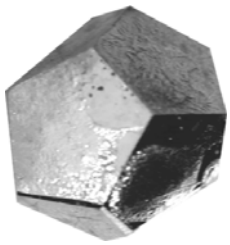
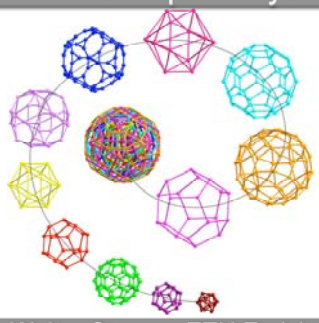
Quasicrystals - The Crystallographer's Point of View



Walter Steurer, ETH Zurich 1

What you probably never wanted to know about quasicrystals



Walter Steurer, ETH Zurich 2

What is a crystallographer?

Crystallographer as seen by others

Crystallographer as seen by myself

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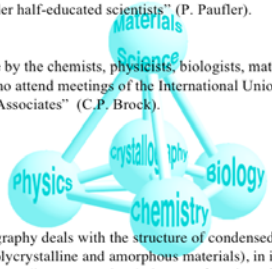
What is crystallography?

"… almost nobody knows what it is or, even worse, … the term associates old-fashioned science under half-educated scientists" (P. Paufler).

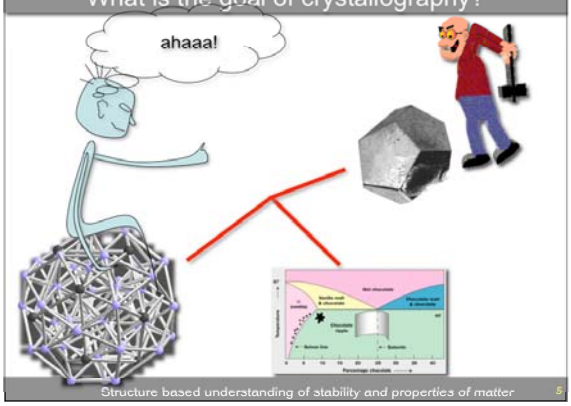
"It is the science done by the chemists, physicists, biologists, mathematicians, and materials scientists who attend meetings of the International Union of Crystallography and its Regional Associates" (C.P. Brock).



"*Summary*: Crystallography deals with the structure of condensed matter on atomic scale (real crystals, polycrystalline and amorphous materials), in its stable as well as in its metastable states. It studies structural ordering as a function of chemical composition, temperature, pressure, electric or magnetic fields, time… It relates physical, chemical or biological properties to structural order. "

125th anniversary of Zeitschrift für Kristallographie 217 (2002) 267-383. 4

What is the goal of crystallography?



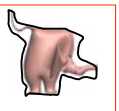
Structure based understanding of stability and properties of matter 5

How I think a physicist sees a QC structure

Well, I have a very nice structure model indeed. Yes, I know it's only a first approximation. However, it fits the data nicely with just a single scale factor. I can model now everything.

Experimental data

Really nice model



Nice fit

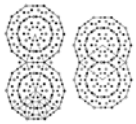
The *toy model*  nicely (?) reproduces measured properties

Model-based understanding of stability and properties of the ~~quasicrystal~~ model 6

What do we want to know about a QC structure?

Physicist: idealized factors governing structure formation and physical properties

idealized structure models and their properties - toy models such as the Burkov model, Elser model ...



Burkov Phys. Rev. Lett. 67 (1991) 614; Elser Phil. Mag. B73 (1996) 641 7

How I think a mathematician sees a QC structure

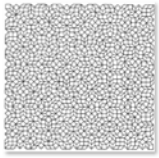
The physicist says it's an elephant or perhaps a rhino. I have nice generating and growth algorithms, such as the $\mathcal{K}^*$-one for all kinds of infinite elephants. They apply very well even to fractal dragons iff they are ....

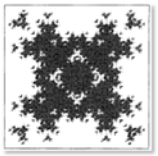
Full understanding of ideal structures with funny feelings that nature may not be ideal. 8

What do we want to know about a QC structure?

Mathematician: idealized geometrical-structure building principles - mathematical objects

infinite tilings or *n*D structures and their mathematical properties





Godréche et al., Jorunal de Physique I France 3 (1993) 1921 9

How I think a materials scientist sees a QC structure

The physicist says it's an elephant with interesting properties. Fabrication of perfect elephants is much too expensive. Perhaps an approximant will do it as well. The local structure of an elephant and a pig is quite similar ....

Experimental data

Nice fit

Nice fit as well

Pragamatic understanding of stability and properties of matter 10

What do we want to know about a QC structure?

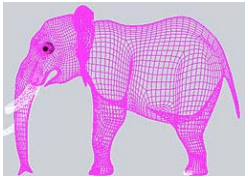
Materials Scientist: real structure/microstructure-property relationships

tailoring of materials and real properties based on simplified idealized structure models. Similar properties of QC and approximants are taken into account. The micro-structure of real multiphase materials become the focus of attention.

(Micro)structure based understanding of stability and properties of matter 11

How I know a crystallographer sees a QC structure

First we solve the idealized average structure. There are a lot of split bones and overlapping muscles. Therefore, to provide a toy model for physicists we have to model the idealized real structure. Then ....



ideal structure

idealized real structure

Where are the atoms (each single one) in a macroscopic quasicrystal? 12

What do we want to know about a QC structure?

Crystallographer: ordering principles of idealized and real structure

As far as possible model-free structure analysis in order to find out whether or not QCs are quasiperiodic and what kind of disorder is present. One of the goals is to provide realistic models as input for quantum-mechanical calculations.

What do we want to know about a QC structure?

We want to know everything we need to build a model that describes reality reasonably well.

Mathematician: idealized geometrical-structure building principles - mathematical objects

Physicist: idealized factors governing structure formation and physical properties

Materials Scientist: real structure/microstructure-property relationships

Crystallographer: ordering principles of idealized and real structures

Structural peculiarities of quasicrystals

Long-range order

- Are QC strictly quasiperiodic or on average only or....
- Is *n*D description really applicable? If yes, are atomic surfaces dense or fractal or ...
- How does long-range order vary with temperature, pressure ...

Disorder

- Does disorder in quasicrystals differ from that in crystals?
- What is the structural meaning of phasons and phason fluctuations?

Structural peculiarities of quasicrystals

Long-range order (the ordering of clusters)

Knowing the structure of a (quasi)crystal means knowing the coordinates of ≈ 10^{20} atoms. At present, the maximum number of unique experimental data accessible from diffraction experiments on quasicrystals is smaller than ≈ 10^4. This means, we need models constraining the number of free parameters to << 10^4.

