Crystallography in the 21st century

2014

international year of crystallography

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Crystals built from ‘molécules intégrantes’
Wilhelm Röntgen

Max Laue
Father and son Bragg

\[2d\sin\theta = n\lambda\]
Lattice periodicity

\[ r(n, j) = r_j + n_1a_1 + n_2a_2 + n_3a_3 \]

\[ \rho(r) = \rho(r + n_1a_1 + n_2a_2 + n_3a_3) \]

Unit cell: region in space such that every atomic position can be brought here by lattice translations.

Atomic positions

\[ r(n, j) \]
Reciprocal space  =  Dual space

Basis of lattice: $a_i \rightarrow$ Basis of reciprocal lattice $a_i^*$

Reciprocal lattice

$$a_i.a_j^* = \delta_{ij}$$

$$H = \sum_{i=1}^{3} h_i a_i^*$$

Lattice periodic function $f(r) = \sum_{H \in \Lambda^*} \hat{f}(H) \exp(iH.r)$

Brillouin Zone

- Unit cell of the reciprocal lattice

- Wigner-Seitz cell of the reciprocal lattice: all points of the reciprocal space closer to the origin than to any other point of the reciprocal lattice
Bloch theorem

\[ \Psi(r) = \exp(i k \cdot r) U(r) \]

U(r) periodic, k in the Brillouin Zone
Diffraction

Scattering amplitude

\[ F(H) = \sum_{n,j} f_j(H) e^{-W} \exp(iH.(n + r_j)) = \Delta(H \in \Lambda^*) \sum_j f_j(H) e^{-W} \exp(iH.r_j) \]

Intensity

\[ I(H) = |F(H)|^2 \]

Problem of the phases:
only absolute value is measured.

End 20th century: ways to solve (Karl and Hauptman, Sütő)
Rotation symmetry - Point group

Identity
5 rotations over multiples of 60 degrees
6 reflections
Point group 6mm has order 12

Rotations+Translation-symmetry - Space group

Elements
\((R | a)\) with \(R\) from the point group
and a a translation, not necessarily a lattice translation
$(E, 0), \left(\frac{m_x}{2}a_1 + \frac{1}{2}a_2\right), \left(\frac{m_y}{2}a_1 + \frac{1}{2}a_2\right), (-E, 0)$
Selection rules

Density is invariant under elements of the space group

\[ \rho(r) = \rho(gr) = \rho(Rr + t) \]

Scattering function is Fourier transform

\[ \rho(r) = \int_H \hat{\rho}(H) \exp(iH.r) \]

Transformation in the reciprocal space the is

\[ \hat{\rho}(H) = \exp(-iH.t)\hat{\rho}(R^{-1}H) \]

If \( R^{-1}H=H \) and \( \exp \neq 1 \), then the intensity vanishes

Space group gives conditions for the existence of Bragg peaks. Therefore, symmetry is important!
Instrumental techniques

Original X-ray tube

Diffractometer

Structure determination

Charge Coupled Device (CCD) camera
BIG instruments

Neutron diffraction
Electron diffraction
Synchrotron radiation

Femtosecond-pulses
Free-electron laser
More and more complicated structures determined

Examples

NaCl

Zeoliet
Addition of Na3 to complete the structure of Na$_2$CO$_3$
$\beta$-Mg$_2$Al$_3$ “The Monster”

Samson phase 1168 atoms / unit cell
Biological systems

DNA
Watson, Crick en Wilkins
Nobel prize 1962
Herpes Simplex Virus Type 1

Crystallographic structure of human fatty acid synthase

Very complex, but always lattice periodic
Quasicrystals: 1982

The difference: to the right a point symmetry that is not compatible with lattice periodicity!
5-fold symmetry is not compatible with lattice periodicity

$\tau \approx 0.618$
1982: quasicrystals

Dan Shechtman

10-fold symmetry in the diffractogram

Icosahedral symmetry
Roger Penrose

Dick (N.G.) de Bruijn

Also: Peter Kramer 3D icosahedral space filling (Acta Cryst. 1982)

Alan Mackay

Peter Kramer
Optical diffraction pattern
Mackay 1982

Indexable with 4 indices
Quasicrystals are not periodic but quasi-periodic

Fibonacci-chain: quasiperiodic
S
L
LS
LSL
LSLLS
LSLLSLSL
LSLLSLSLLSLLS

....................

