Department of Physics, University of Siegen

Lecture course on crystallography, 2015*

****THIS LECTURE CONTAINS OPTIONAL MATERIAL***

Modern experimental methods for crystal structure determination and refinement

1895: Discovery of X-rays by W.C Roentgen

1895 **Wilhelm Conrad Röntgen**

The discovery of a new radiation type, which can easily pass through the substances.

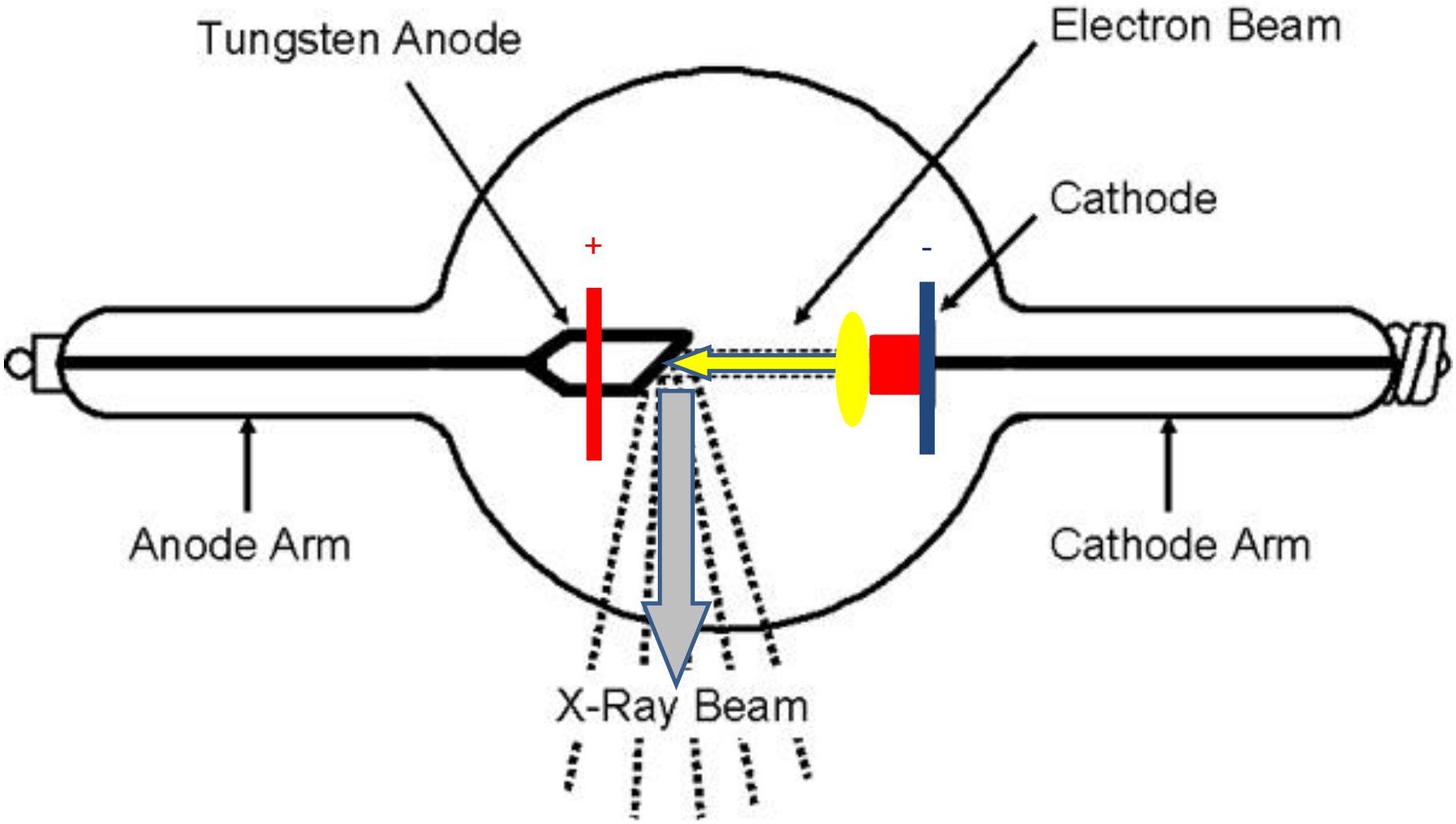
1901

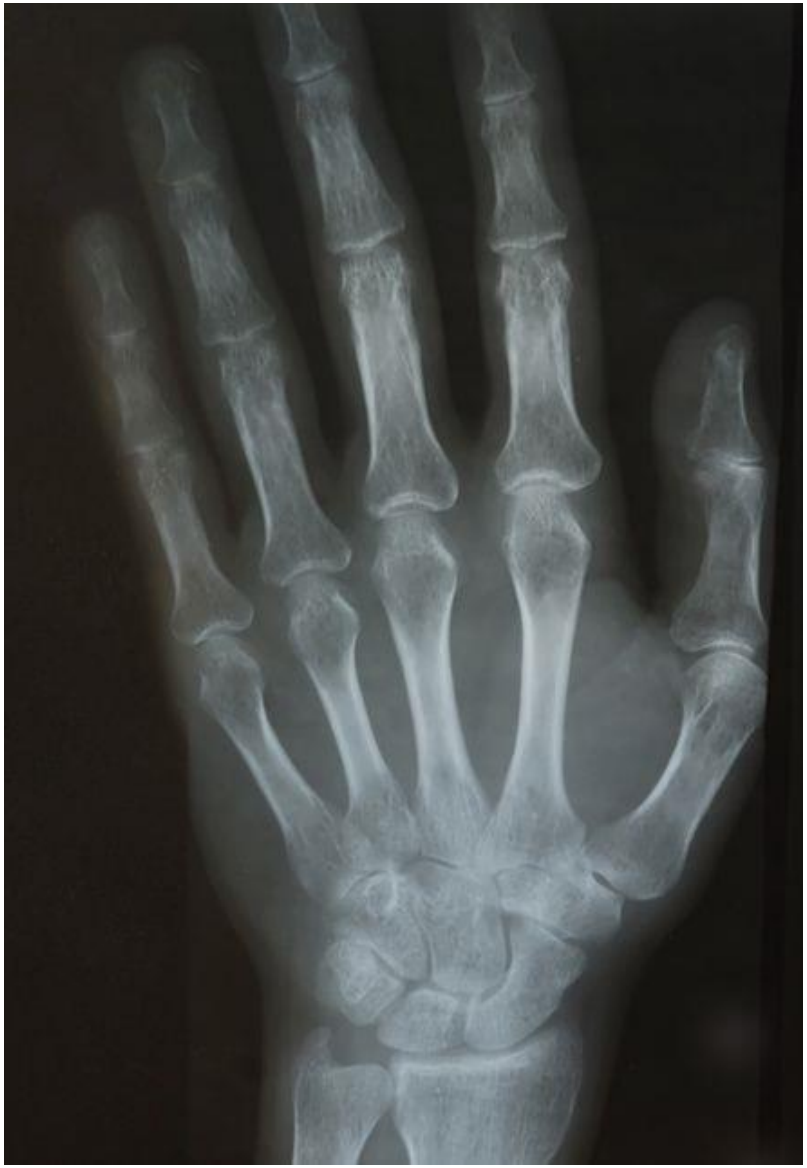
Nobel prize in physics

"in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him"

Röntgen rays = X-rays

Generation of X-rays





The amazing properties of X-rays to be invisible to a human eye but penetrate easily through matter remained unexplained for some time.

One of the hypotheses was suggesting that X-rays are the electromagnetic waves with the wavelength much shorter than the wavelength of ***visible light****.*

1912: Discovery of X-ray diffraction by crystals

1912 **Max von Laue**

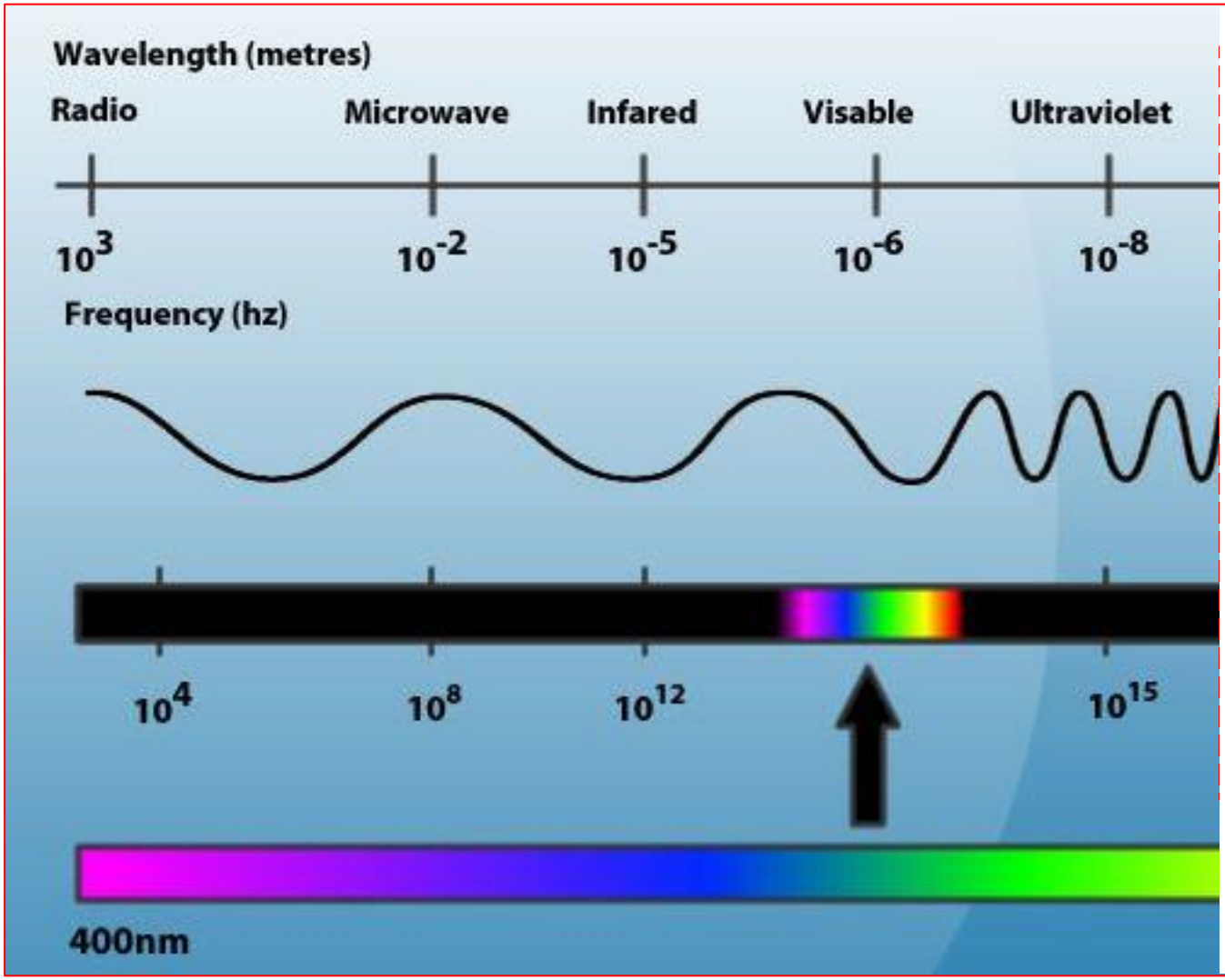
1914

Nobel Prize in Physics

"for his discovery of the diffraction of X-rays by crystals"

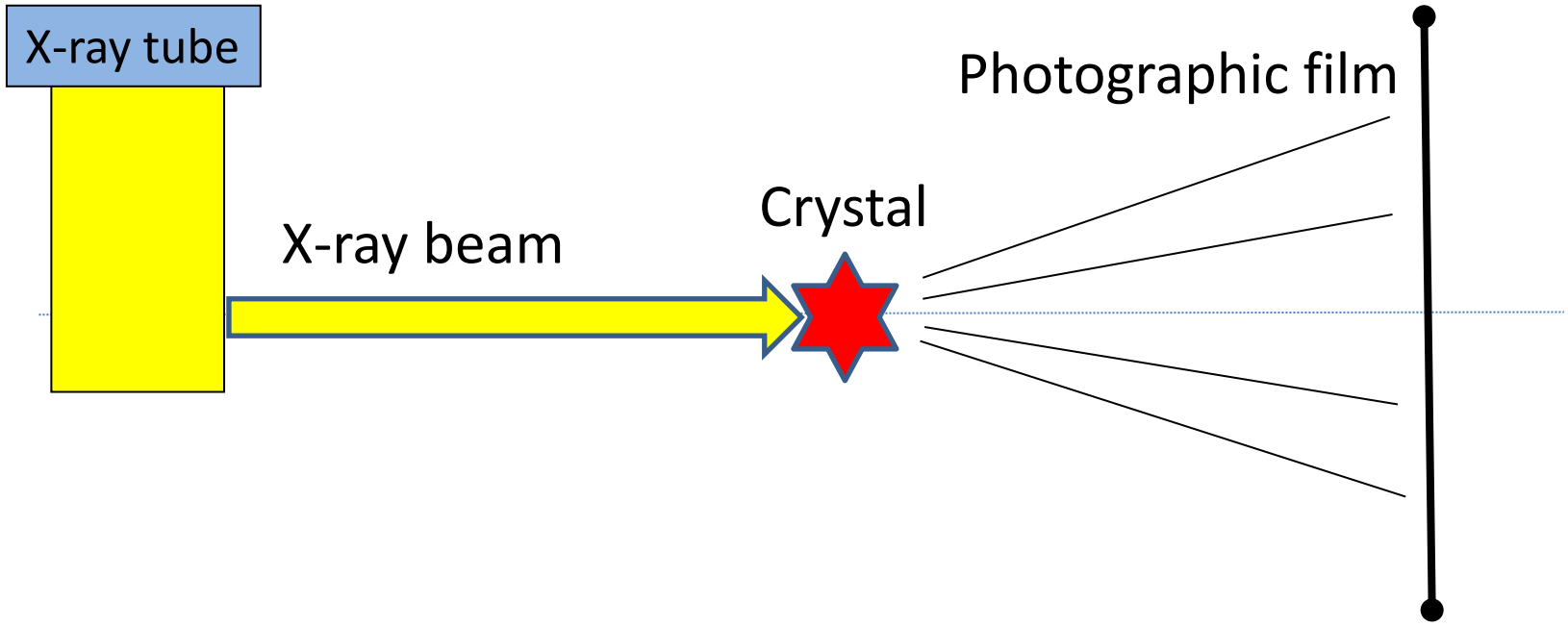
1912 is the birth of Solid State Physics

Spectrum of electromagnetic waves



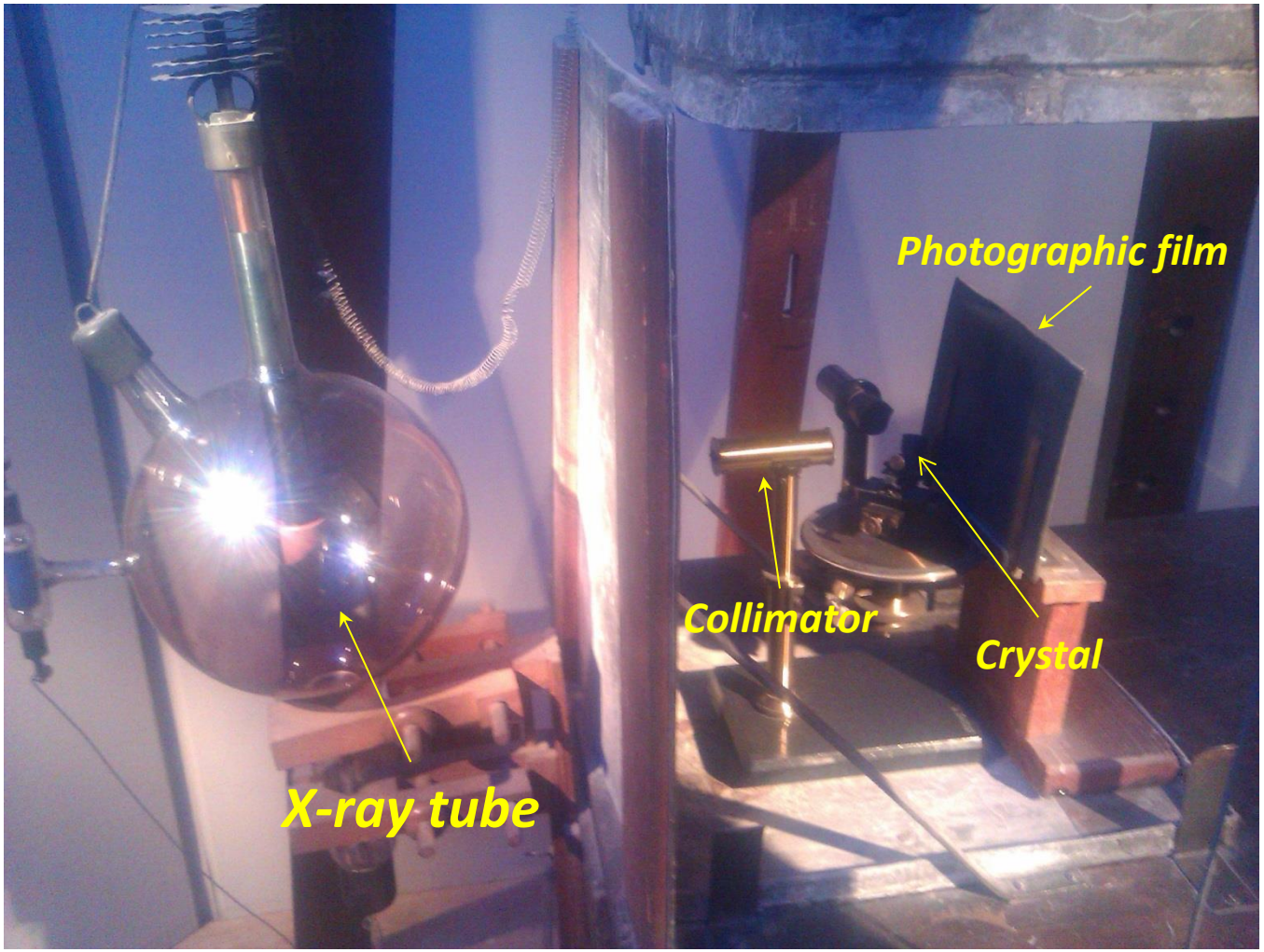
Do X-rays have the same (wave) nature as visible light?