Nowadays, ab-initio quantum-mechanical modeling is possible for approximants only (< 1000 atoms). Consequently, the property that is typical for quasicrystals, *i.e.* the quasiperiodic long-range order, cannot be studied in this way at present and near future.

Expected number of reflections

Total number of Bragg reflections $N_{int} = (4\pi a^3)/(3d_{min}^3)$.

For a 500x500x500 Å^3 approximant unit cell (≈9 000 000 atoms) and standard resolution $d_{min}=\lambda$ (for MoKα λ=0.70926 Å, $\theta_{max}=30°$) we get

N_{int} = 1 526 527 042 reflections

In case of a primitive (face-centred) icosahedral phase this corresponds to

$N_{unique} = N_{int}/(120x32)$ = 6 114 636 (191 082) unique reflections.

In case of a decagonal phase with 8 Å periodicity this corresponds to

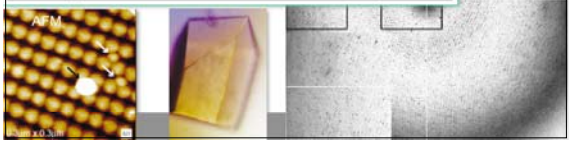
$N_{unique} = N_{int}/(62.5x40)$ = 610 610 unique reflections.

Preliminary analysis of crystals of panicum mosaic virus (PMV) by X-ray diffraction and atomic force microscopy

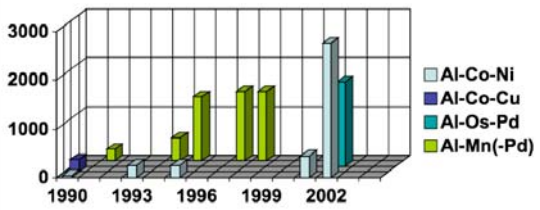
Débora L. Makino, Steven B. Larson and Alexander McPherson*

Acta Cryst. (2005). D61, 173–179

Wavelength (Å)	1.000
Space group	$P2_1$
Z	4
Unit-cell parameters (Å, °)	a = 411.74, b = 403.90, c = 412.46, β = 89.65
No. observations	17212205
No. unique reflections	2279719
Crystal mosaicity (°)	0.373–0.544
Resolution range (Å) (θ_{max} ≈10°)	50.01–2.71 (2.81–2.71)
Completeness (%)	63.0 (4.9)
R_{merge} (%)	13.6 (34.6)
$I/\sigma(I)$	6.8 (2.5)
Redundancy	7.55 (3.14)

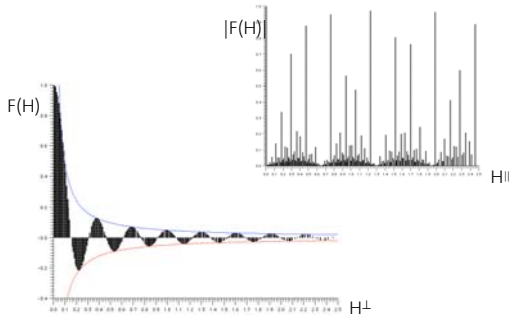


Quantitative structure analyses of decagonal phases



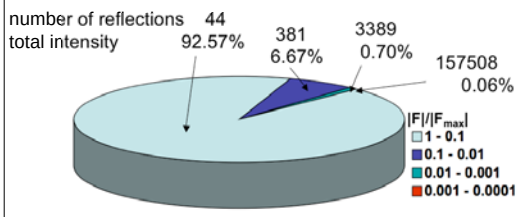
Number of reflections used for structure analyses as a function of time 19

Intensity statistics of the Fibonacci sequence



Number of weak reflections grows with $|H|^2$, that of strong one with $|H|$ 20

Intensity statistics of the Fibonacci sequence

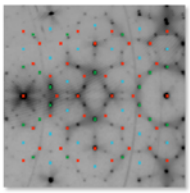


Al, B = 1 Å², S = 2.5 Å, for 161 322 reflections within $0 \le \sin\theta/\lambda \le 2$

Number of weak reflections grows with $|H|^2$, that of strong one with $|H|$ 21

Long-range order

The smallest distances between Bragg reflections in d-Al-Co-Ni corresponds to netplane distances < 100 Å. This means, long-range order can be determined *a priori* on that scale only.



The accessible range of experimental information on long-range order is larger for imaging methods (HRTEM, HAADF-STEM, AFM, STM,..).

A priori determination of long-range order 22

Structural peculiarities of quasicrystals

Short-range order (the structure of clusters)

The method of choice for obtaining a starting model are electron microscopic methods, in particular for decagonal phases.

The novel Ultra-High-Resolution Transmission Electron Microscopes (UHRTEM) with full correction of spherical aberration will allow to get much better images in future. For instance, for a 200 keV microscope (Zeiss), a resolution of 0.8 Å is possible.

However, compared to diffraction methods, the accuracy is very low (laterally: ≈ 0.5 Å, vertically: no spatial resolution at all).

Determination of local order 23

Structural peculiarities of quasicrystals

Disorder

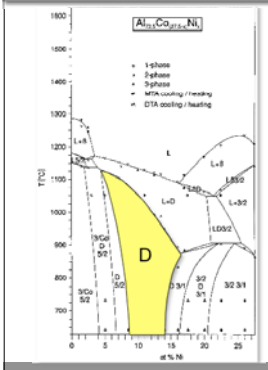
A principal problem is that in most cases non-equilibrium structures are studied. Usually, a QC is prepared from the melt, HT annealed, quenched.

During cooling to RT partial relaxation takes place due to a different efficient atomic volume at HT and RT (atomic vibrations). Chemical disorder, thermal vacancies and random phason fluctuations are not equilibrated.

Structural disorder of the displacive and/or the substitutional type may be present anyway, also at equilibrium conditions.

Structural disorder 24

Inherent disorder: system Al-Co-Ni



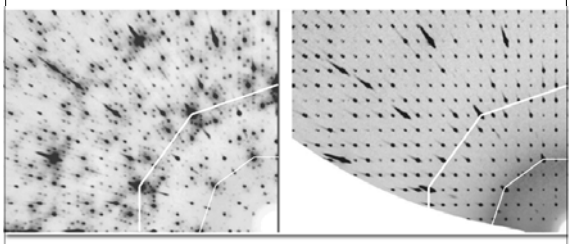
If a single phase has a broad stability range, chemical disorder must be present.

This leads locally to relaxations and, possibly, to element-specific short-range order.

