graphene, which could be used as a template for trapping regular arrays of nanoparticles. The system under investigation was a monolayer of graphene deposited on ruthenium(0001). From the literature, there was a dispute as to whether there were 13 times 13 graphene unit cells sitting on top of 12 by 12 ruthenium cells, or whether there were 12 by 12 graphene cells on 11 by 11 ruthenium cells. For the sake of brevity, we call these 13 on 12 and 12 on 11, respectively. Neither low energy electron diffraction or scanning tunneling microscopy have provided sufficient resolution to settle these burning issues.

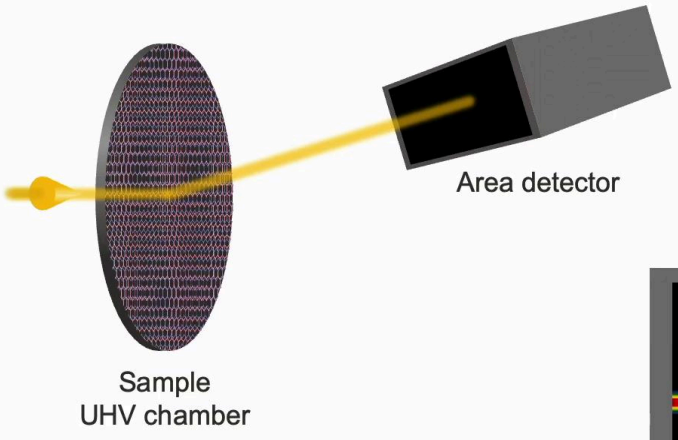
Notes

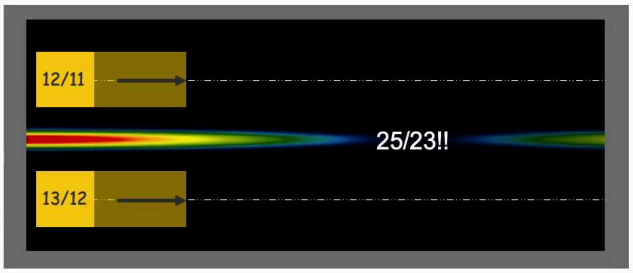
Summary

4m 28s

Example – graphene on ruthenium

- Experiment
  - Glancing-incident beam
  - Alignment calibrated to bulk Ru-substrate diffraction signal
    - Accuracy 0.0002 r.l.u.
  - In-plane position of superstructure rods





See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

The sample was prepared under ultra-high vacuum conditions and transferred also in ultra-high vacuum to another UHV chamber with an X-ray transparent beryllium dome. Exact crystallographic alignment of the sample was possible through calibration with the strong ruthenium substrate bulk diffraction signals to an accuracy and reciprocal space of about two parts in 10,000. Now, once calibration was completed, we moved the area detector to a region where it could capture both a possible 13 upon 12 or a 12 upon 11 signal, depending on which one it really was. We used Post-it notes on the computer screen panel for the detector output at both of these positions and held our breath as we opened the shutter to allow the sample to be illuminated by X-rays. Would it be 13 on 12 or would it be 12 on 11? Boom. It was neither. But in fact, an almost unbelievable 25 on 23 structure. This contains 1,250 carbon atoms alone.