1912: The experiment of Max von Laue



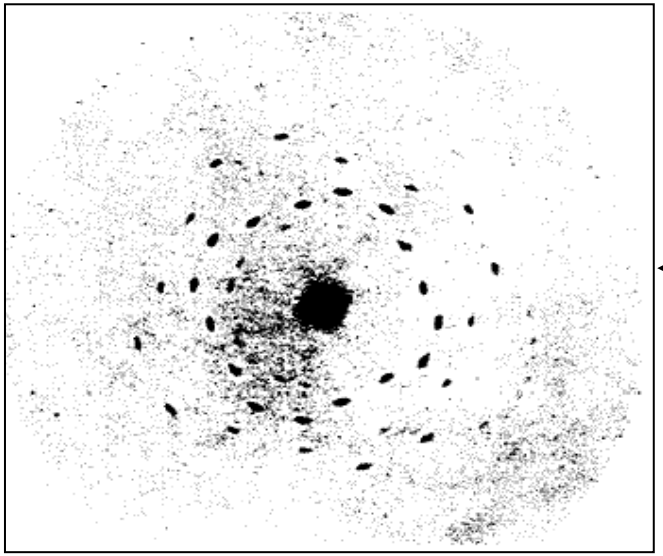
An X-ray beam was directed onto a copper sulphate crystal. The experiment was performed by Friedrich and Knipping

Original experimental setup of Laue, Friedrich und Knipping



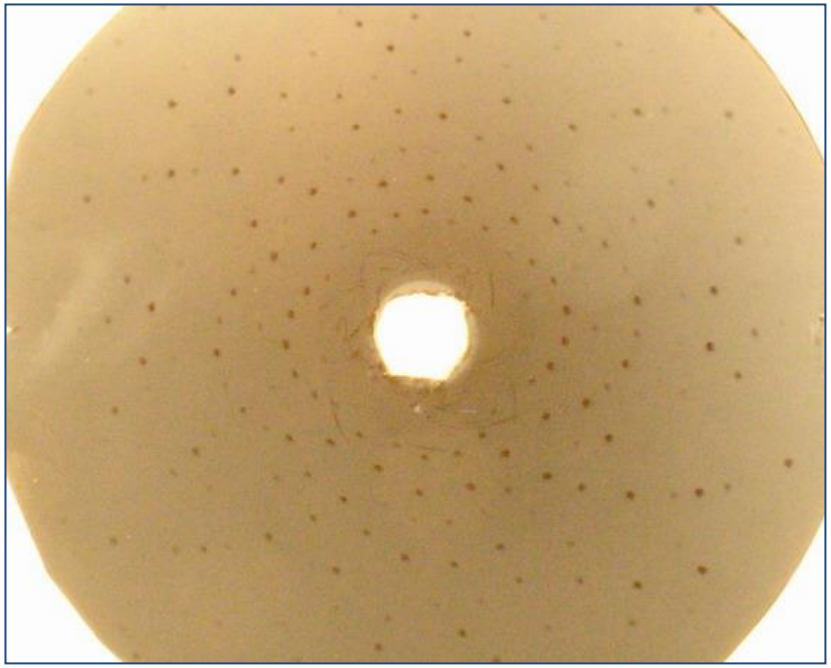
Exhibited in Deutsches Museum, München

Laue pattern: diffraction of X-rays by a crystal



The first Laue pattern: diffraction of X-rays on a $CuSO_4$ crystals obtained by Max von Laue, Friedrich and Knipping

A modern Laue pattern: diffraction of X-rays on quartz (SiO_2) crystal



The BASIC physical principles of X-ray diffraction

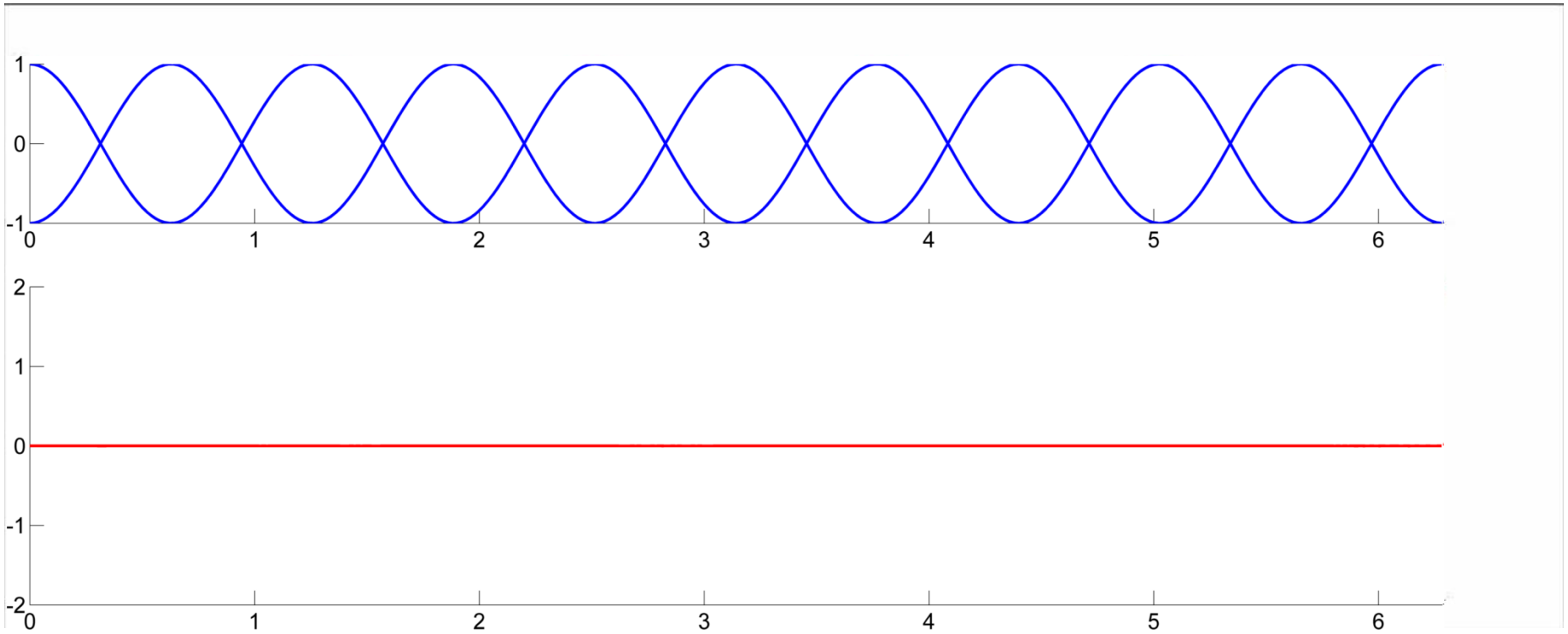
X-rays are electromagnetic waves with the wavelength of the order λ=1 Å (10^{-10} m)

X-rays are scattered by electrons (Thomson scattering)

The waves scattered at different crystal sites interfere with each other. The sum of two waves depends on the phase difference between them

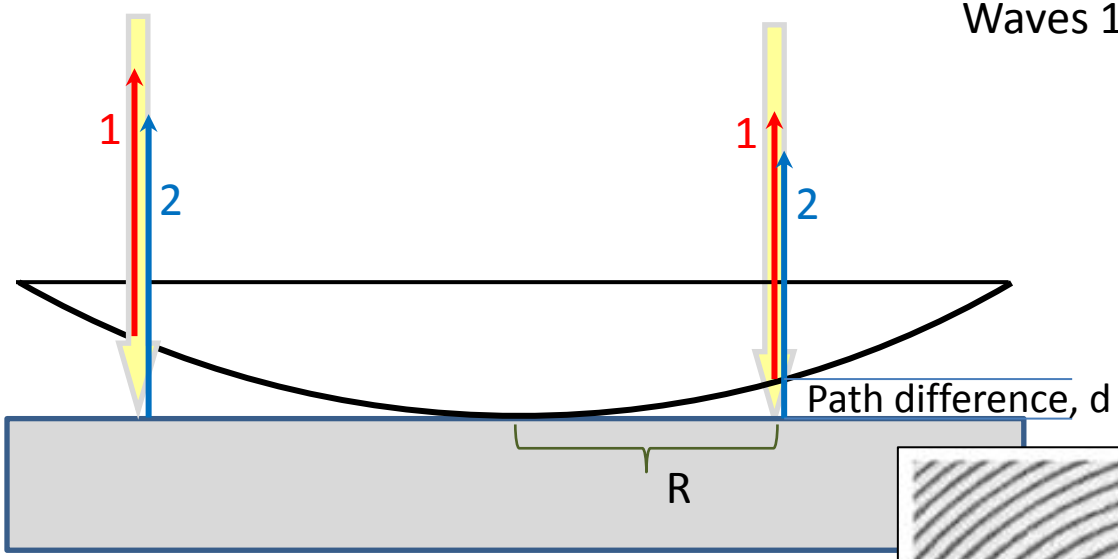
Interference / diffraction of waves

Interference of light is a physical phenomena occurring when two waves of the same wavelength sum up with each other. One defines **CONSTRUCTIVE** and **DESTRUCTIVE** interference



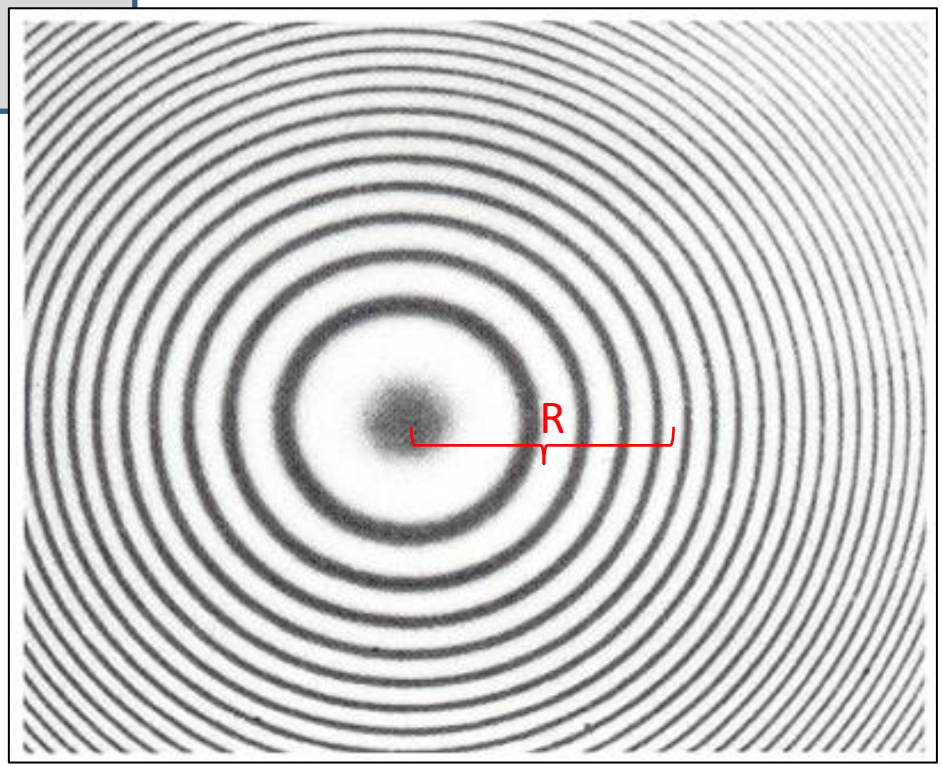
Important parameter: phase shift between wave 1 and wave 2