Number S’s / Number L’s  ->  $\tau=(\sqrt{5}-1)/2$ Golden rule
Quasicrystals and quasiperiodic tilings can be obtained from a lattice periodic structure in more dimensions: the superspace.

This holds also for the Fibonacci chain

Embedding and unit cell of the Fibonacci chain

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LSL.LS.LSL.LSLLS.LSLLS.LSLLS.LSLLS.LSLLS...
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Vertical lines: atomic surfaces, y=0 physical space
Two-dimensional example

Eight-fold Ammann-Beenker tiling

Diffraction pattern and projection of the 4D Brillouin Zone
Small quasicrystals

Large quasicrystal AlMnPd

Clusters in a CdYb icosahedral quasicrystal
Aperiodic crystals were found already 20 years earlier.

- incommensurate spin waves
- incommensurate crystals:
  an incommensurate modulation:
  1964 de Wolff et al. discover $\gamma$-$\text{Na}_2\text{CO}_3$ with sharp diffraction peaks at positions $k$:

\[ k = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m(\alpha\mathbf{a}^* + \beta\mathbf{b}^*) \]

- incommensurate composites
  1978 $\text{Hg}_3\delta\text{AsF}_6$ with Hg-chains;

diffraction peaks at

\[ k = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\gamma\mathbf{c}^* \]

$\gamma$ is irrational: structure is incommensurate:
quasiperiodic en aperiodic
Also these aperiodic crystals are the intersection of a periodic structure in super space with the 3D physical space.

Modulated phase as intersection in 4D space

n-dimensional crystallography
Physics of aperiodic crystals

No 3D Brillouin Zone: use nD BZ or ‘approximants’

Ammann-Beenker tiling
aperiodic

Periodic approximant to aperiodic A-B tiling
Approximate irrational number by a series of rationals:
e.g. $\sqrt{1/2} \approx 2/3, 5/7, 12/17, \ldots$
Physical properties of aperiodic crystals

There is an nD BZ but no 3D BZ

Listen to Denis Gratias on this!

Electron states in a 1D modulated chain
APPLICATIONS

Ferroelectrics
smart cards

Multiferroics
data management, spin-dipole coupling

Spin structures

Biological structures, medicine, pills

Quasicrystals
low wear, low friction

Incommensurate phases transducers

One has to know the structure

Medicine

Smart card

Exhaust
Two-dimensionale space groups
in the Alhambra

octagonal Gunbad-i Kabud tomb tower
in Maragha, Iran (1197 C.E.)
Maurits Escher

Figure 228. Three-colored network pattern: M. Escher’s “Lizards.” This pattern has the symmetry of the two-dimensional Bieber group P6\(\text{mm}\). The complete hexagonal cell of the group can be obtained from three contiguous “rhombic” cells. The contour of one of the cells can be discerned in the pattern.
Polyhedra and 5-fold symmetry
Summary

Crystallography has seen a spectacular growth in these 100 years.

It has given an essential contribution to our knowledge of minerals, materials and biological structures.

The notion of ‘crystal’ has changed:
first: “minerals with symmetrically ordered flat faces”
then: “materials with lattice periodicity and a unit cell”
now: “materials with sharp peaks in the diffraction pattern”.

This development is partially due to the development of big instruments: the use of neutrons and synchrotron radiation.

The development of new materials would not have been possible without the use of new crystallographic techniques.

Therefore, there was a good reason for announcing 2014 as the International Year of Crystallography!