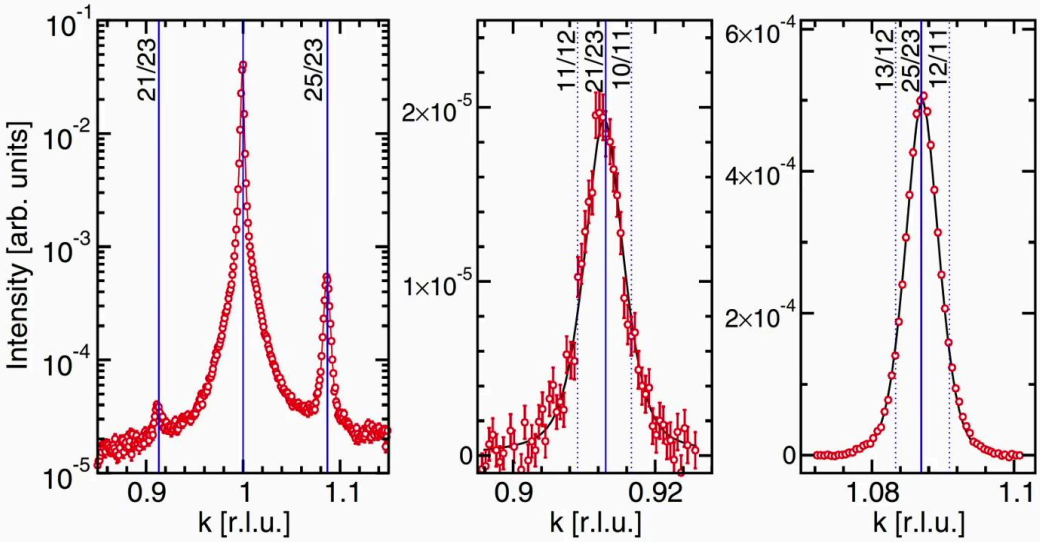
Notes

Summary

6m 12s

Example – graphene on ruthenium

- In-plane data (scans at a constant out-of-plane scattering vector $Q_\perp$)



See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

Satellites on either side of the ruthenium 0 1 crystal truncation rod, or CTR, in the in-plane scan in the k direction, can be seen on the left-hand side plot. The primary graphene 0 1 signal at k equals 1.087 reciprocal lattice units is, in itself, actually no proof of a commensurate reconstruction, as in principle, the graphene could float above the ruthenium substrate without any definitive registry with it. However, the presence also of a signal at an equal distance on the other side of the ruthenium CTR at 0.913 reciprocal lattice units indicates that a real construction must exist. The two zoom-ins of the reconstruction peaks, which are part of their respective superstructure rods, clearly show that the reconstruction be neither 12 on 11 nor 13 upon 12.

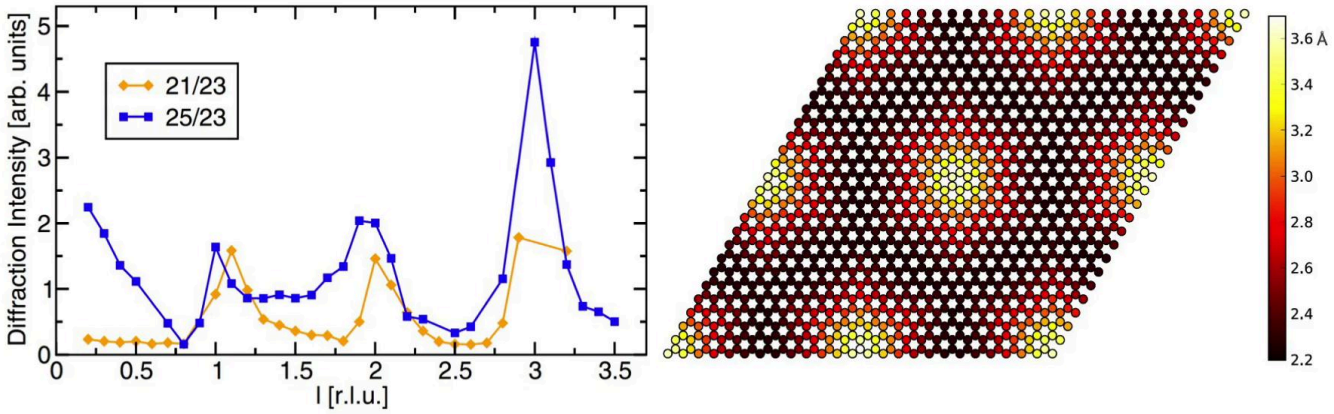
Notes

Summary

7m 20s

Example – graphene on ruthenium

- Out-of-plane data (scans along the l direction for fixed h and k)
  - Probes out-of-plane positions of top Ru layer and graphene
  - (0 25/23 L) and (0 21/23 L) rods
  - Model to data indicates corrugation amplitude ~ 1.4 Å