Newton rings

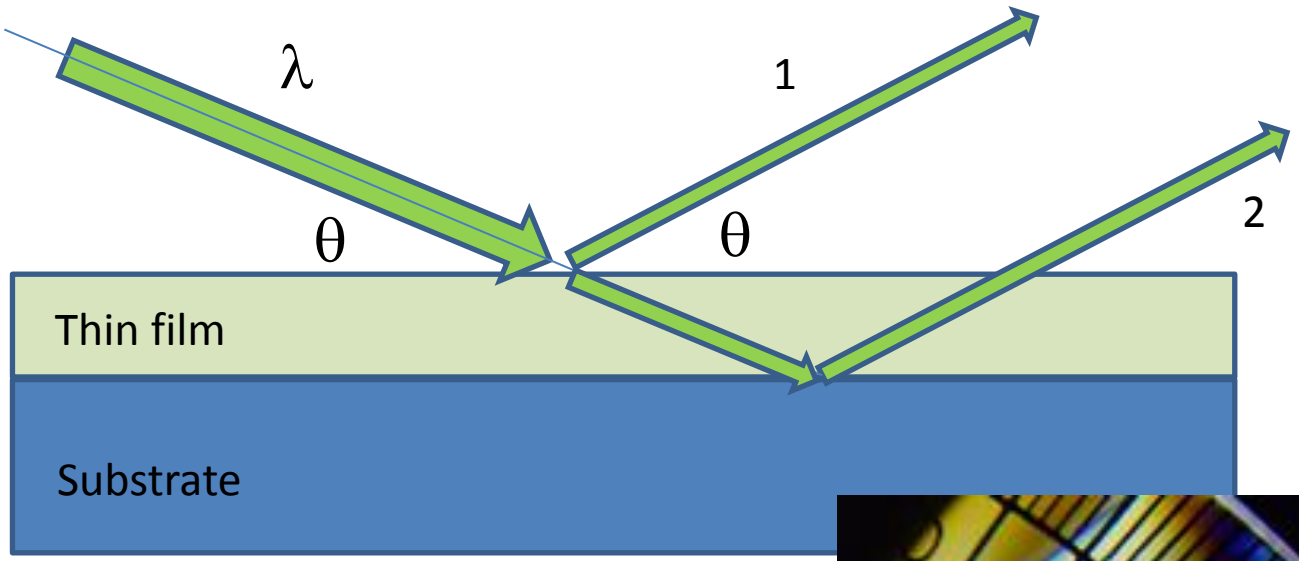


Waves 1 and 2 overlap with each other at the phase shift, δ

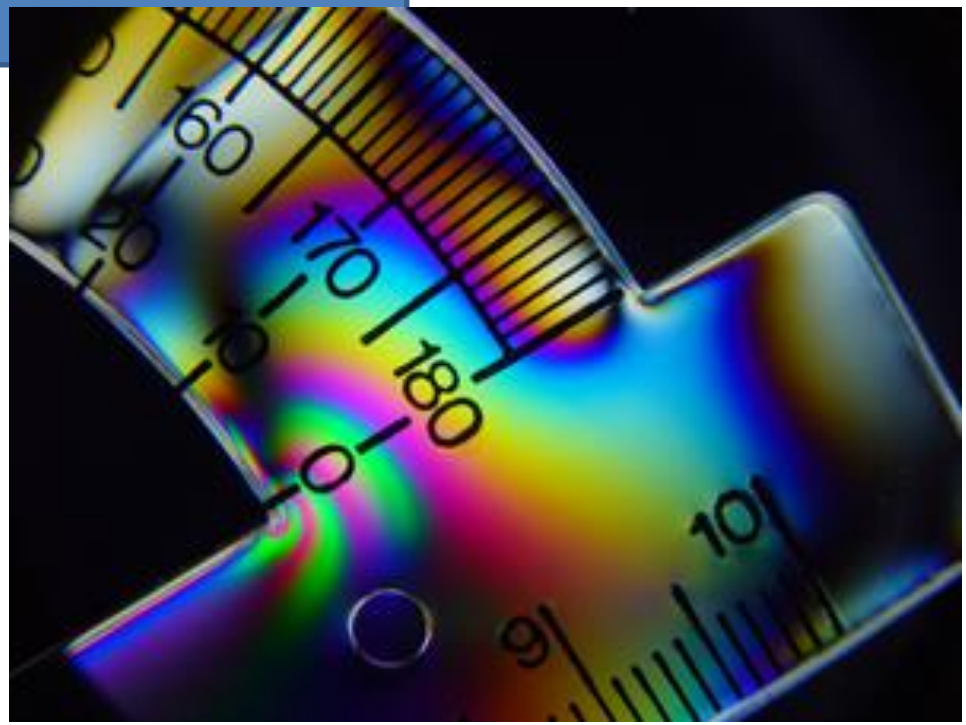
$$\delta = 2\pi\, d / \lambda$$



Further examples

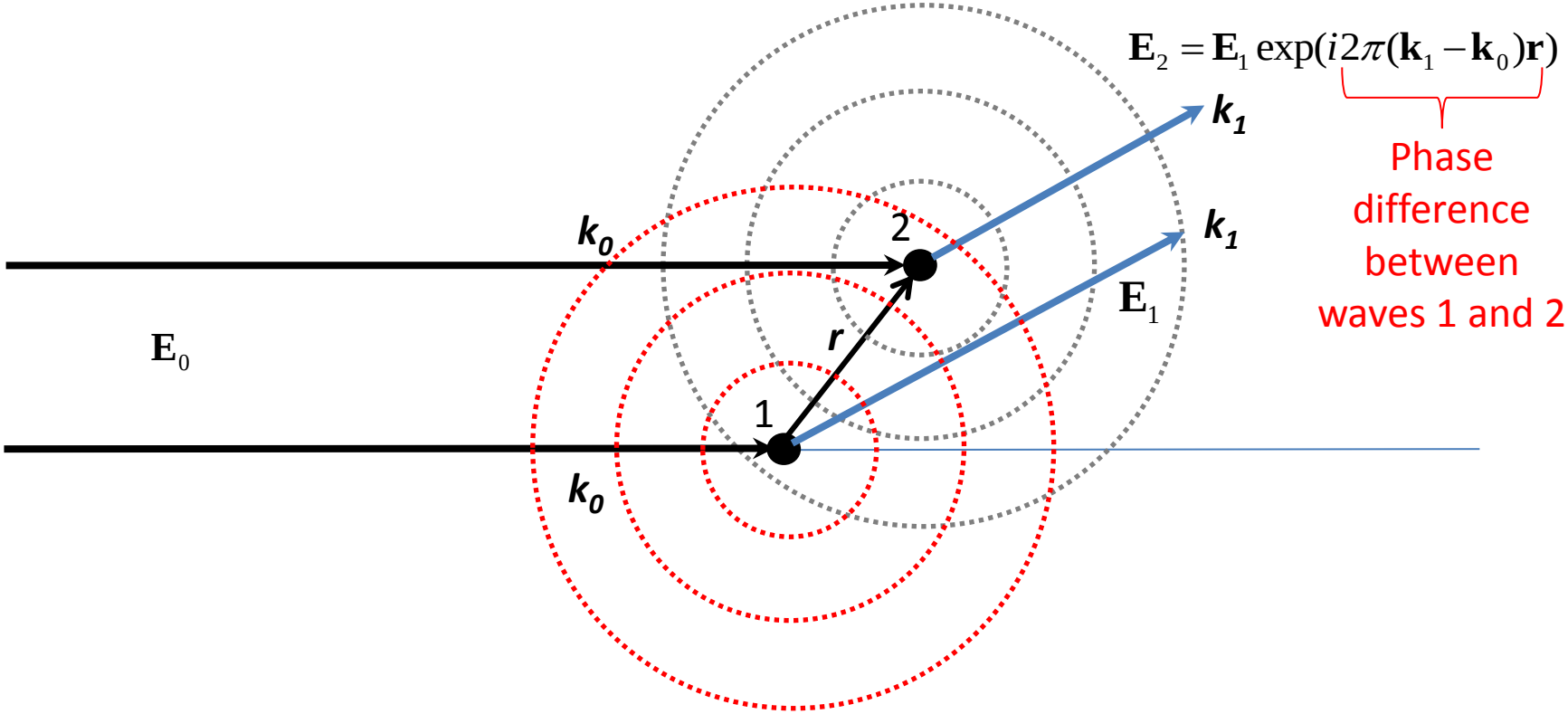


$$2\,d\sin\theta = n\lambda$$



Physical principle of scattering techniques*

Suppose that a monochromatic X-ray beam with wavelength λ hits a crystal. The primary beam is described by the wave vector $\boldsymbol{k_0}$ the scattered beam is described by the wave vector $\boldsymbol{k_1}$. ***The length of both wave vectors is 1/λ***

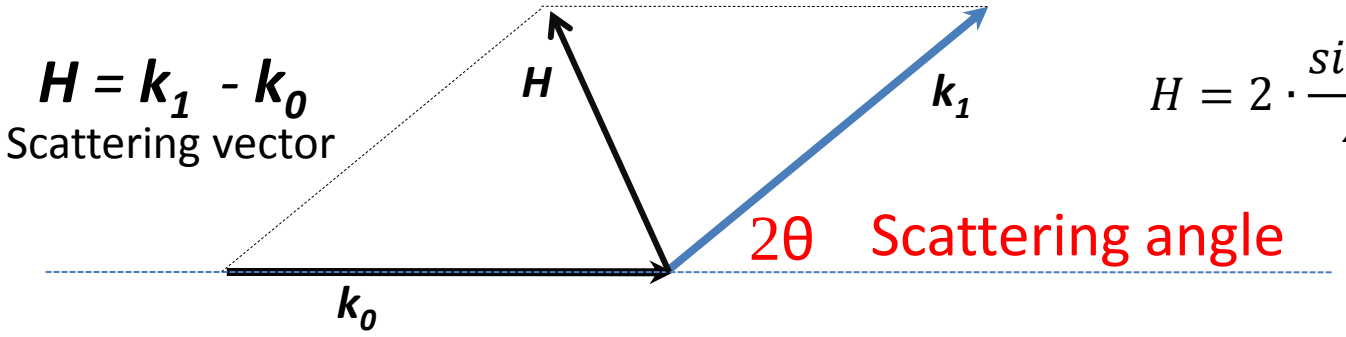


The sum of the electric field vectors from the waves scattered at electrons 1 and 2 is

$$\mathbf{A}(\mathbf{k}_1,\mathbf{k}_0) = \mathbf{E}_1\{1+\exp(2\pi i(\mathbf{k}_1-\mathbf{k}_0)\mathbf{r}\} = \mathbf{E}_1\{\exp(2\pi i(\mathbf{k}_1-\mathbf{k}_0)\mathbf{0} + \exp(2\pi i(\mathbf{k}_1-\mathbf{k}_0)\mathbf{r}\}$$

the amplitude of scattering depends on the DIFFERENCE between the wave vectors

Scattering vector and scattering angle*



$$H = 2 \cdot \frac{sin\theta}{\lambda}$$

The amplitude of X-ray scattering is usually described as a function of a scattering vector ***H (instead of k_1 and k_0).*** Replacing two separate scatters (see previous page) by distributed density:

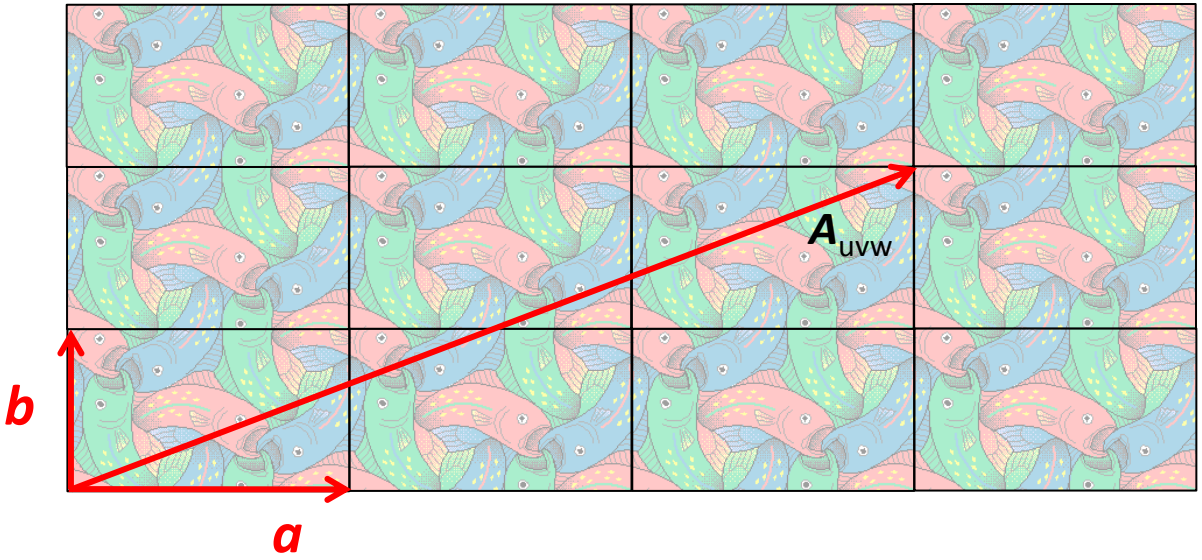
$$A(\mathbf{H}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{H}\mathbf{r}) dV$$

With ρ(r) being an ELECTRON DENSITY so that ρ(r)dV is the amount of electrons in the small volume dV. The intensity of the X-ray scattering is the square of the absolute value of electric field so that

$$I(\mathbf{H}) \sim | A(\mathbf{H}) |^2$$

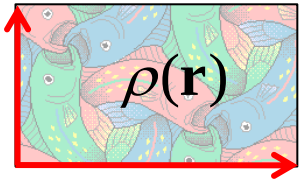
Scattering by a crystal (periodic system)*

Consider the *scattering amplitude*, A(**H**), for the periodic crystal. In this case electron density can be described by LATTICE and UNIT CELL



Lattice translation

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{A}_{uvw})$$



The sum (integration) over the whole crystal can be reduced to the integration over the single unit cell only:

$$A(\mathbf{H}) = \int_{(unit\,CELL)} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H}\mathbf{r}) dV \cdot \sum_{uvw} \exp(2\pi i \mathbf{H}\mathbf{A}_{uvw})$$

Contribution of the single UNIT CELL (F) ***CRYSTAL LATTICE (L)***

Contribution of the crystal lattice*

$$L(\mathbf{H}) = \sum_{uvw} \exp(2\pi i \mathbf{H}\mathbf{A}_{uvw})$$ **The sum is carried out over all lattice points**

It is convenient to decompose the scattering vector by the reciprocal lattice basis, *a *b** and *c** so that H= *h* a* + *k* b* + *l* c*. In this case the dot product between vectors H and A is reduced to**

$$\boldsymbol{HA}_{uvw} = hu + kv + lw$$

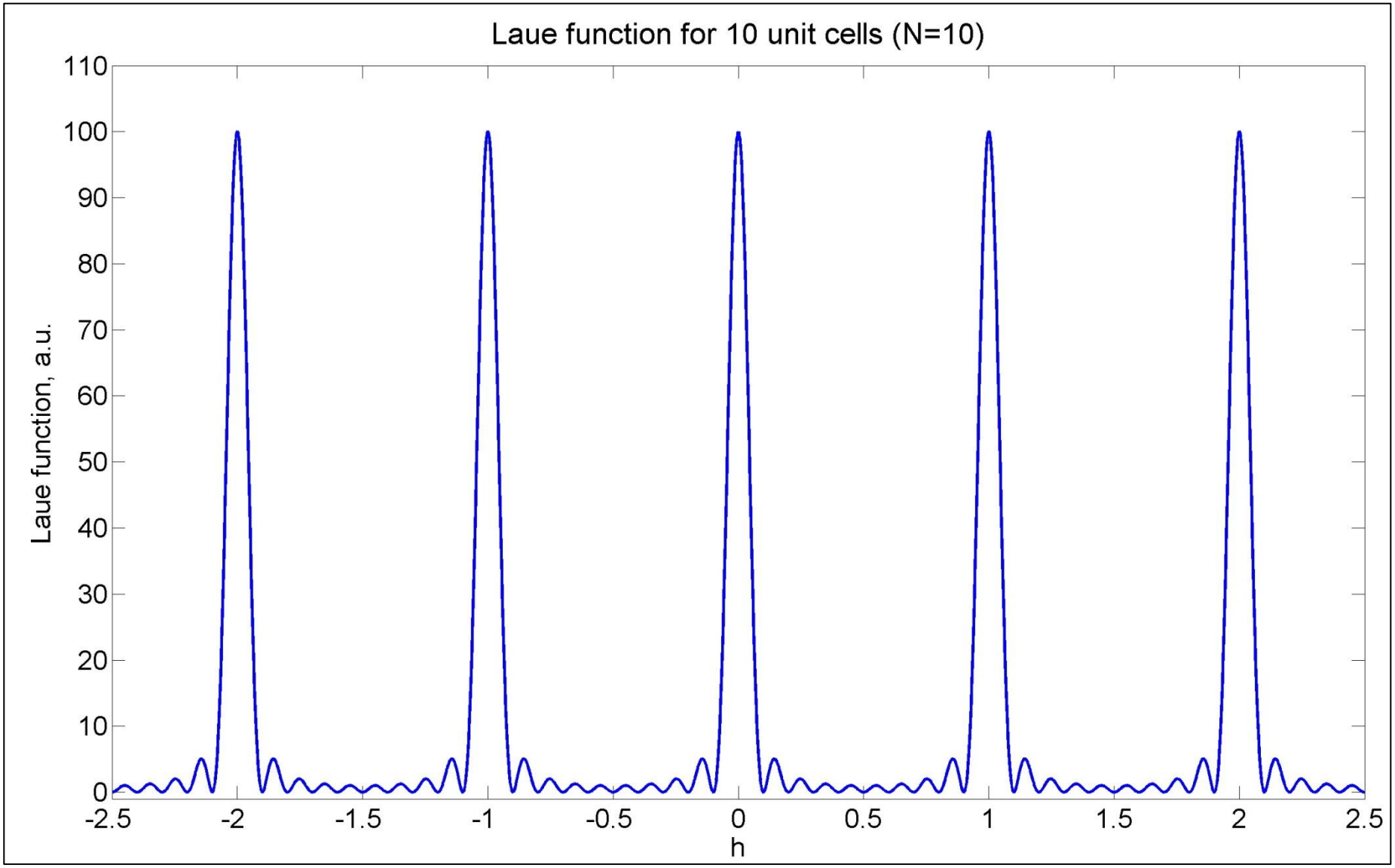
$$L(\mathbf{H}) = \sum_{u} \exp(2\pi i h u) \sum_{v} \exp(2\pi i k v) \sum_{v} \exp(2\pi i l w)$$

It can be easily shown that in the case of an X-ray beam that illuminates N_a N_b *and* N_c *unit cells* in the directions ***a b*** and ***c*** then

