· 2014

international year of crystallography

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Crystallography in the 21st century





Abbé Ha<u>üy</u>

Crystals built from 'molécules intégrantes'

Wilhelm Röntgen



Max Laue





Father and son Bragg





Lattice periodicity

$$\mathbf{r}(\mathbf{n},j) = \mathbf{r}_j + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

 $\rho(\mathbf{r}) = \rho(\mathbf{r} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)$

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

Atomic positions







Reciprocal space = Dual space

Basis of lattice: $\mathbf{a}_i \rightarrow \text{Basis}$ of reciprocal lattice \mathbf{a}_i^*

Reciprocal lattice

 $\mathbf{a}_i.\mathbf{a}_j^*=\delta_{ij}$

$$\mathbf{H} = \sum_{i=1}^{3} h_i \mathbf{a}_i^*$$

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

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

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k}.\mathbf{r})U(\mathbf{r})$$

U(r) periodic, k in the Brillouin Zone

Diffraction

H belongs to reciprocal lattice

Scattering amplitude

 $F(\mathbf{H}) = \sum_{\mathbf{n},j} f_j(\mathbf{H}) e^{-W} \exp(i\mathbf{H}.(\mathbf{n} + \mathbf{r}_j)) = \Delta(\mathbf{H} \in \Lambda^*) \sum_j f_j(\mathbf{H}) e^{-W} \exp(i\mathbf{H}.\mathbf{r}_j)$

Intensity

$$I(\mathbf{H}) = |F(\mathbf{H})|^2$$

Atomic diffraction factor

Debye-Wallerfactor

Problem of the phases: only absolute value is measured.

End 20th century: ways to solve (Karl and Hauptman, Süto)

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



$$(E,0), (m_x, \frac{1}{2}a_1 + \frac{1}{2}a_2), (m_y, \frac{1}{2}a_1 + \frac{1}{2}a_2), (-E, 0)$$

Selection rules

Density is invariant under elements of the space group

 $\rho(\mathbf{r}) = \rho(g\mathbf{r}) = \rho(R\mathbf{r} + \mathbf{t})$

Scattering function is Fourier transform

$$ho(\mathbf{r}) = \int_{\mathbf{H}} \hat{
ho}(\mathbf{H}) \exp(i\mathbf{H}.\mathbf{r})$$

Transformation in the reciprocal space the is

 $\hat{\rho}(\mathbf{H}) = \exp(-i\mathbf{H}.\mathbf{t})\hat{\rho}(R^{-1}\mathbf{H})$

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



Structure determination



Diffractometer



Charge Coupled Device (CCD) camera

BIG instruments

Neutron diffraction









Electron diffraction





Synchroton radiation





More and more complicated structures determined

Examples







Addition of Na3 to complete the structure of Na_2CO_3



β -Mg₂Al₃ "The Monster"

Samson phase 1168 atoms / unit cell

Biological systems



DNA Watson, Crick en Wilkins Nobel prize 1962









Crystal structure of the largest protein solved by crystallographic ab initio methods (PDB code 1E8U). Secondary structure elements are reported in colors: red for α -elices, yellow for β -sheet,

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



1982: quasicrystals



Dan Shechtman



1982



10-fold symmetry in the diffractogram





Roger Penrose





Dick (N.G.) de Bruijn SCIENTIFIC AMERICAN





Alan Mackay



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

Peter Kramer

Optical diffraction pattern Mackay 1982

Indexable with 4 indices

Quasicrystals are not periodic but quasi-periodic

.



Number S's / Number L's -> $\tau = (\sqrt{5-1})/2$ Golden rule

Quasicrystals and quasiperiodic tilings can be obtained fromt a lattice periodic structure in more dimensions: the superspace.

This holds also for the Fibonacci chain



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 AIMnPd

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
 γ-Na₂CO₃ with sharp
 difraction peaks at positions k:



$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^* + m(\alpha\mathbf{a}^* + \beta\mathbf{b}^*)$$



- incommensurate composites 1978 Hg_{3-δ}AsF₆ with Hg-chains;

diffraction peaks at

$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + \ell\mathbf{c}^* + m\gamma\mathbf{c}^*$$

γ 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,





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

Exhaust





35

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 Belov group $P6^{(3)}$. 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.





Gerard Caris Maastricht

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!