See D. Martoccia *et al.*, PRL (2008) DOI: 10.1103/PhysRevLett.101.126102

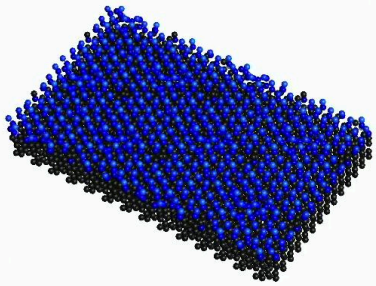
Lastly, the two superstructure rods were recorded as a function of the out-of-plane reciprocal lattice vector l. These plots provide information on the out-of-plane atomic positions of the carbon and ruthenium atoms and indicated a corrugation amplitude of approximately 1.4 angstroms between the valleys and peaks of the graphene corrugation. The four sub-cells within the super cell can't map translationally onto one another as from the SXRD data, it is clear that the number of unit cells of ruthenium 23, as well as on graphene 25, along with the edges of the supercell, are all odd. One is therefore forced to conclude that the graphene supercell must consist of four translationally inequivalent sub-cells.

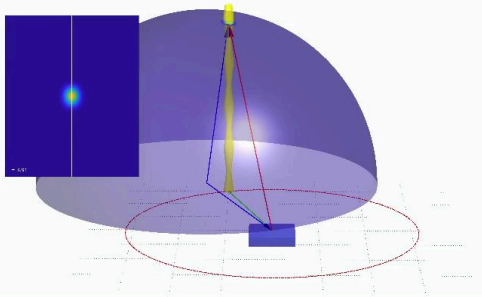
Notes

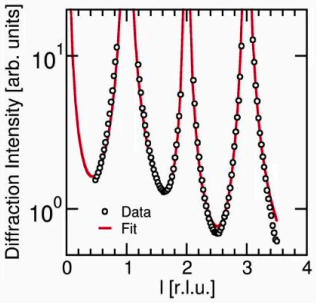
Summary

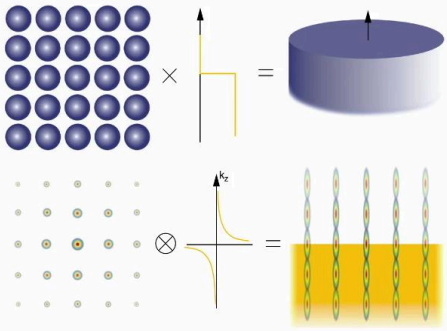
8m 25s

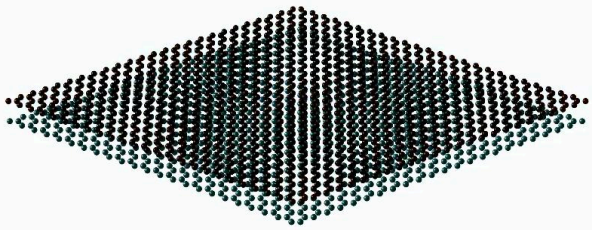
Summary of this section











In these two videos dealing with surface X-ray diffraction, we first considered why surfaces and interfaces might be interesting, even in principle, then made different arguments how and why surface diffraction signal arises. We then looked at how one records surface X-ray diffraction data and then what types of signal we can expect, including CTRs and superstructure rods. We finished with an example of surface X-ray diffraction about the curious case of corrugated structure of graphene grown on ruthenium.

Notes

Summary

9m 17s

In the next section...

In the next and final section of this week, we will look at small-angle X-ray scattering, a technique for determining the mesoscale structure of particles on the nanometre scale and the related technique of X-ray reflectivity.

Notes

Summary

9m 52s