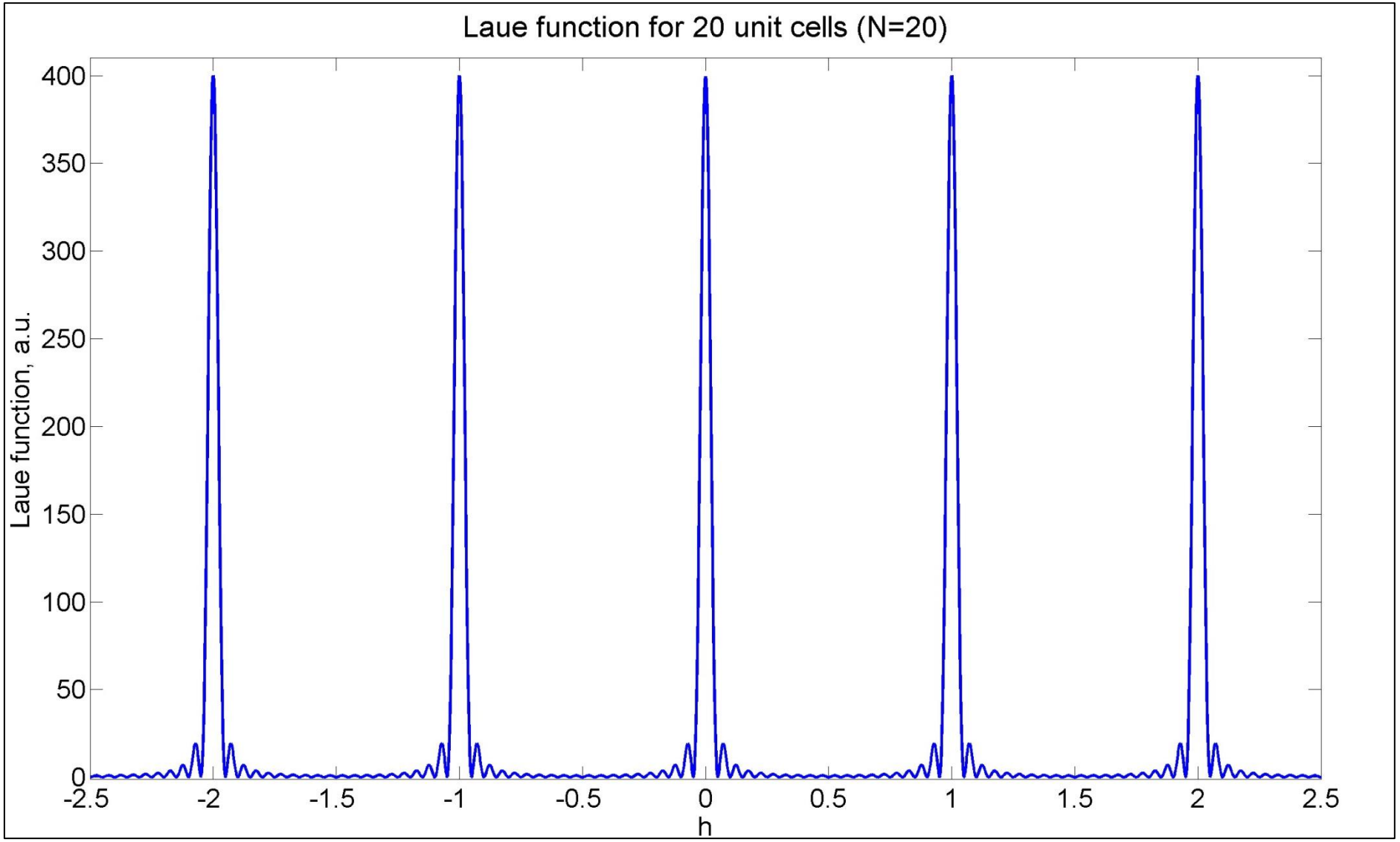
$$\left|L(hkl)\right|^2 = \frac{\sin^2(\pi N_a h)}{\sin^2(\pi h)} \cdot \frac{\sin^2(\pi N_b k)}{\sin^2(\pi k)} \cdot \frac{\sin^2(\pi N_c l)}{\sin^2(\pi l)}$$

LAUE INTERFERENCE FUNCTION

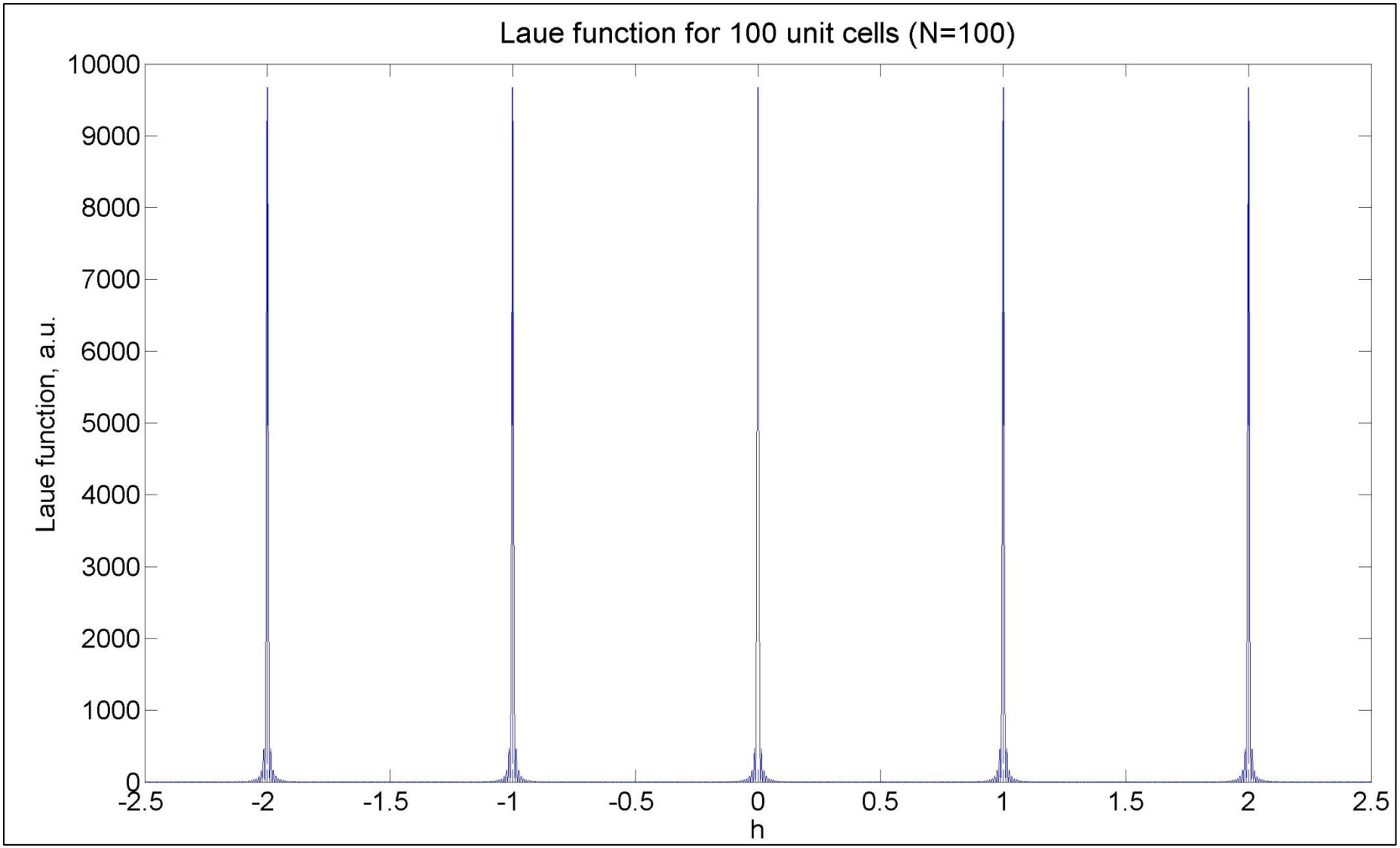
Laue interference function*



Laue interference function*



Laue interference function*



Conclusion: LAUE EQUATION

The intensity of scattering by a crystal is non-zero for the scattering vectors ***H whose reciprocal lattice coordinates are integers. That means, the scattering from a crystal (with a given lattice) is described by the corresponding RECIPROCAL LATTICE***

LAUE EQUATION for the diffraction by a crystal

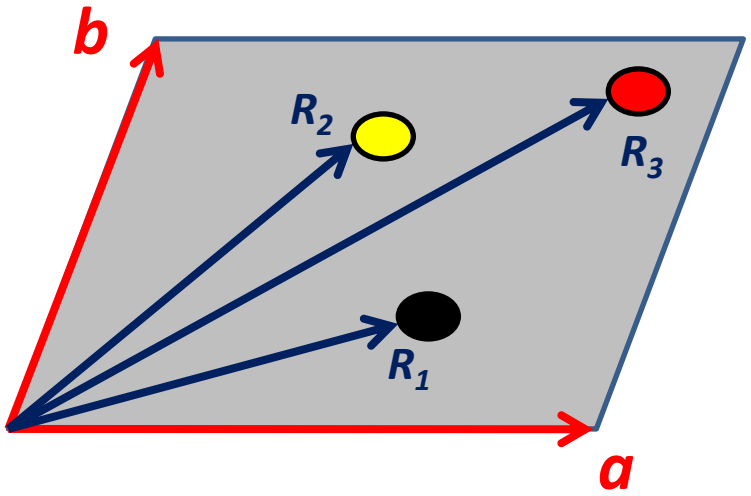
$$\boldsymbol{k_1 - k_0 = h\,a^* + k\,b^* + l\,c^*}$$

h, k and l are indices of reflection

SCATTERING ⟶ DIFFRACTION

Contribution of the UNIT CELL*

Electron density in the unit cell is the sum of the electron densities of the constituting atoms. Suppose that atoms occupy the sites in the unit cell at the positions $\boldsymbol{R}_1$, $\boldsymbol{R}_2$, ... $\boldsymbol{R}_n$. Each atom has its own electron density around the nucleus position. We suppose that electron density of a single / isolated atom μ is $\rho_\mu(\mathbf{r})$



$$\rho(\mathbf{r}) = \sum_{\mu=1}^{n} \rho_\mu(\mathbf{r} - \mathbf{R}_\mu)$$

The scattering amplitude by the single unit cell is then given by

$$F(\mathbf{H}) = \int_{(unit\,CELL)} \rho(\mathbf{r}) \exp(2\pi i \mathbf{H}\mathbf{r}) dV \rightarrow \int_{(unit\,CELL)} \sum_{\mu} \rho(\mathbf{r} - \mathbf{R}_\mu) \exp(2\pi i \mathbf{H}\mathbf{r}) dV$$

ATOMIC SCATTERING FACTOR

Atomic scattering factor is the amplitude of the X-ray scattering by a single (isolated) atom

$$f_\mu(\mathbf{H}) = \int \rho_\mu(\mathbf{r}) \exp(2\pi i \mathbf{H}\mathbf{r}) dV$$

Atomic scattering factor depends only on the type of atom μ and can be calculated for each atom in the periodic table

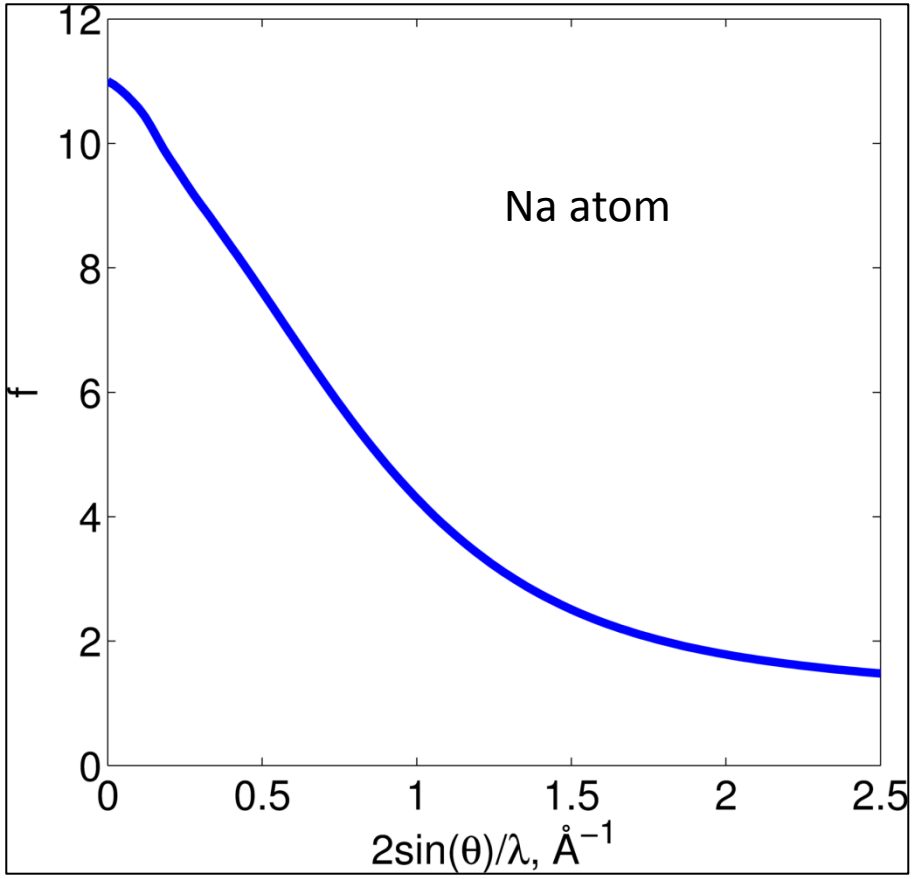
Electron density of single atoms is calculated by means of QUANTUM CHEMISTRY methods and tabulated for each atom of the periodic table.

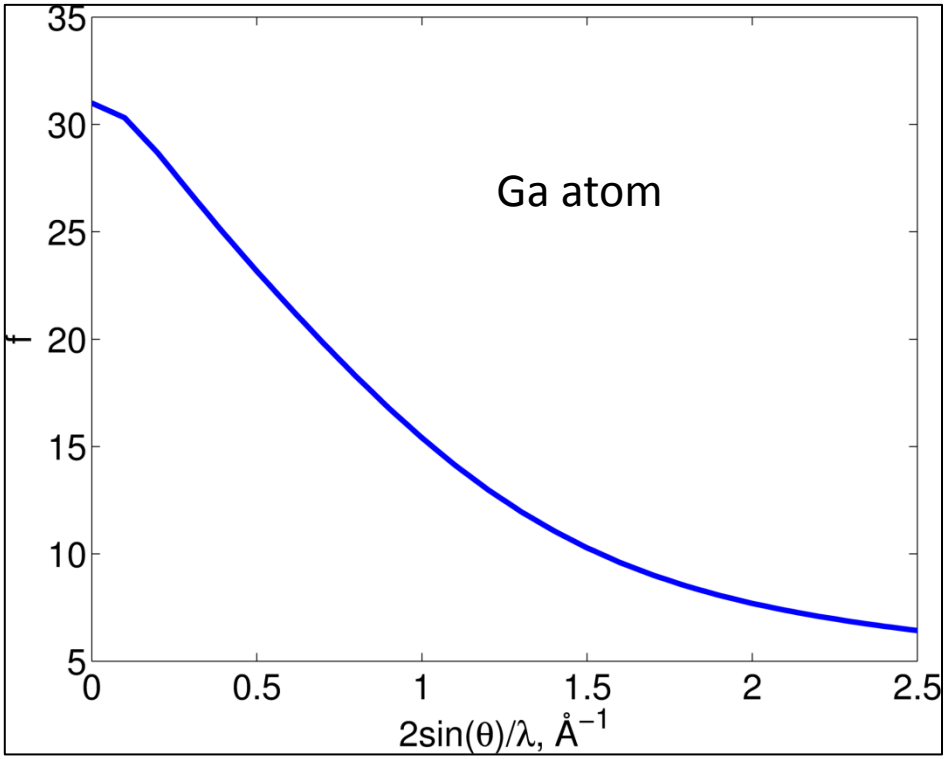
Official source: International Tables for Crystallography: Volume C

Unofficial but mostly used nowadays source:
Crystallography group in Buffalo

http://harker.chem.buffalo.edu/group/ptable.html

EXAMPLES of ATOMIC SCATTERING FACTORS*





STRUCTURE FACTOR

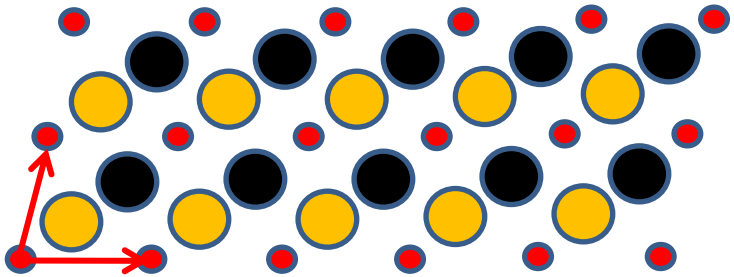
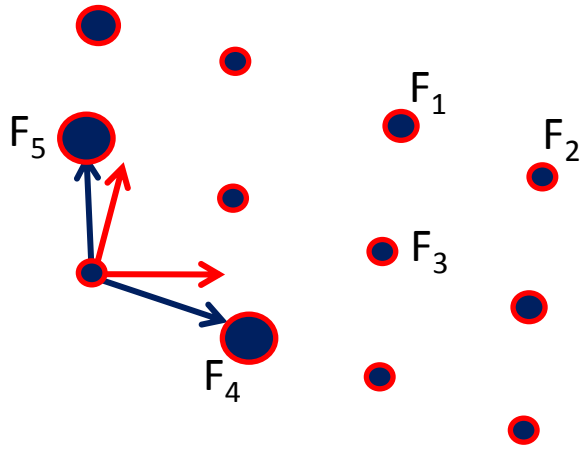
USING THE DEFINITION of ATOMIC SCATTERING FACTOR and the position of each atom in the unit cell, $[x_\mu, y_\mu, z_\mu]$ we can rewrite the amplitude of scattering by the single unit cell as

$$F(hkl) = \sum_{\mu=1}^{n} f_\mu(\mathbf{H}) \exp\left(2\pi i(hx_\mu + ky_\mu + lz_\mu)\right) \qquad \text{STRUCTURE FACTOR}$$

THE SQUARE OF THE STRUCTURE FACTOR DEFINES THE INTENSITY OF THE REFLECTION with the indices h,k and l.