Gödecke & Lück (1996) 25

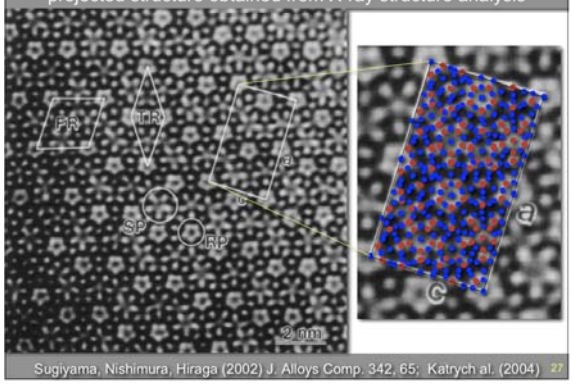
Decagonal Al-Co-Ni versus W-$Al_{72.5}Co_{20}Ni_{7.5}$

$Al_{72.5}Co_{20}Ni_{7.5}$, the so-called W-phase is the largest known approximant to the stable decagonal quasicrystal (*QC*) in the system Al-Co-Ni (a = 39.668 Å, b = 8.158 Å, c = 23.392 Å, b = 90.05°, space group Cm).



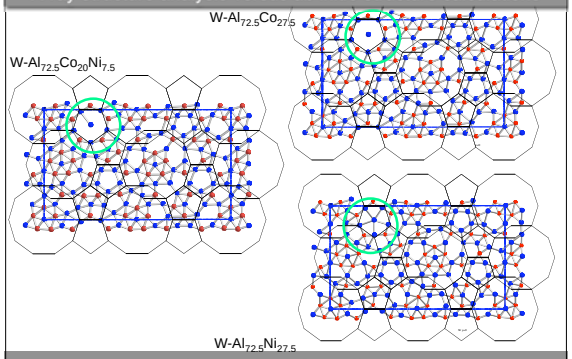
Katrych and Steurer (2004); Sugiyama et al., J. Alloys Comp. 342 (2002) 65 26

HAADF-STEM image of W-$Al_{72.5}Co_{20}Ni_{7.5}$ compared to the projected structure obtained from X-ray structure analysis



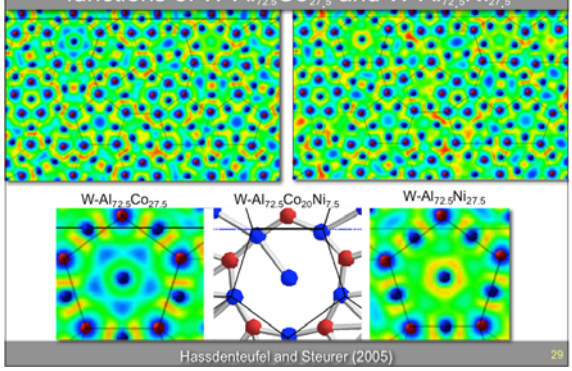
Sugiyama, Nishimura, Hiraga (2002) J. Alloys Comp. 342, 65; Katrych al. (2004) 27

W-$Al_{72.5}Co_{20}Ni_{7.5}$ X-ray structure analysis versus *ab initio* structure calculations



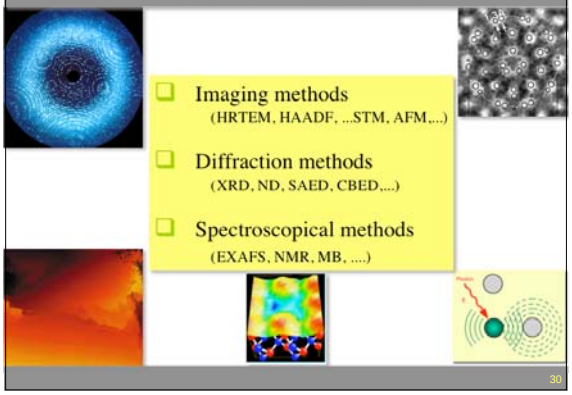
Hassdenteufel and Steurer (2005) 28

Comparison of the electron localization functions of W-$Al_{72.5}Co_{27.5}$ and W-$Al_{72.5}Ni_{27.5}$



Hassdenteufel and Steurer (2005) 29

Structural characterization of materials



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Structural characterization of materials

Diffraction methods
globally averaged local and global structure

X-ray	neutron	electron
$V<10^{-3}$ mm^3	$V>10^{1}$ mm^3	$V<10^{-9}$ mm^3
very high Resolution	very high Resolution	low Resolution
$<10^{-4}$ Å	$<10^{-4}$ Å	$<10^{-2}$ Å

x_i, p_i, u_{ij}, i,j=1..3 plus n order parameters

The only way for studying QC structurally at high pressures and/or temperatures

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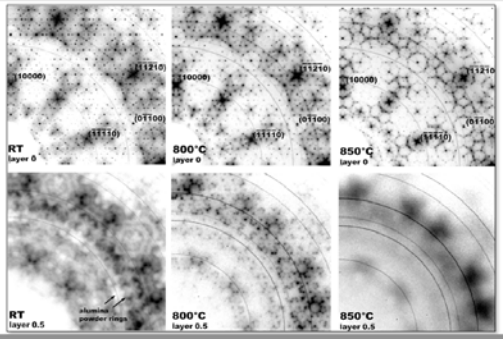
HT-Data collection and reciprocal space reconstruction



Steurer et al. Chimia 55 (2001) 528

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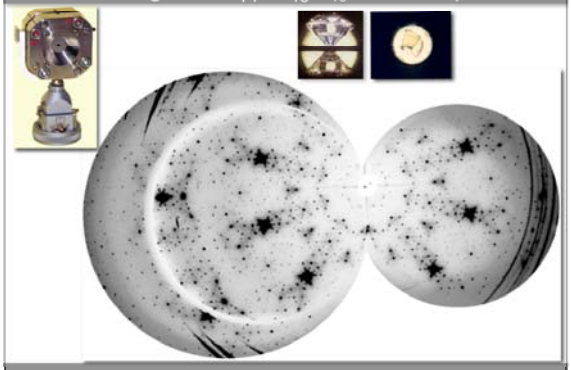
Decagonal $Al_{71}Co_{13}Ni_{16}$ at 10.7 Gpa



Krauss et al. Philos. Mag. Lett. 83 (2003) 525

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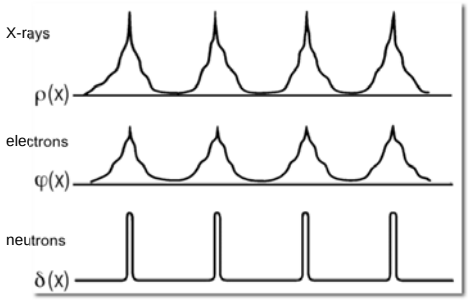
Interaction potential