STRUCTURE FACTOR is an ACTUAL LINK BETWEEN CRYSTAL STRUCTURE (atomic positions x_μ, y_μ and z_μ) and INTENSITY OF X-ray DIFFRACTION

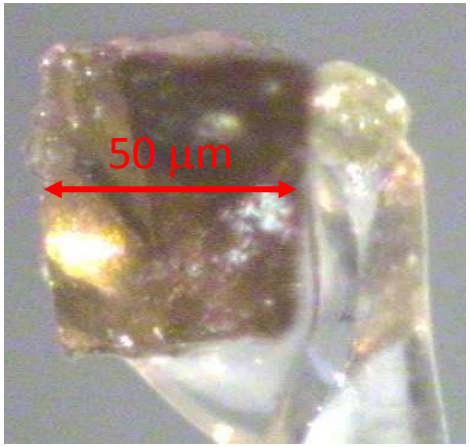
A bit of terminology: real AND reciprocal space

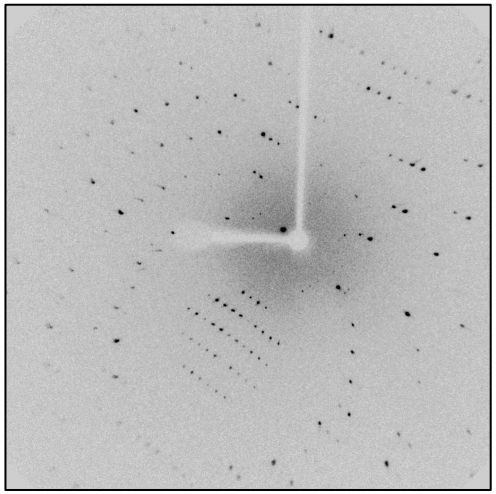
Real space	Reciprocal space
Description of real crystal structure, i.e. distribution of electron density or atomic positions $\rho(\mathbf{r})$	*Distribution of diffraction intensity as a function of the scattering vector* $A(\mathbf{H})$
CRYSTAL STRUCTURE 	**RECIPROCAL LATTICE** 

Investigation of crystal structures by means of X-ray diffraction technique

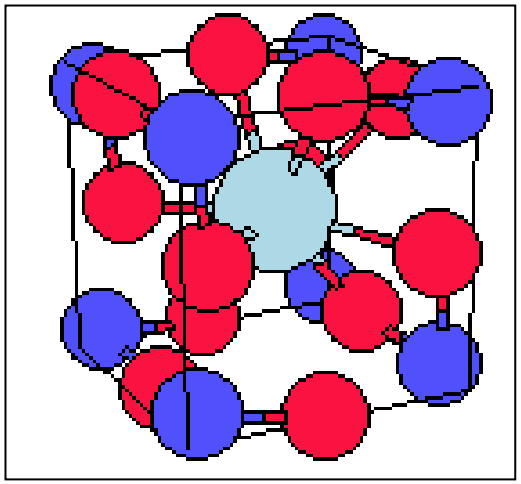
Diffraction images

X-ray beam





Crystal structure



Data analysis

The main goals of an X-ray diffraction experiment

Crystal lattice constants and symmetry

A COLLECTION OF INFORMATION ABOUT RECIPROCAL SPACE

↓

Locating positions of the diffraction maxima, i.e. reciprocal lattice points

↓

Reconstruction of the reciprocal lattice

↙ ↘

Determination of the Bravais type of crystal lattice

Finding the orientation of lattice vectors, a*, b* and c*

↓

The main goals of an X-ray diffraction experiment

Physics

Determination of intensities of individual reflections

↓

Analysing the SYMMETRY of RECIPROCAL SPACE

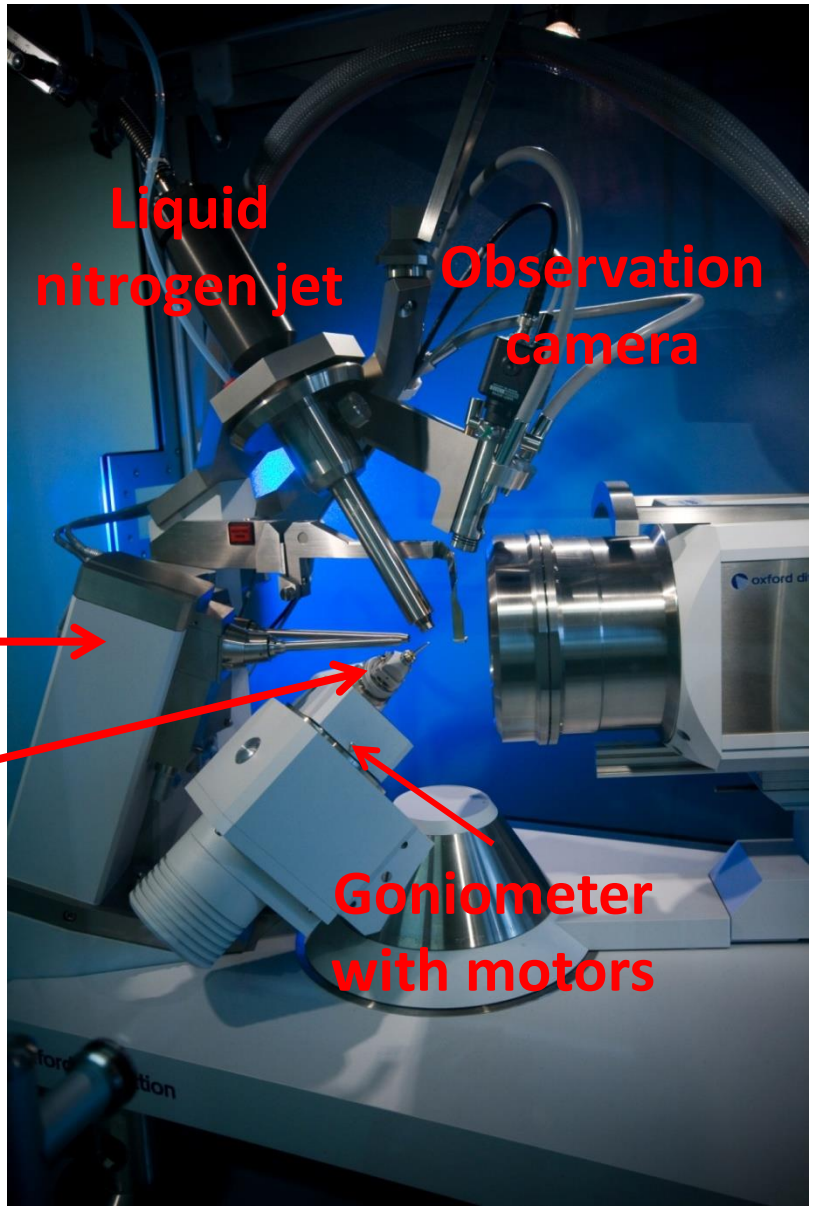
↓

ASSIGNMENT OF THE SPACE GROUP OF INVESTIGATED CRYSTAL

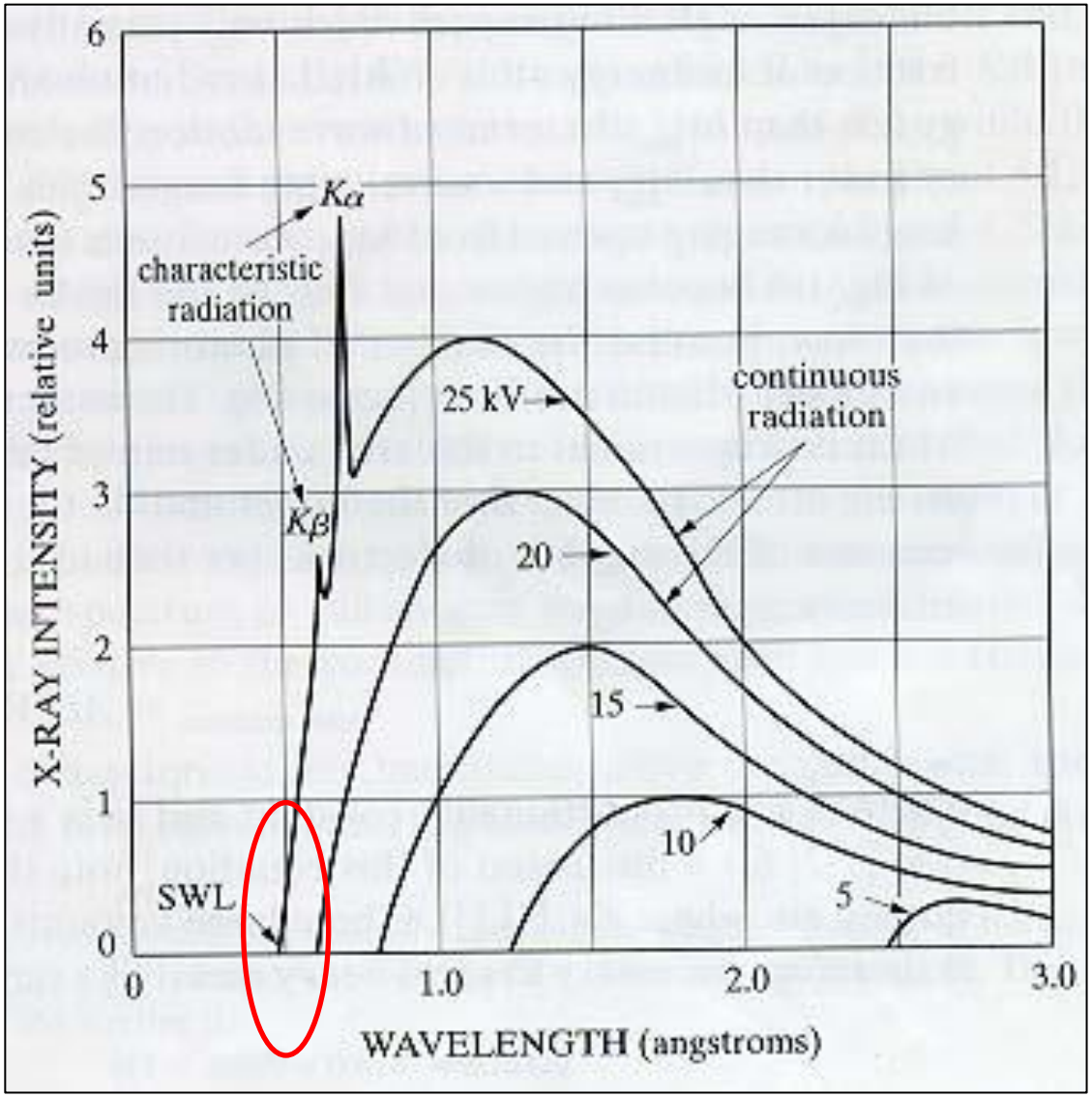
↓

STRUCTURE SOLUTION (determination or refinement of atomic positions in the unit cell)

X-ray diffractometer



Spectra of the X-ray beam



Shortest wavelength of the white X-ray beam (highest energy of an X-ray photon) is determined by the highest energy of electron hitting the target.

$$\lambda_{\min} = \frac{hc}{eU}$$

λ_{min} (Å) = **12.39** / U (kV)

Shortest wavelength

Monochromatic X-ray beams

The wavelength of the CHARACTERISTIC X-ray beam depends on the material of the target and the electron shells involved in the transition

Anode type	Radiation	Wavelength, Å	Energy, keV
Cu	Cu, Kα	1.5406	8.0423
Mo	Mo, Kα	0.7107	17.433
Fe	Fe, Kα	1.9351	6.402
Ag	Ag, Kα	0.5477	22.162

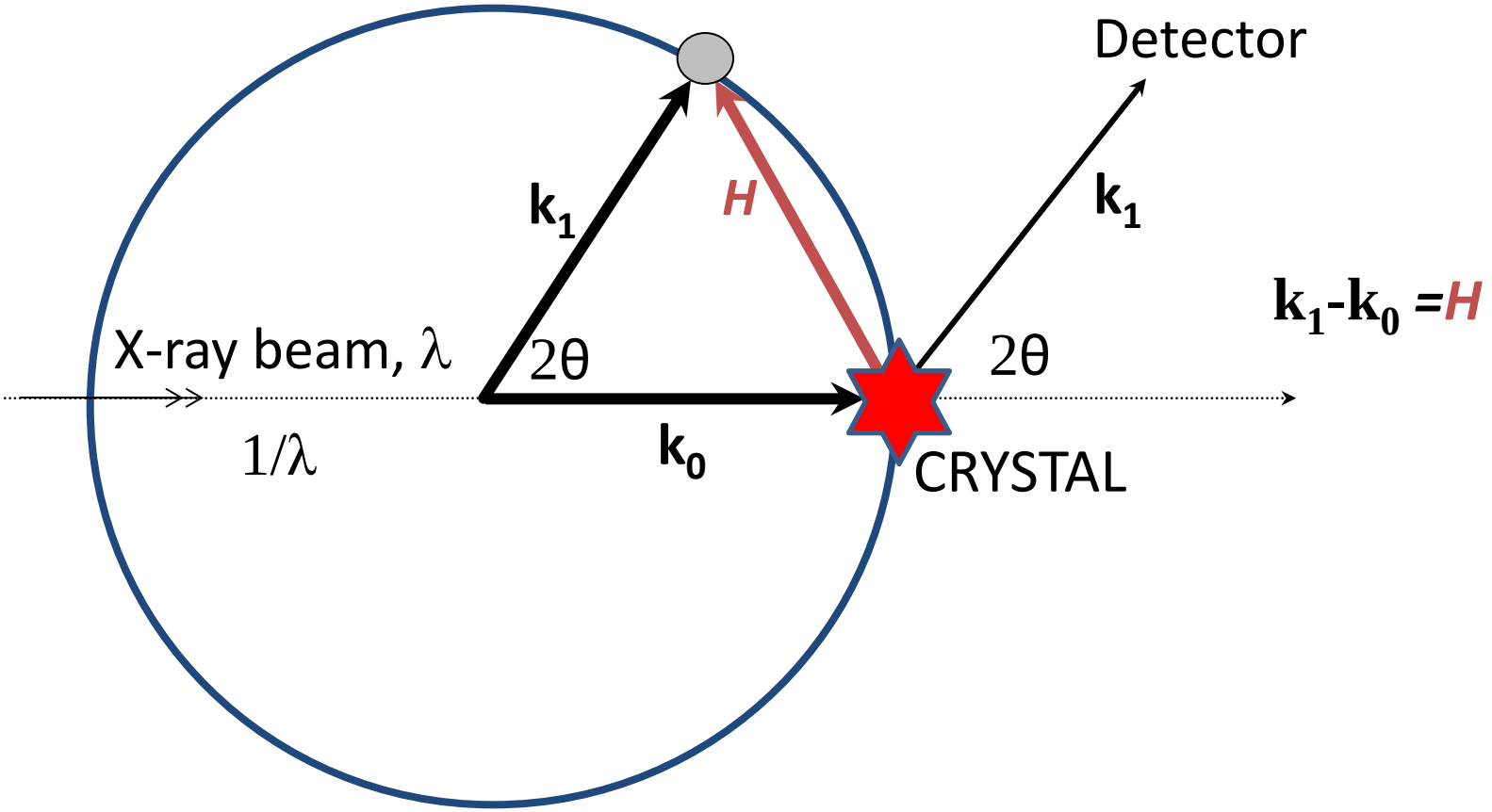
Diffraction in the monochromatic X-ray beam

The majority of modern X-ray diffraction techniques use a monochromatic X-ray beam ($\Delta\lambda / \lambda \approx 10^{-4}$ Å).

Which part of the reciprocal space is available from the X-ray diffraction pattern obtained from a STILL CRYSTAL???

The answer is given by the EWALD CONSTRUCTION

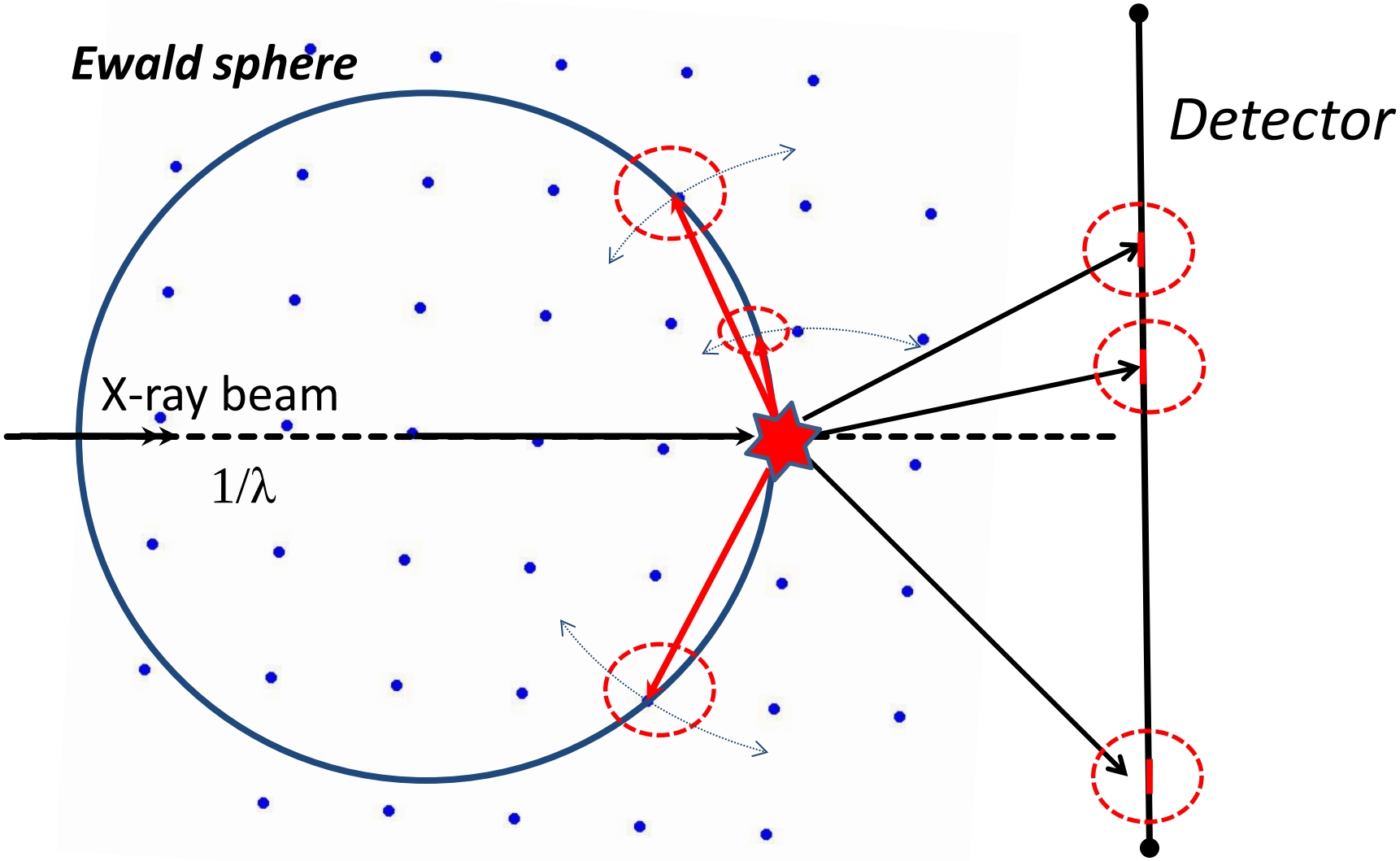
Ewald sphere



The wavelengths of the primary X-ray beam and the diffracted beam are the same, therefore $|k_0|=|k_1|=1/\lambda$. Therefore the scattering vector $H=k_1-k_0$ always points to the surface of the sphere of radius $1/\lambda$ with the center at the point $-k_0$. This sphere is referred to as an Ewald sphere

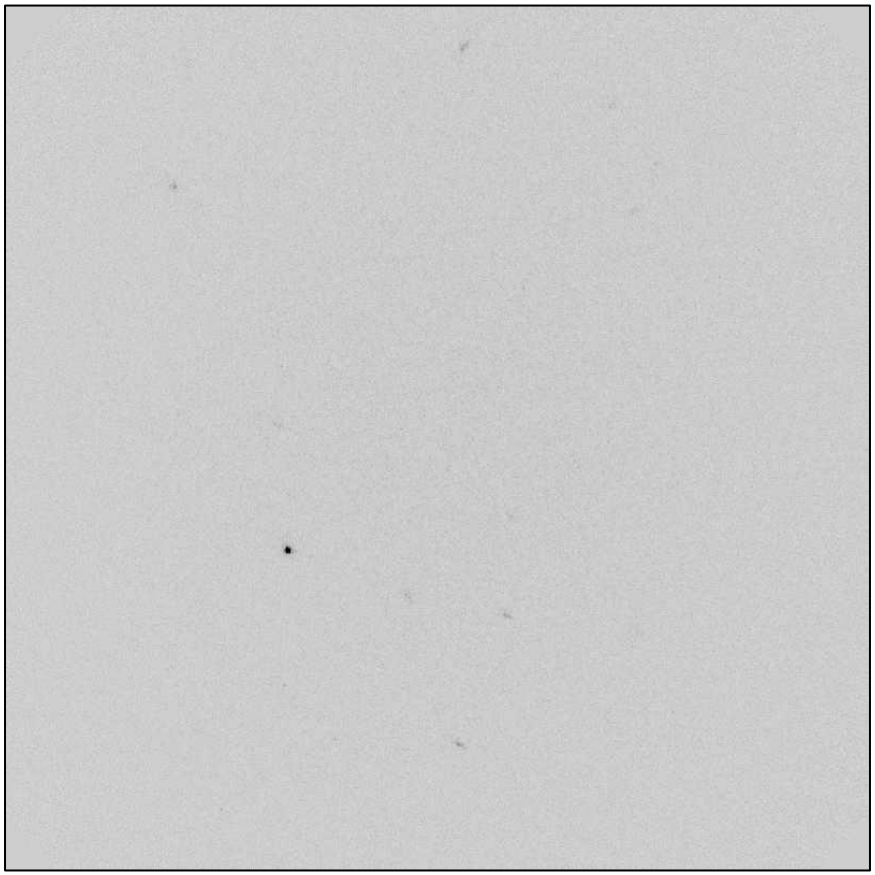
X-ray diffraction from a rotated crystal

What happens if we rotate a crystal by a certain angle whilst collecting an image from the detector?

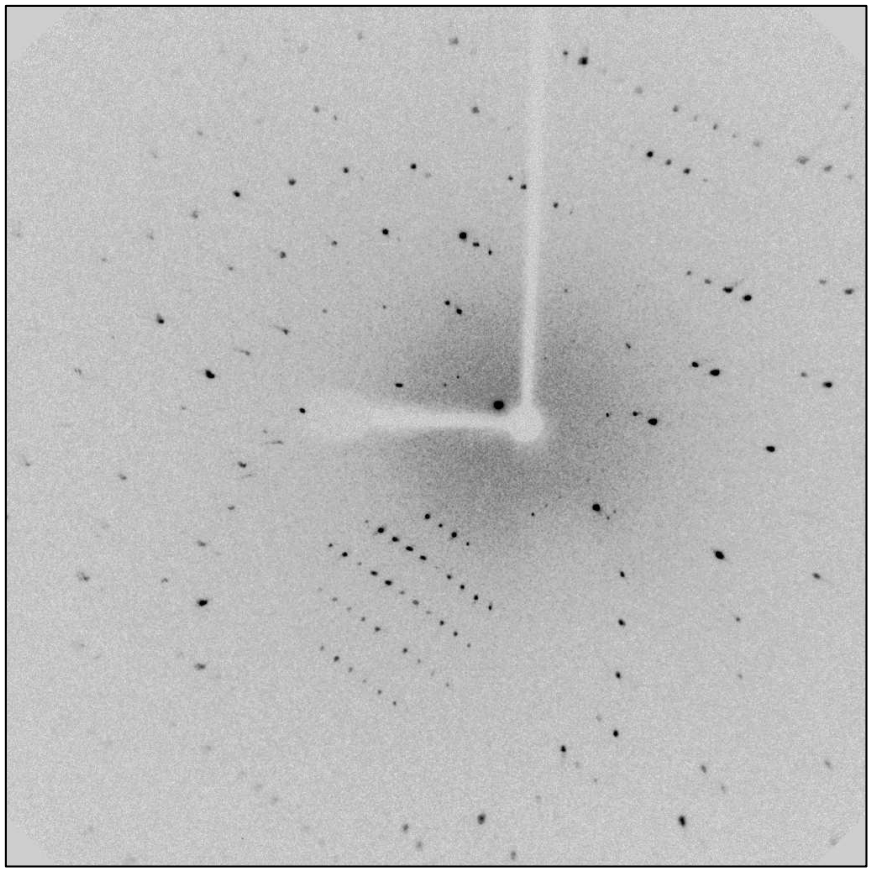


Rotation photographs (taken at single crystal diffractometer, rotation angle 1 degree)

a=b=c=3.8 Å $\alpha = \beta = \gamma$ =90 deg



a=10.2 Å b=15.4 Å c=18.3 Å



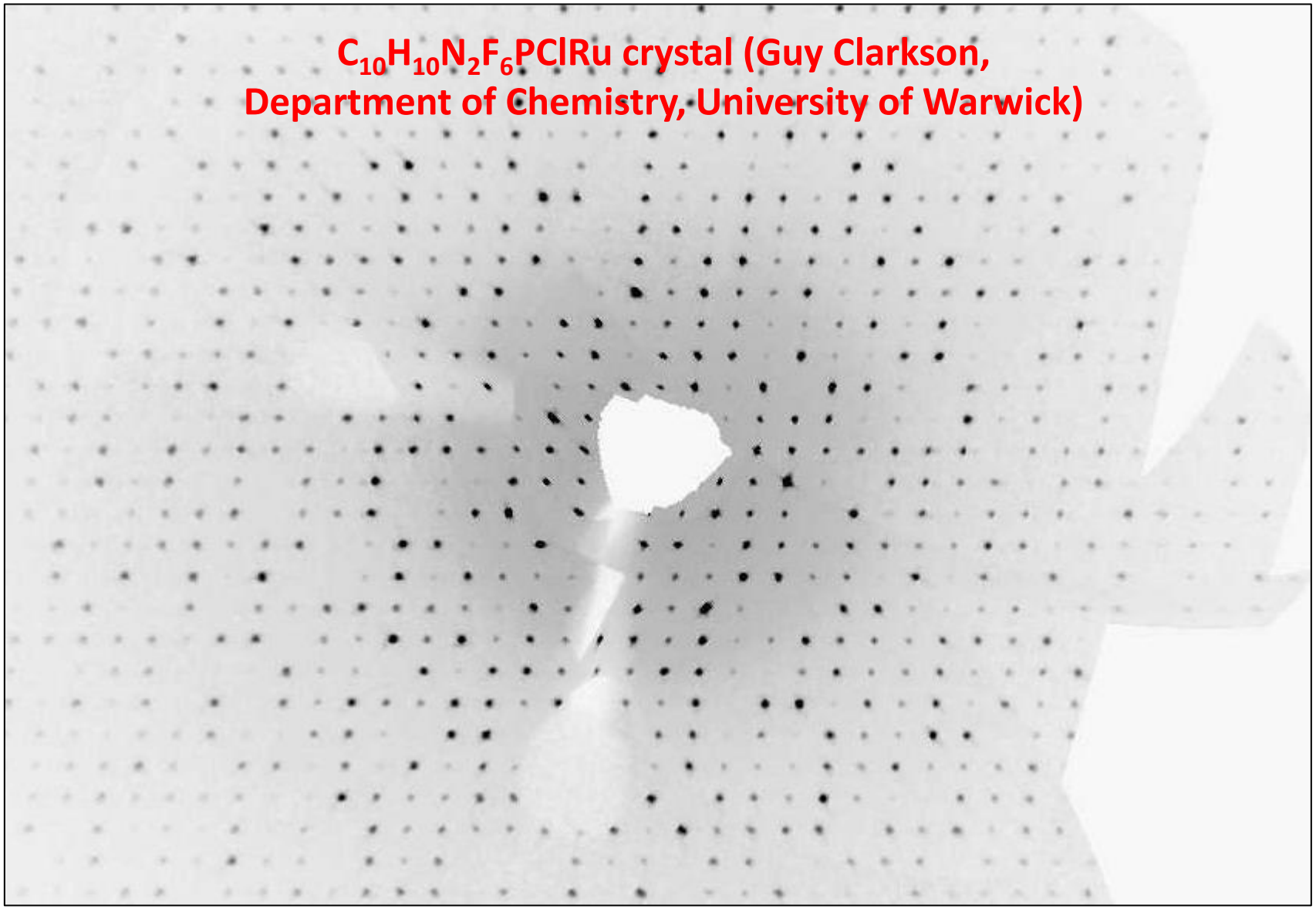
Modern X-ray diffraction experiment

Taking the number of ROTATION PHOTOGRAPHS with very small step at different orientations of a crystal. Taking images frame by frame

Reconstructing reciprocal space

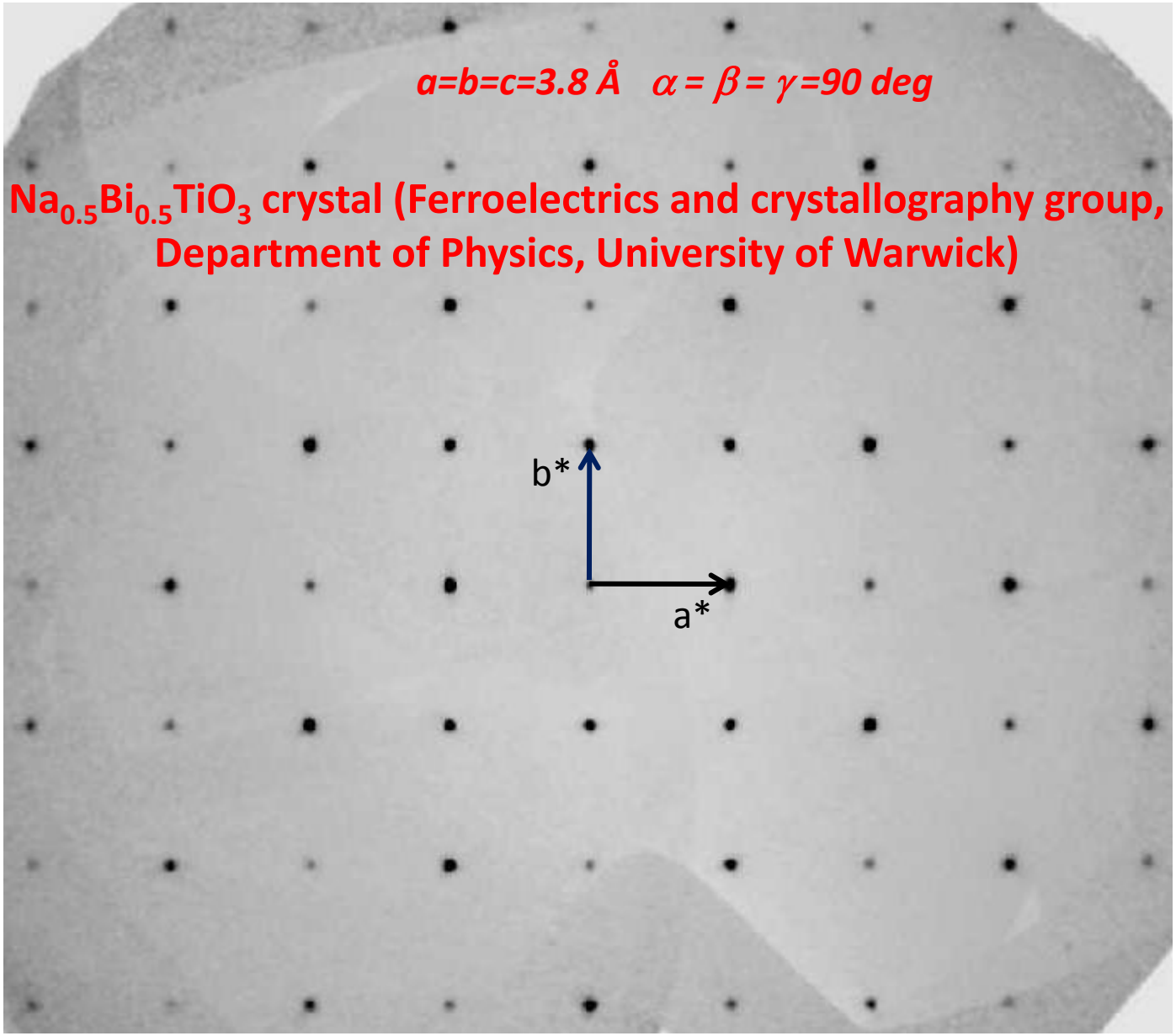
Calculating distribution of intensities in the selected sections of the reciprocal space