Diffraction methods

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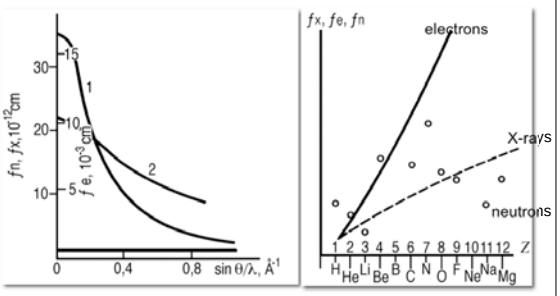
Scattering power



Diffraction methods

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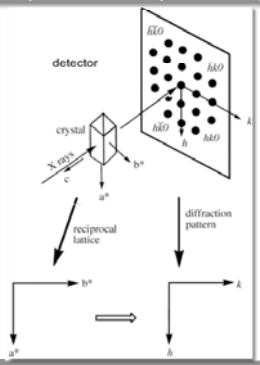
Direct space - reciprocal space



Crystal setup

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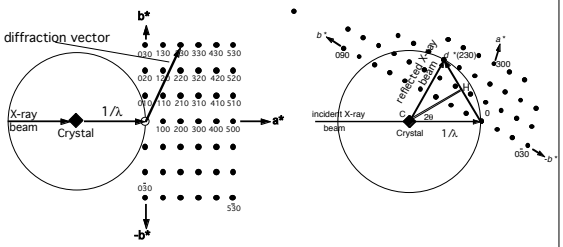
Ewald construction



Geometrical visualization of Bragg's condition $2d \sin\theta = n\lambda$

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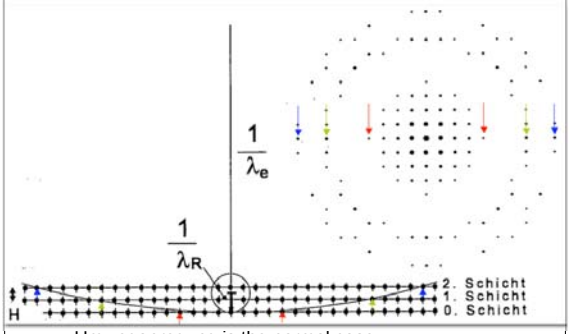
Ewald construction for electron diffraction



Umweganregung is the normal case

Reflection are streaks along the incoming electron beam

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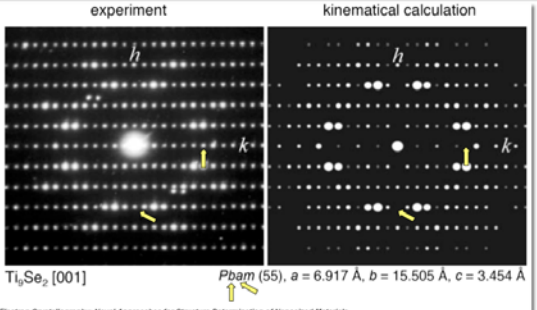
Systematic absences may be masked by dynamical diffraction effects



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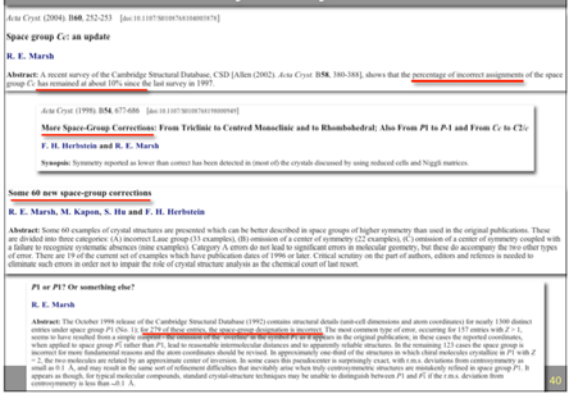
Problems of symmetry determination



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Structural characterization of materials

Electron microscopic methods
projected local structure

HRTEM, HAADF-STEM,....

low to medium resolution possible

Qualititative information about the projected local structure => creation and verification of structure models.

The only way for the determination of the local projected real structure of QC

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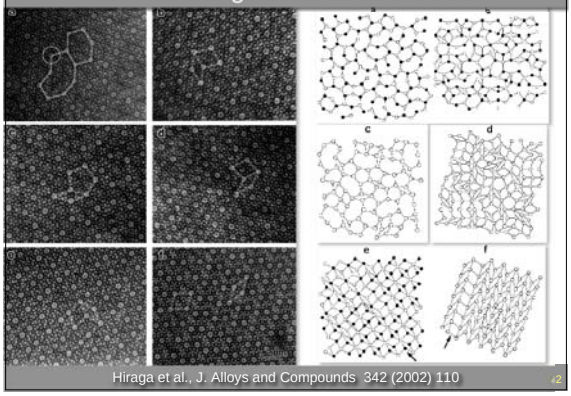
Medium-range order in d-Al-Co-Ni



Hiraga et al., J. Alloys and Compounds 342 (2002) 110

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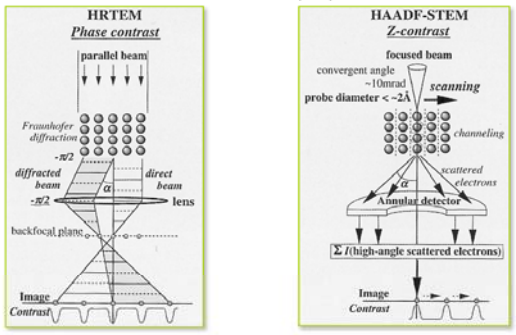
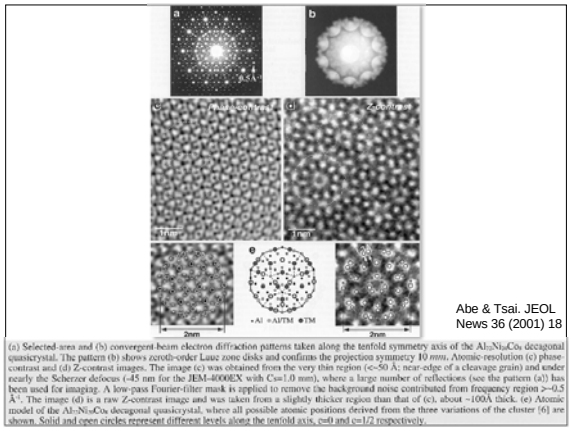
HRTEM *versus* HAADF-STEM