Reconstruction of reciprocal space: Example 1

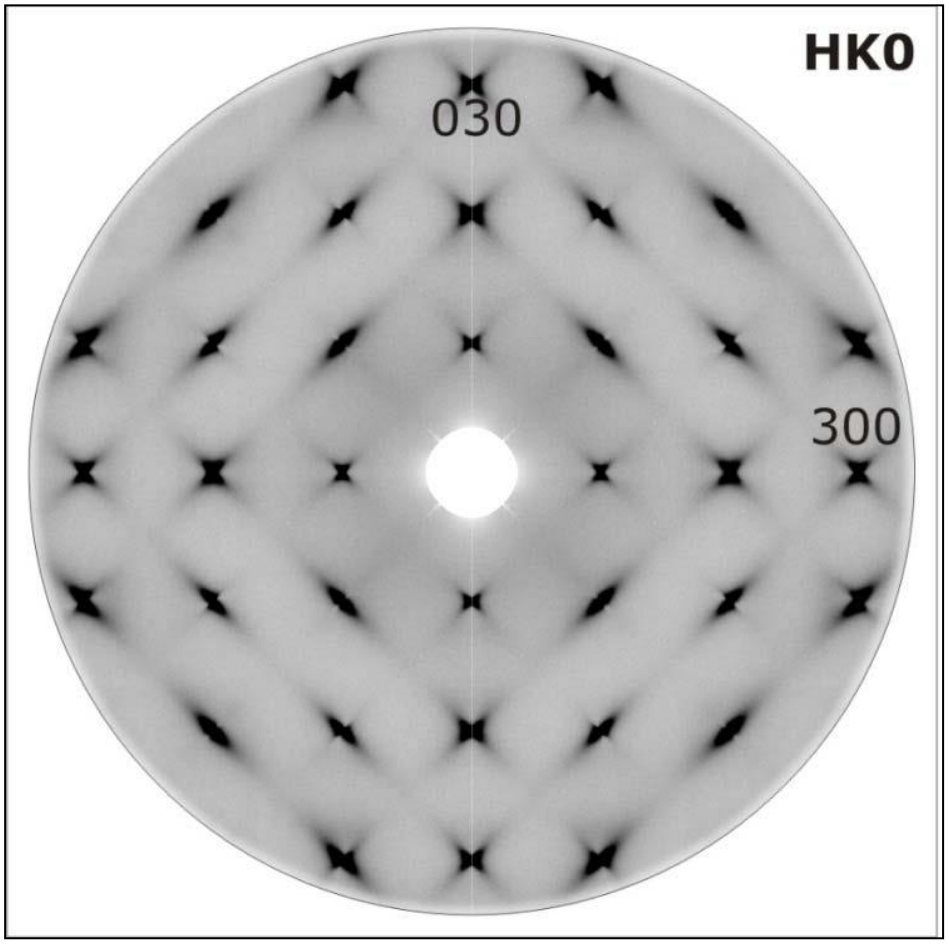


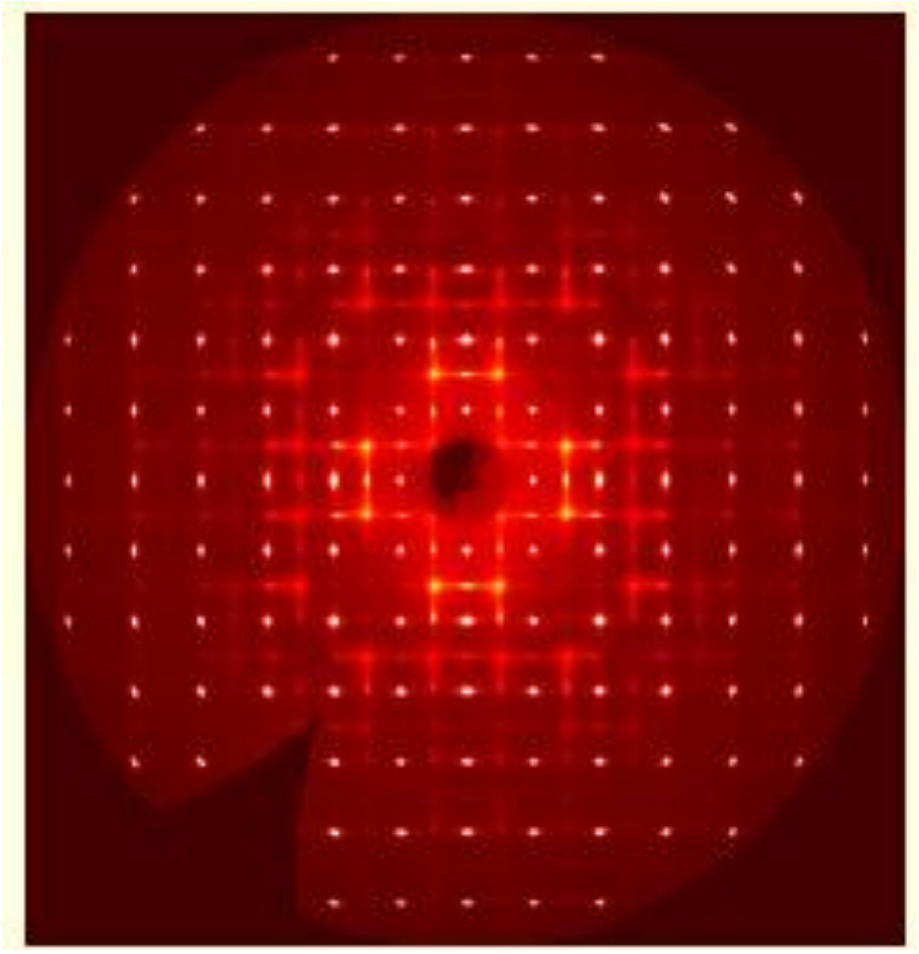
a=37.05 b=8.69 c=20.7 Å α=90 β=95.97 γ=90 deg

Reciprocal space of a crystal: Example 2



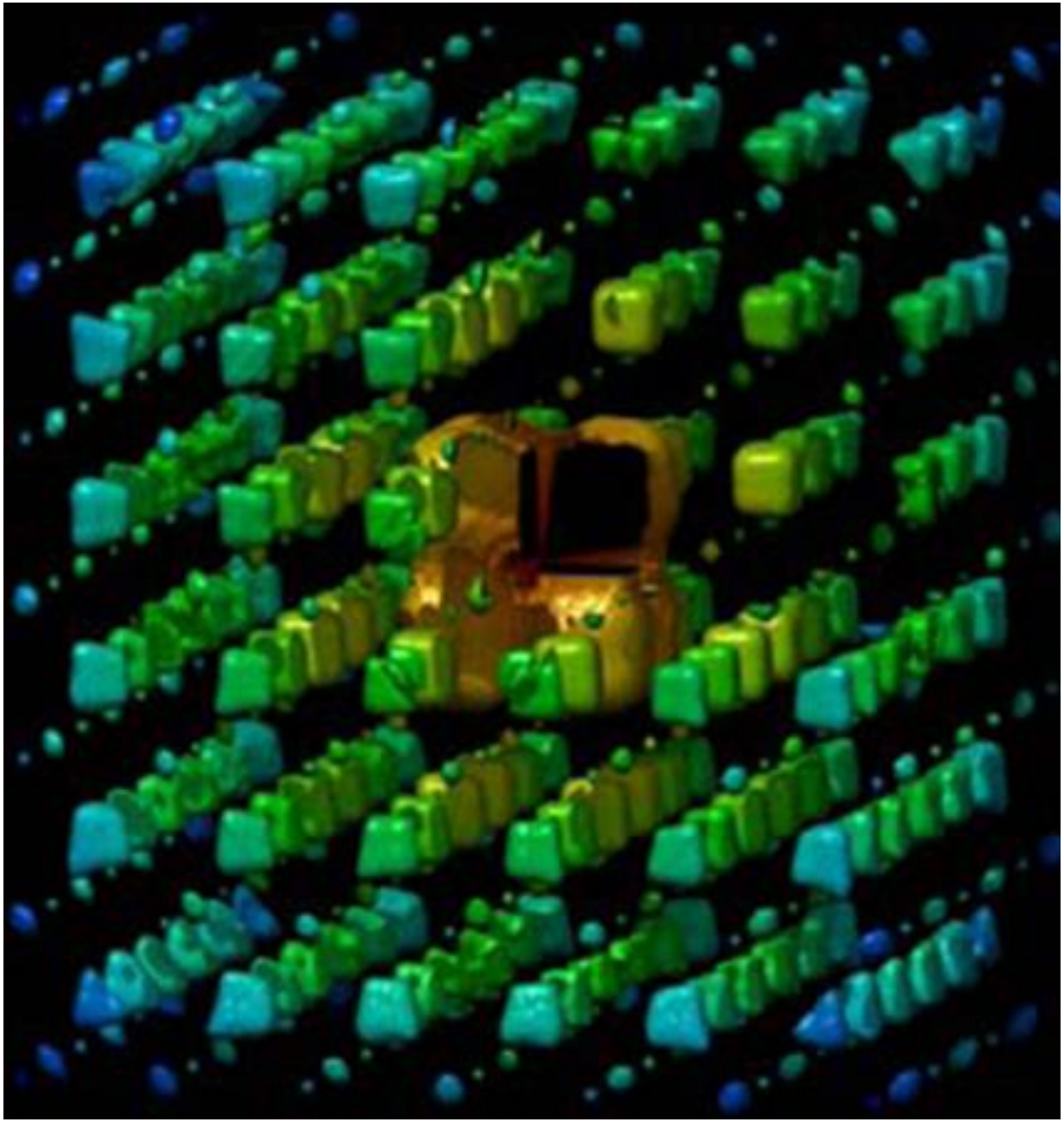
Examples of reciprocal space reconstruction



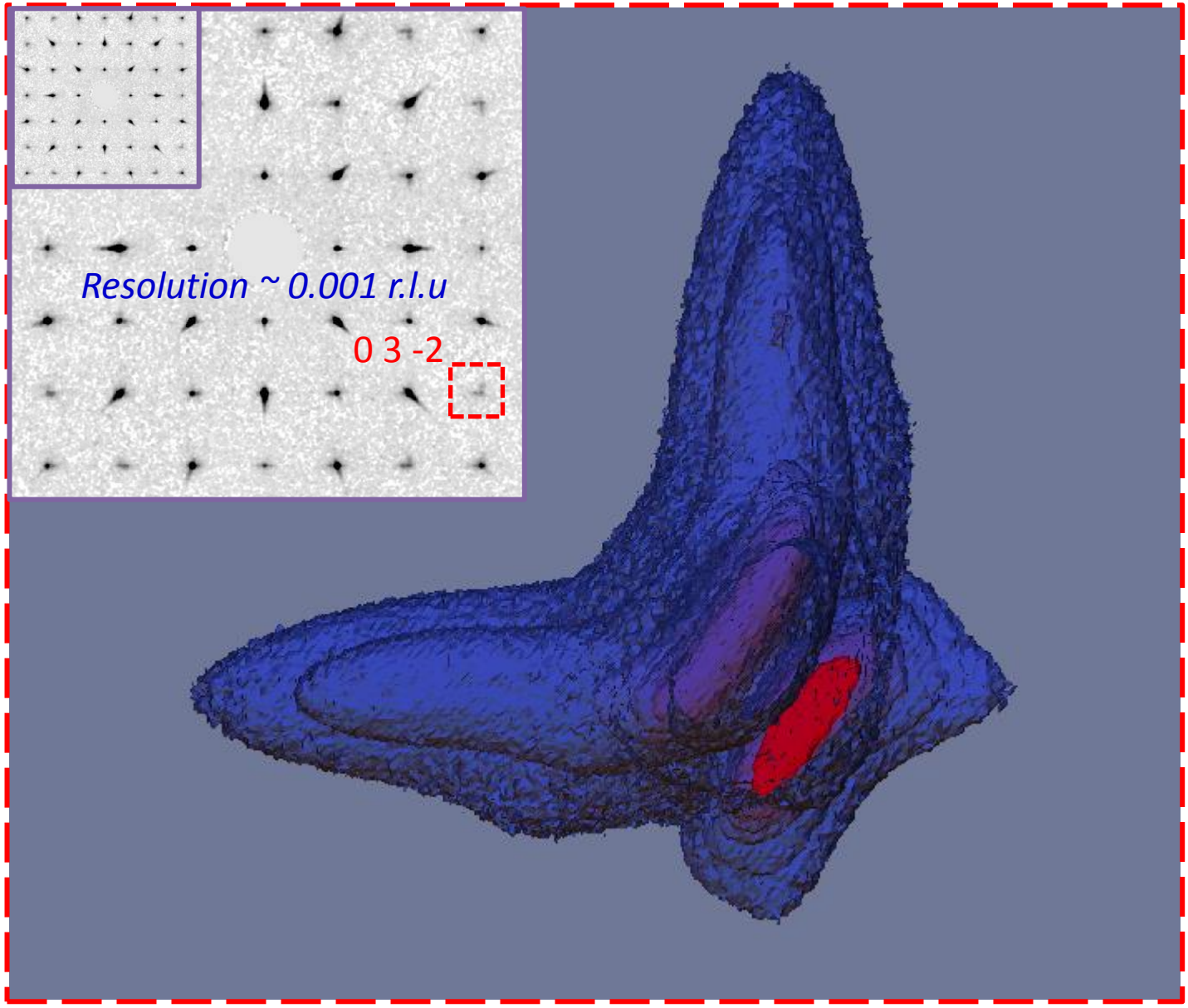


Chernyshev, D., Bosak, A. European Synchrotron Radiation Facility

Examples of DXS (BM01A @ ESRF)



Results: diffuse scattering around 0 3 -2

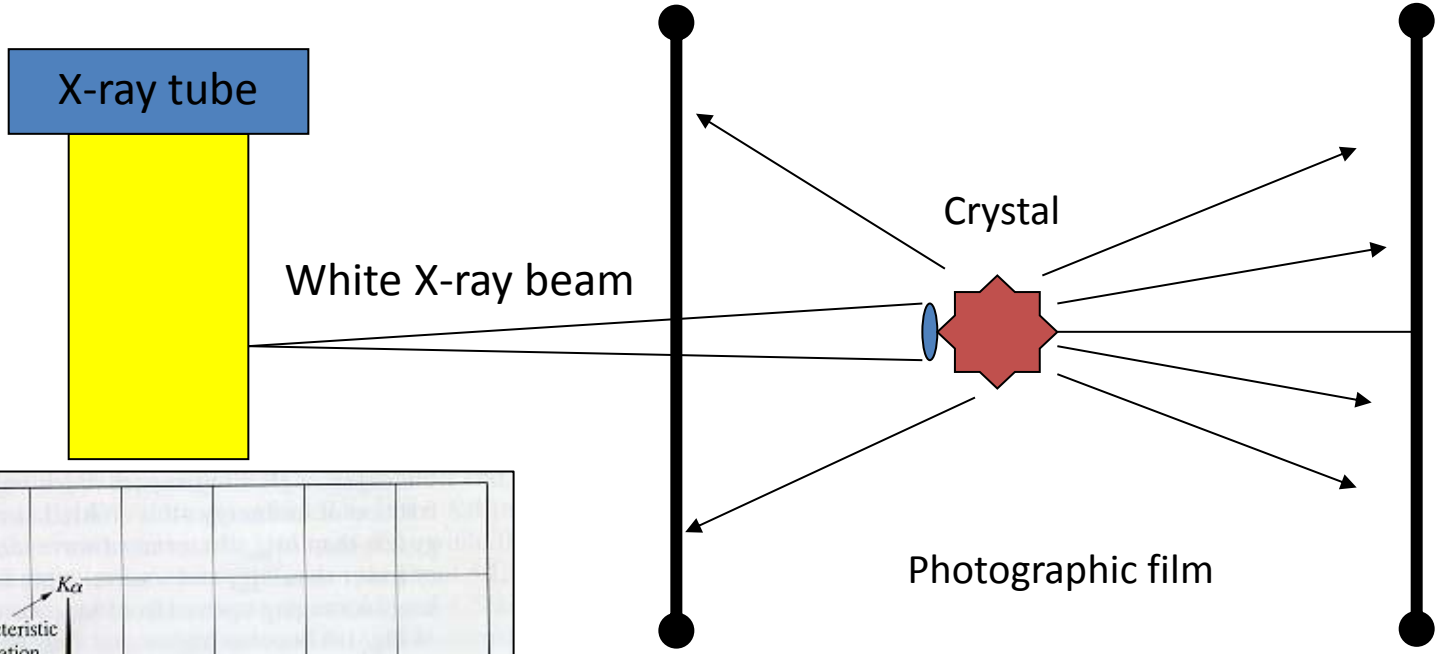


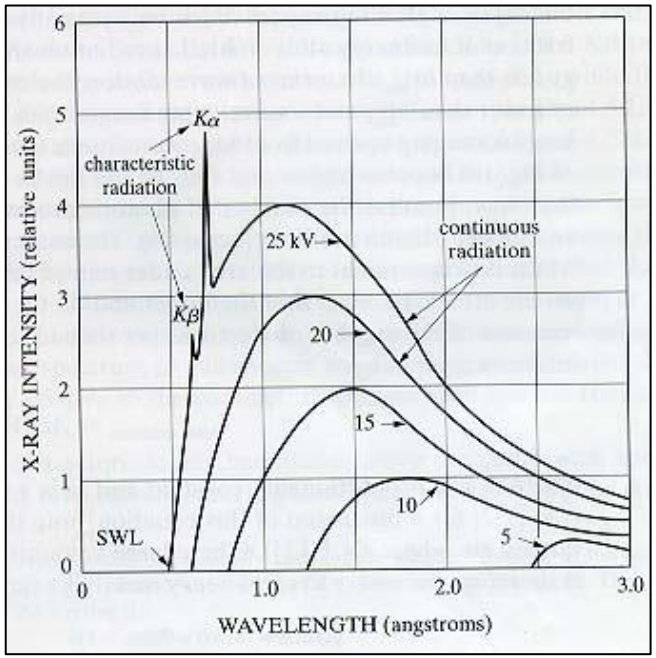
Diffraction in the POLYCHROMATIC X-ray beam

The diffraction in the polychromatic beam was historically the first method of X-ray crystallography. Although it does not allow for the accurate quantitative studies (some recent exceptions are available) it can be preferential for simple task such as testing the quality of a crystal and defining the orientation of the crystallographic axes.