Abe & Tsai. JEOL News 36 (2001) 18

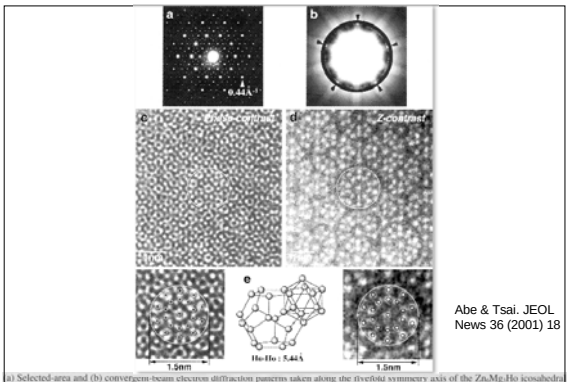


Local information about the projected structure (averaged over 5 to 10 nm) 43



Abe & Tsai. JEOL News 36 (2001) 18

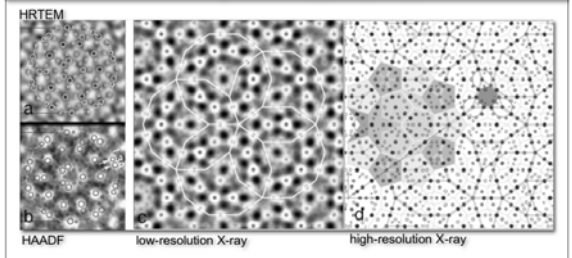
(a) Selected-area and (b) convergent-beam electron diffraction patterns taken along the tenfold symmetry axis of the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal. The pattern (b) shows zeroth-order Laue zone disks and confirms the projection symmetry 10 *mm*. Atomic-resolution (c) phase-contrast and (d) Z-contrast images. The image (c) was obtained from the very thin region (<~50 Å; near-edge of a cleavage grain) and under nearly the Scherzer defocus (-45 nm for the JEM-4000EX with C_S=1.0 mm), where a large number of reflections (see the pattern (a)) has been used for imaging. A low-pass Fourier-filter mask is applied to remove the background noise contributed from frequency region ρ>~0.5 $Å^{-1}$. The image (d) is a raw Z-contrast image and was taken from a slightly thicker region than that of (c), about ~100Å thick. (e) Atomic model of the $Al_{72}Ni_{20}Co_8$ decagonal quasicrystal, where all possible atomic positions derived from the three variations of the cluster [6] are shown. Solid and open circles represent different levels along the tenfold axis, z=0 and z=1/2 respectively.



Abe & Tsai. JEOL News 36 (2001) 18

(a) Selected-area and (b) convergem-beam electron diffraction patterns taken along the rivefold symmetry axis of the Zn_xMg_yHo icosahedral quasicrystal. The pattern (b) shows higher-order Laue zone disks which clearly reveal fivefold rotational symmetry, as indicated by arrowheads. Atomic-resolution (c) phase-contrast and (d) Z-contrast images. The observation conditions for the both imagings, the defocus value and the sample thickness, are almost the same as those of fig. 2 (c) and (d). (e) A representative local Ho configuration found in the proposed structural model [11] of the Zn_xMg_yHo icosahedral quasicrystal.

Decagonal $Al_{70.6}Co_{6.7}Ni_{22.7}$



Images of the projected structure of decagonal Al-Co-Ni: (a)HRTEM, (b) HAADF (Abe & Tsai, JEOL News 39,2001,18); (c) X-ray data based low-resolution (1 Å) electron density map with the high-resolution (0.15 Å) map shown in (d) overlaid.

Cervellino et al., Acta Cryst. B58 (2002) 8 46

Structural characterization of materials

Spectroscopical methods
globally averaged local structure

NMR, EXAFS, Mössbauer,….

very high resolution possible

↓

Quantitative information about the averaged local structure => verification of structure models.

Accurate information on the local surrounding of target atoms 47

Structural characterization of materials

Surface structure analysis
local structure

STM, AFM, …., LEED, RHEED, XRD,…

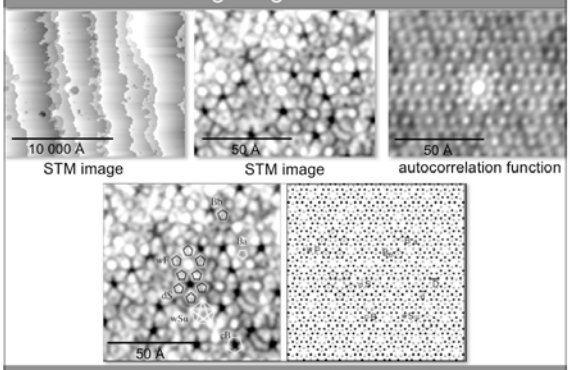
low to high resolution possible

↓

Information on the surface structure that may also be helpful for determining the bulk structure.

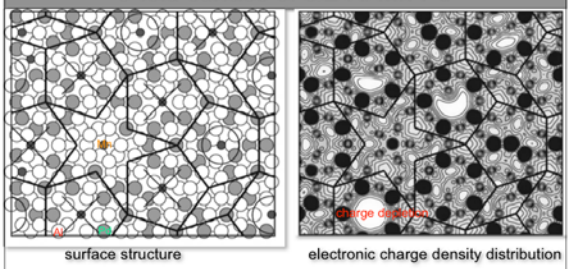
Information on different length scales, from sro to lro 48

Short- and long-range order in i-Al-Mn-Pd



Papdopolos et al., Phys. Rev. B 66 (2002) art. Nr. 184207 49

5-fold surface of 3/2-Al-Mn-Pd



STM only shows a kind of electronic charge distribution as a function of the tunneling current. The image obtained reflects the electronic surface structure rather than the atomic structure.

Krajci & Hafner, Phys. Rev. B **71** (2005) Art. Nr. 054202 50

The long way from a quasicrystal to its structure

- crystal growth
- thermal equilibration

⇩

- X-ray data collection - Bragg reflections
- structure solution - average structure
- structure refinement - average structure
- structure modeling - idealized structure

⇩

- X-ray data collection - diffuse intensities
- structure solution - disordered structure
- structure refinement - disordered structure
- structure modeling - disordered structure

⇩

- modeling based on first-principles calculations

There is no quantitative QC structure determination without diffraction methods 51

What do we want to know about a crystal structure?

- Coordinates
  input for first-principles calculations
- Electron density distribution
  chemical bonding
- Dynamics: thermal vibrations
  interaction potentials
- Disorder: displacive (phasonic), substitutional
  entropic contribution

and

their variation with temperature, pressure,….

The defect structure is not part of a crystal structure 52

Crystal growth and thermal equilibration

Depending on the growth method, as-grown crystals are usually chemically not fully homogenous (*e.g.* radial gradient in composition).

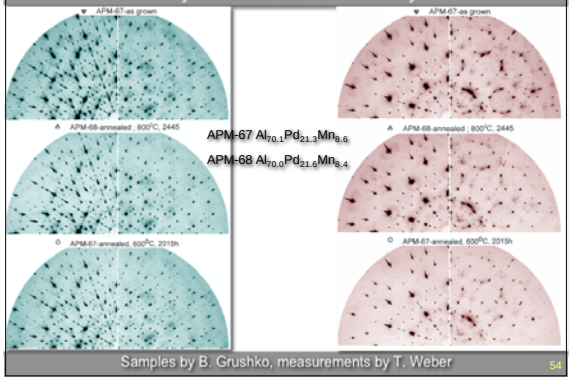
Thermal annealing leads (close) to an equilibrium state at a given temperature (not too far from melting temperature).

An ideal crystal is a mathematical object. A perfect crystal is in its thermodynamic equilibrium state. This can also be a disordered state! The usual crystal shows more or (in rare cases) less imperfections.

Problem:
By quenching from the annealing temperature, the HT-structure with all its inherent disorder (thermal vacancies, phason flips,...) is frozen in. On the way to RT, the structure partially relaxes until it arrives in a metastable state. The larger the crystals *(e.g.* Czochralski grown) the larger the problem due to a smaller cooling rate.

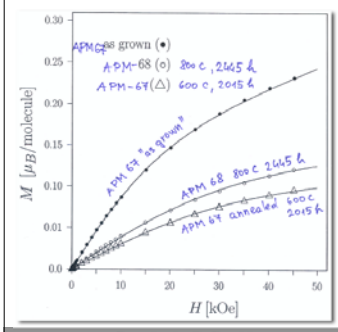
flowchart 53

X-Ray diffraction patterns with 2- and 5-fold symmetry for three, differently annealed ico-Al-Pd-Mn crystals.



Samples by B. Grushko, measurements by T. Weber 54

Magnetization as a function of the magnetic field at 5 K for three, differently annealed ico-Al-Pd-Mn crystals.

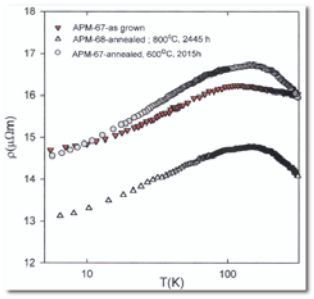


APM-67 $Al_{70.1}Pd_{21.3}Mn_{8.6}$

APM-68 $Al_{70.0}Pd_{21.6}Mn_{8.4}$

Samples by B. Grushko, measurements by J. Dolinsek

Resistivity as a function of temperature for three, differently annealed ico-Al-Pd-Mn crystals.



APM-67 $Al_{70.1}Pd_{21.3}Mn_{8.6}$

APM-68 $Al_{70.0}Pd_{21.6}Mn_{8.4}$

Samples by B. Grushko, measurements by J. Dolinsek

Structure solution - average structure

Regular crystal structure analysis:

- determination of short-range order, i.e. the atomic arrangement in a single unit cell, is sufficient.

Quasicrystal structure analysis:

- determination of both short- and long-range order is necessary, i.e. the structure of "clusters" as well as of "cluster" odering.

X-ray data collection - Bragg reflections

The high perfection of QC (small mosaicity, *i.e.* sharp reflections), basically allows the collection of data with a sufficient resolution to determine atomic positions in a box 500 x 500 x 500 Å^3, *i.e.* for ≈ 9'000'000 atoms.

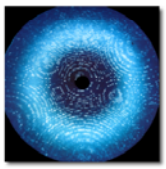
A full data set of that resolution of an F-centered ico phase would include ≈ 190'000 unique reflections.

Problem:
The main problem in case of QC is multiple scattering (Umweganregung). It is a severe problem for weak reflections. Reflections with large perp-space components are almost all very weak reflections and the most important ones for determining the long-range order of QC.

Multiple scattering can be overcome if the QC is oriented asymmetrically and several data sets are collected at slightly different wave lengths.

Strong reflections suffer from extinction. However, this is a minor problem.

Example NAD$^+$ synthetase



$P2_1$, a=52.28, b=84.97, c=59.64 Å, β=110.5°

No. of measured reflections	790 765
No. of unique reflections	231 200
with I > 4 σ(I)	170 606
No. of reflections in refinement	205 215
No. of parameters	47 101
No. of restraints	57 173
No. of non-H atoms (excl. waters)	4 518
R-factor	0.116

Symersky et al, Acta Cryst. D58 (2002) 1138

Structure solution - average structure

Structure solution means solution of the phase problem. Only the amplitudes $|F|$ of complex structure factors $F = |F|\exp(i\phi)$ can be determined from the intensities $|F| = \sqrt{I}$

There are many ways to solve a structure:

- trial and error (starting model from HRTEM,...)
- direct methods (statistical methods, MEM, LDM,...)
- Patterson methods (heavy-atom method)
- Multi-wavelength technique ....

The result is a crude model of the average structure - a subset of correctly phased structure factors.

Problem:
Since phasing, in particular for non-centrosymmetric structures, is only successful for stronger reflections, the structure solution gives a only a first model for the structural components with the largest weight (positions of heavy atoms, major building blocks). Often, it contains averaged structure motifs, artifacts and in the worst cases many Patterson peaks.

Average-structure solution by MEM

Solving decagonal structures requires the fundamental maximum entropy equations (Bricogne 1984)

$$q_i = \frac{p}{Z\left(\lambda_1,\ldots,\lambda_{N_C}\right)} \exp\left(\sum_{n=1}^{N_C} \lambda_n \frac{\partial C_n}{\partial q_i}\right) \quad (5)$$

$$Z\left(\lambda_1,\ldots,\lambda_{N_C}\right) = \sum_{i=1}^{N_P} p \exp\left(\sum_{n=1}^{N_C} \lambda_n \frac{\partial C_n}{\partial q_i}\right) \quad (6)$$

to be solved in five dimensions for all N_P grid points q_i restricted to all N_C constraint equations C_n by Lagrange multipliers λ_n. Two different constraint equations are necessary to take all structure factors derived from the symmetry minimum solution and all the observed structure amplitudes simultaneously into account. Assuming the noise to be gaussian the known structure factors $F_{obs}(\boldsymbol{H})$ can be constrained by

$$C_1 = \sum_{\boldsymbol{H}} \frac{1}{\sigma^2} \left| F_{obs}(\boldsymbol{H}) - F_{clc}(\boldsymbol{H}) \right|^2 = \chi^2. \quad (7)$$

Haibach et al., Acta Crystallogr. A (1996) 277 61

Average structure solution by MEM

with their corresponding standard deviations σ. The second constraint equation (compare Sakata & Sato 1990) only depends on the structure amplitudes and restrains all unknown phases to

$$C_2 = \sum_{\boldsymbol{K}} \frac{1}{\sigma^2} \left| \left| F_{obs}(\boldsymbol{K}) \right| - \left| F_{clc}(\boldsymbol{K}) \right| \right|^2 = \chi^2. \quad (8)$$

Substituting (7) and (8) into equation (5) results in a five-dimensional algorithm

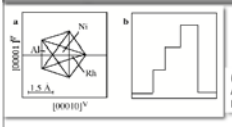
$$q_i = \frac{p}{Z\left(\lambda_1,\lambda_2\right)} \exp\left[-2\lambda_1 \sum_{\boldsymbol{H}} \frac{1}{\sigma^2} \left| F_{obs}(\boldsymbol{H}) - F_{clc}(\boldsymbol{H}) \right| \cos\left(2\pi \boldsymbol{H}\boldsymbol{x}_i - \varphi_\Delta\right) \right.$$

$$\left. -2\lambda_2 \sum_{\boldsymbol{K}} \frac{1}{\sigma^2} \left| \left| F_{obs}(\boldsymbol{K}) \right| - \left| F_{clc}(\boldsymbol{K}) \right| \right| \cos\left(2\pi \boldsymbol{K}\boldsymbol{x}_i - \varphi_{clc}\right) \right], \quad (9)$$

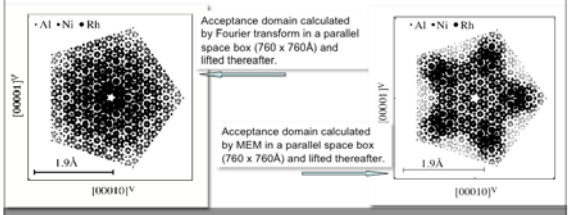
with $\varphi_\Delta = \arctan\left\{ \mathrm{Im}\left[F_{obs}(\boldsymbol{H}) - F_{clc}(\boldsymbol{H})\right] / \mathrm{Re}\left[F_{obs}(\boldsymbol{H}) - F_{clc}(\boldsymbol{H})\right] \right\}$, the phase of the structure factor difference. This equation can be maximised solving λ_n by Newton's method (Bricogne 1984) or by exponential modelling (Collins & Mahar 1983).

Haibach et al., Acta Crystallogr. A (1996) 277 62

Average-structure solution by MEM



(a) Pentagrammal acceptance domain of hypothetical decagonal Al-Ni-Rh. (b) Section through the acceptance domain along the line drawn in (a).



Haibach et al., Acta Crystallogr. A (1996) 277 63

Structure refinement - average structure

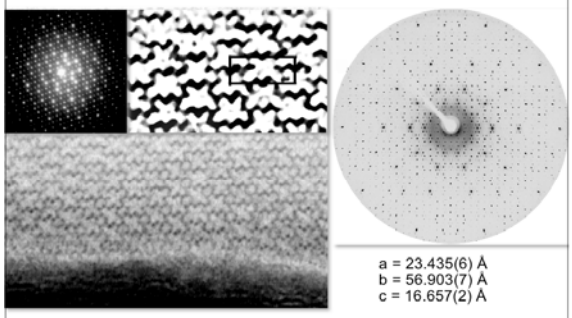
The refinement of the crude structure model resulting from the structure solution procedure gives the best possible model of the average structure. Its quality depends on the quality and size of the data set as well as on the model parameters refined.

The quality of the refinement is difficult to determine but very important for comparing the quality of different models. For QC this is particularly difficult for judging the quality of the Iro-model. One has to use R-factor plots as function of H^{perp}, H^{par}, I and statistical tests.

Problem:
Since Bragg reflections contain only information of the average structure, the average structure has to be refined. This makes modeling much more complicated.

The average structure may contain split atoms and not fully occupied positions 64

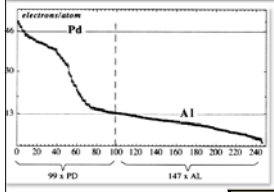
Example HT-Al_3Pd



a = 23.435(6) Å
b = 56.903(7) Å
c = 16.657(2) Å

Edler, Thesis (1997) 65

Example HT-Al_3Pd



C2mm
oC~1300

a = 23.435(6) Å
b = 56.903(7) Å
c = 16.657(2) Å
V = 22212.5 Å^3

Intermediate result:
Difficult assignment of Pd and Al to peaks in the electron density distribution function

Number of unique reflections:	
Measured(I>0)	17115
Observed (I>3σ)	6984
Number of refined parameters	707
R	0.114
wR	0.079

Edler, Thesis (1997) 66

Structure refinement - average structure

SHELXL always refines against F^2. Refinement against ALL F^2-values is demonstrably superior to refinement against F-values greater than some threshold [say $4\sigma(F)$]. More experimental information is incorporated (suitably weighted) and the chance of getting stuck in a local minimum is reduced. In pseudo-symmetry cases it is very often the weak reflections that can discriminate between alternative potential solutions. It is difficult to refine against ALL F-values because of the difficulty of estimating $\sigma(F)$ from $\sigma(F^2)$ when F^2 is zero or (as a result of experimental error) negative. The diffraction experiment measures intensities and their standard deviations, which after the various corrections give F_o^2 and $\sigma(F_o^2)$.

The use of a threshold for ignoring weak reflections may introduce bias which primarily affects the atomic displacement parameters; it is only justified to speed up the early stages of refinement. In the final refinement ALL DATA should be used except for reflections known to suffer from systematic error. Anyone planning to ignore this advice should read Hirshfeld & Rabinovich (1973) and Arnberg, Hovmöller & Westman (1979) first. Refinement against F^2 also facilitates the treatment of twinned and powder data, and the determination of absolute structure.

R-factors and Goodness of fit

$$R1 = \frac{\sum_{i=1}^{n} \left| |F_i^{obs}| - |F_i^{calc}| \right|}{\sum_{i=1}^{n} |F_i^{obs}|}$$

$$wR2 = \left\{ \frac{\sum_{i=1}^{n} w_i \left(|F_i^{obs}|^2 - |F_i^{calc}|^2 \right)^2}{\sum_{i=1}^{n} w_i \left(|F_i^{obs}|^2 \right)^2} \right\}^{\frac{1}{2}}$$

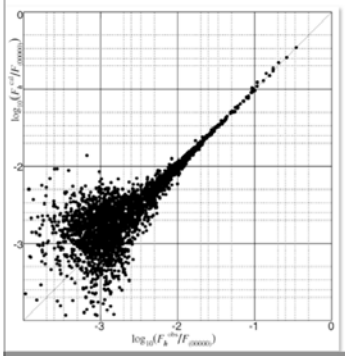
$$S = \left\{ \frac{\sum_{i=1}^{n} w_i \left(|F_i^{obs}|^2 - |F_i^{calc}|^2 \right)^2}{n - p} \right\}^{\frac{1}{2}}$$

where n is the number of reflections and p is the total number of parameters refined. Weighting scheme $w = 1 / [\sigma^2(F_o^2)]$.

One cosmetic disadvantage of refinement against F^2 is that R-indices based on F^2 are larger than (more than double) those based on F.

The R-index for MEM calculations is not a reliability factor. Its value is meaningless.

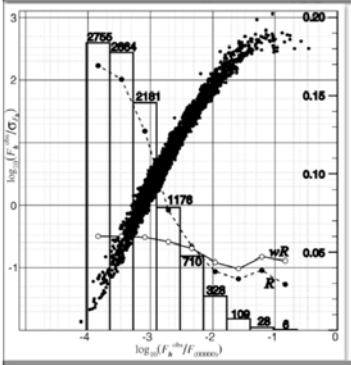
Decagonal $Al_{70.6}Co_{6.7}Ni_{22.7}$



R=0.17, wR=0.06 for 2767 reflections with |F(**H**)|>0

Cervellino, Haibach & Steurer, Acta Cryst. B58 (2002) 8.

Decagonal $Al_{70.6}Co_{6.7}Ni_{22.7}$



Black dots show the distribution of errors on the measured intensity. Columns with numbers: number of reflections over a given |F| threshold.

Full circles, dashed line, right scale: the unweighted R-factor calculated for each of the reflection subsets indicated by the corresponding column.

Empty circles, continuous line, right scale: the weighted R-factor wR calculated for the same reflection subsets.

Cervellino, Haibach & Steurer, Acta Cryst. B58 (2002) 8.

Diffraction methods - weak reflections

Weak reflections in periodic structure analysis

Due to atomic scattering factor and temperature factor large $q^{\parallel}$-reflections are weak. They are important for high-resolution electron density maps but not for atomic positions.

Weak reflections in quasiperiodic structure analysis

Additional to weak reflections of the type described above, all reflection intensities are rapidly falling off with $q^{\perp}$ independent from $q^{\parallel}$.

Problem

All diffraction experiments on high-quality single crystals suffer from multiple diffraction effects, which may strongly increase intensities of weak reflections. This is a special problem for quasicrystals with their dense reciprocal space.

Structure modeling - idealized structure

The refined model usually does not account for disorder. Therefore, the fit to the experimental data will not be overwhelming. Difference-Fourier (or better MEM) maps will show where the model did not describe the data properly.

Different idealized models may fit to the experimental data equally well (bad). Local order will result quite reliable, long-range order will not.

Problem:
Till now, even idealized models are based on too small (perp-space) data sets to make reliable assumptions on long-range order.

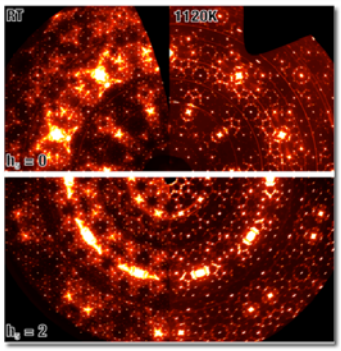
X-ray data collection - diffuse intensities

3D diffuse diffraction data can only be quantitavely collected employing area detectors and synchrotron radiation. Variation with temperature can help distinquishing between static and dynamic disorder.

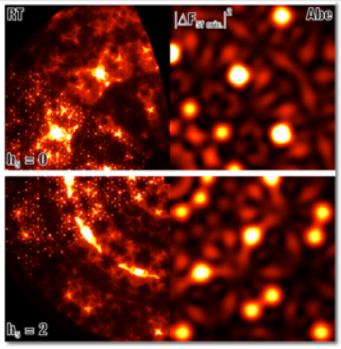
Separation of diffuse scattering of static and dynamic origin by quasielastic or inelastic neutron scattering.

Problem:
Separation of Bragg reflection intensities from diffuse scattering.

X-ray data collection - diffuse intensities



Diffuse intensities - modeling



Structure determination - disordered structur

The disordered structure is usually solved by trial-and-error or, more recently for quasicrystals, by Patterson methods.

Monte Carlo or reverse Monte Carlo techniques, genetic algorithms etc. are used to improve the structure models.

These techniques give automatically disorder models.

Problem:

Separation of diffuse scattering from densly distributed weak Bragg scattering is almost impossible. This problem can only be solved by calculating the integrated intensity of all contributions from diffuse (TDS, PDS, disorder, defects) and Bragg scattering.

Structure modeling - disordered structure

Modeling of the phononic and phasonic contribution to the diffuse scattering in a decagonal quasicrystal

Influence of the phasonic elastic constant k1 on the diffuse scattering of $h_1h_2h_3h_4\emptyset$

Influence of the phonon-phason coupling elastic constant r on the diffuse scattering of $h_1h_2h_3h_4\emptyset$

Modeling based on first-principles

Based on realistic structural parameters modeling by first-principles methods will give realistic results for the relaxed structure and physical properties.

Problem:

Till now, only approximants can be calculated with a maximum number of atoms per unit cell < 1000.

What is our goal (and where are we now)?

Full quantitative determination of at least one quasicrystal structure and its variation with temperature, pressure,.... :

local ordering (close to understanding)
global ordering (halfway)

and

quantum-mechanical modeling
(far from reality)

Realistic model = ideal model plus disorder parameters 79

Where will we be at ICQ10?

We will certainly have toy models, which much better describe experimental observations than actual models do, especially for decagonal Al-Co-Ni.

We will better understand what clusters are and what properties they have. Consequently, we will better understand the local (short-range) order in quasicrystals.

We will still not have solved the long-range order structure of quasicrystals with an accuracy comparable to that of regular structure analysis.

Let's start working! 80