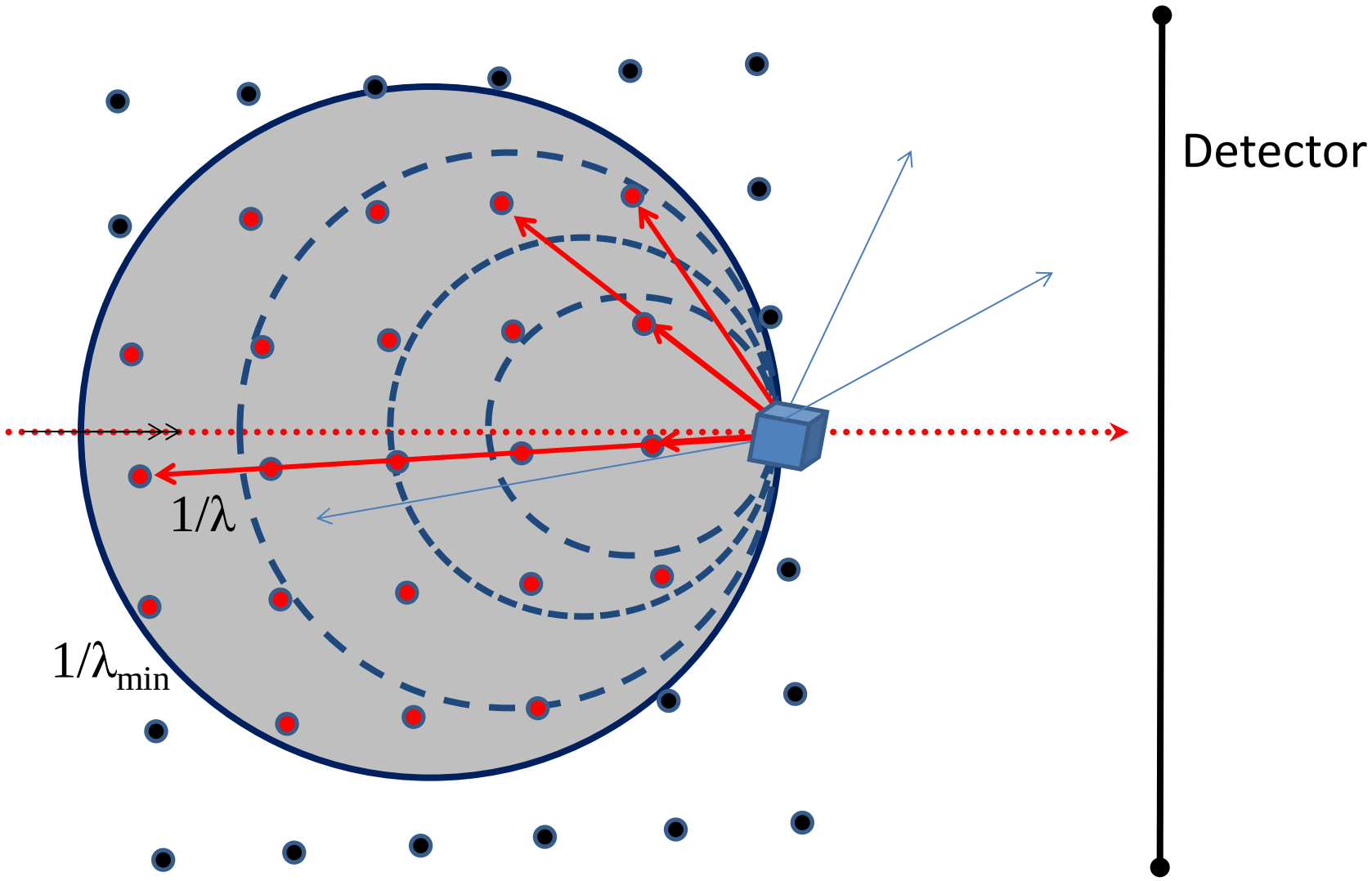
The diffraction in the polychromatic beam is usually referred to as Laue method

The schematic view of the experiment



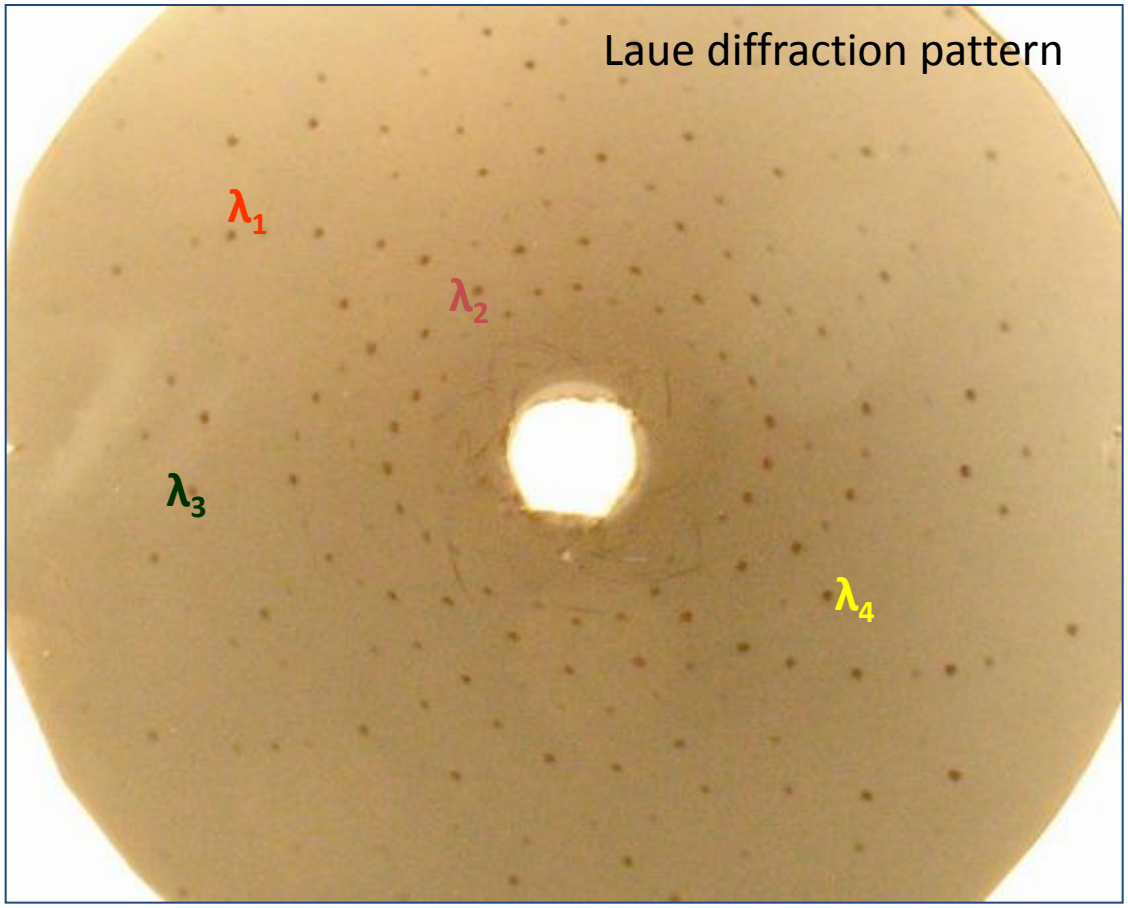


Ewald construction for the Laue method



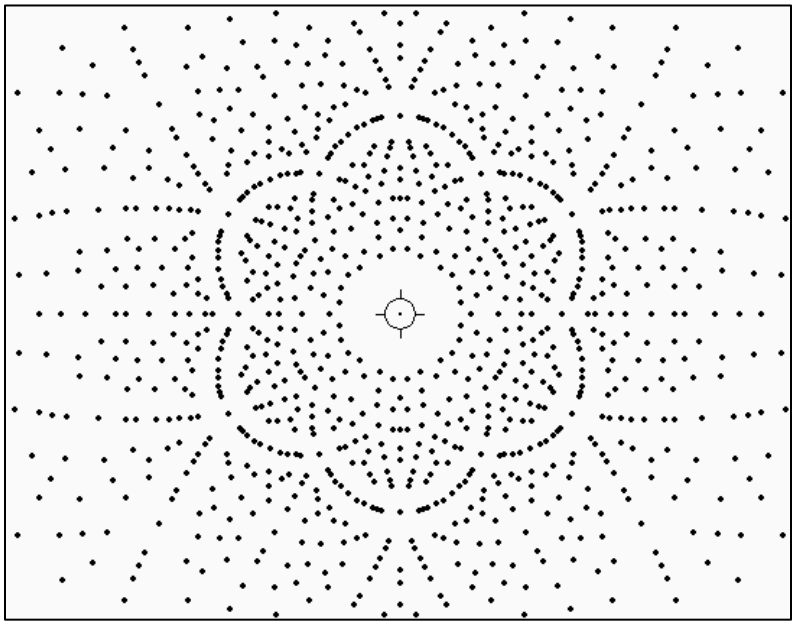
Any reciprocal lattice point within the LARGEST EWALD sphere (of radius $1/\lambda_{min}$ contribute to the Laue pattern)

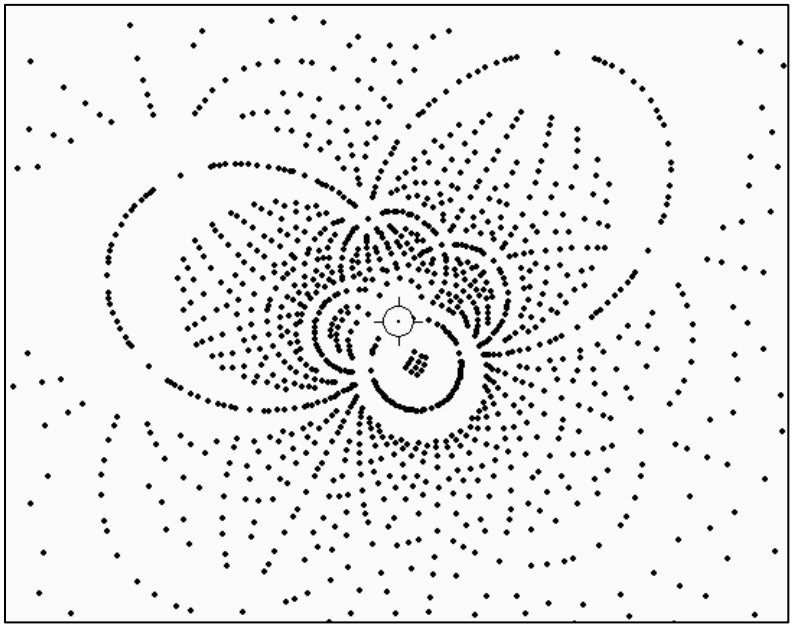
Laue diffraction pattern

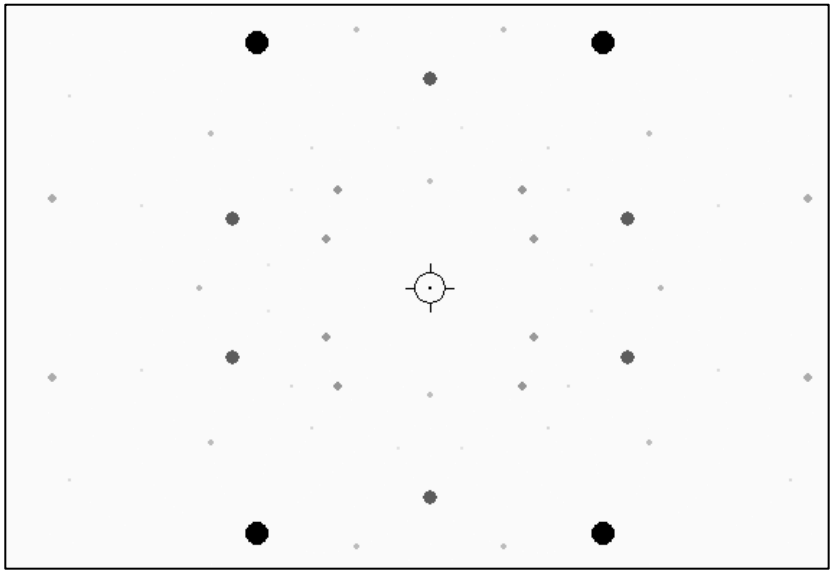


Each Bragg reflection is diffracted at its own wavelength. Usually 2D detectors do not give the information about the wave length therefore each spot reconstructs the direction of reciprocal space only

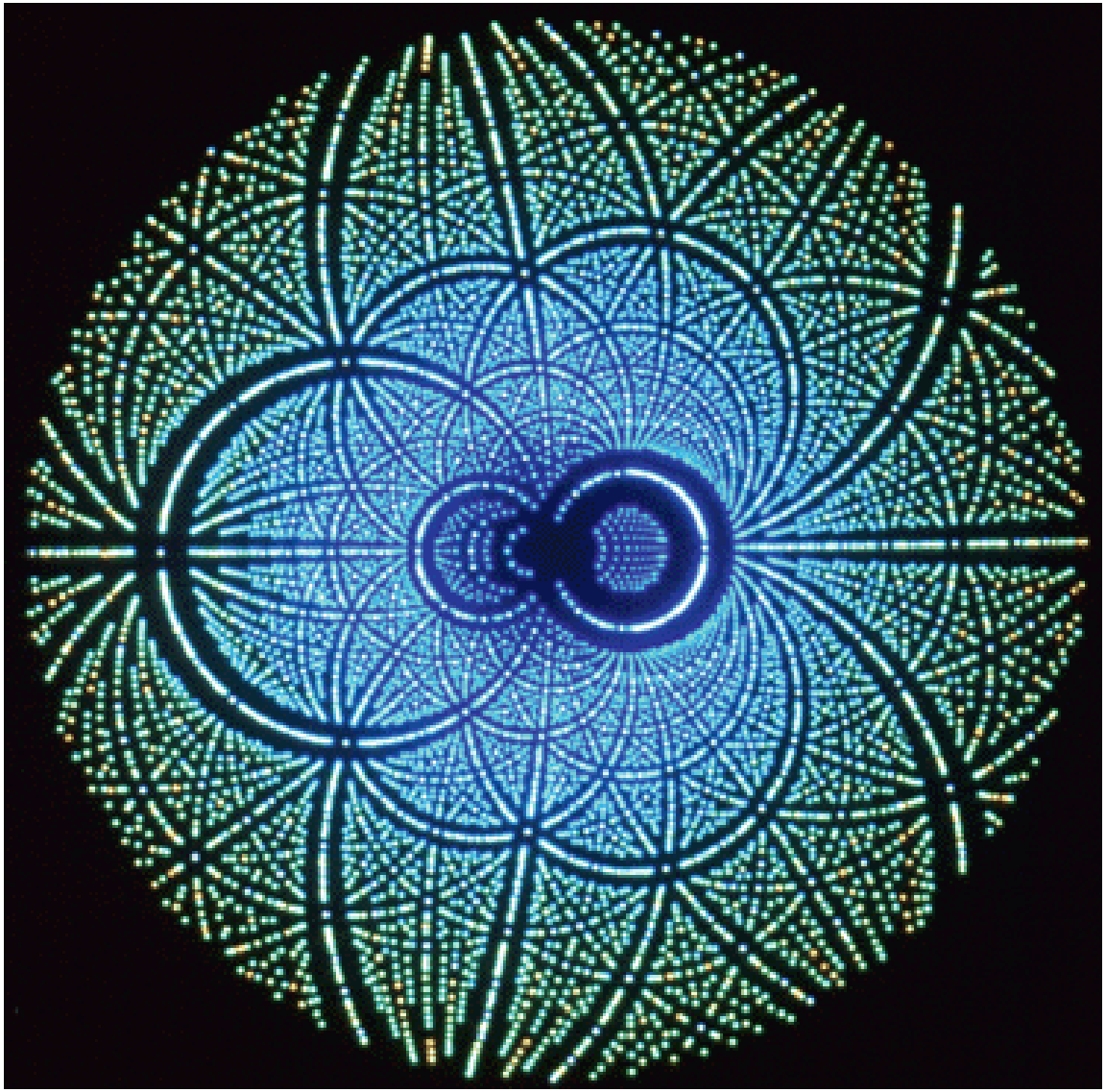
Different Laue diffraction patterns







Laue diffraction from protein crystals



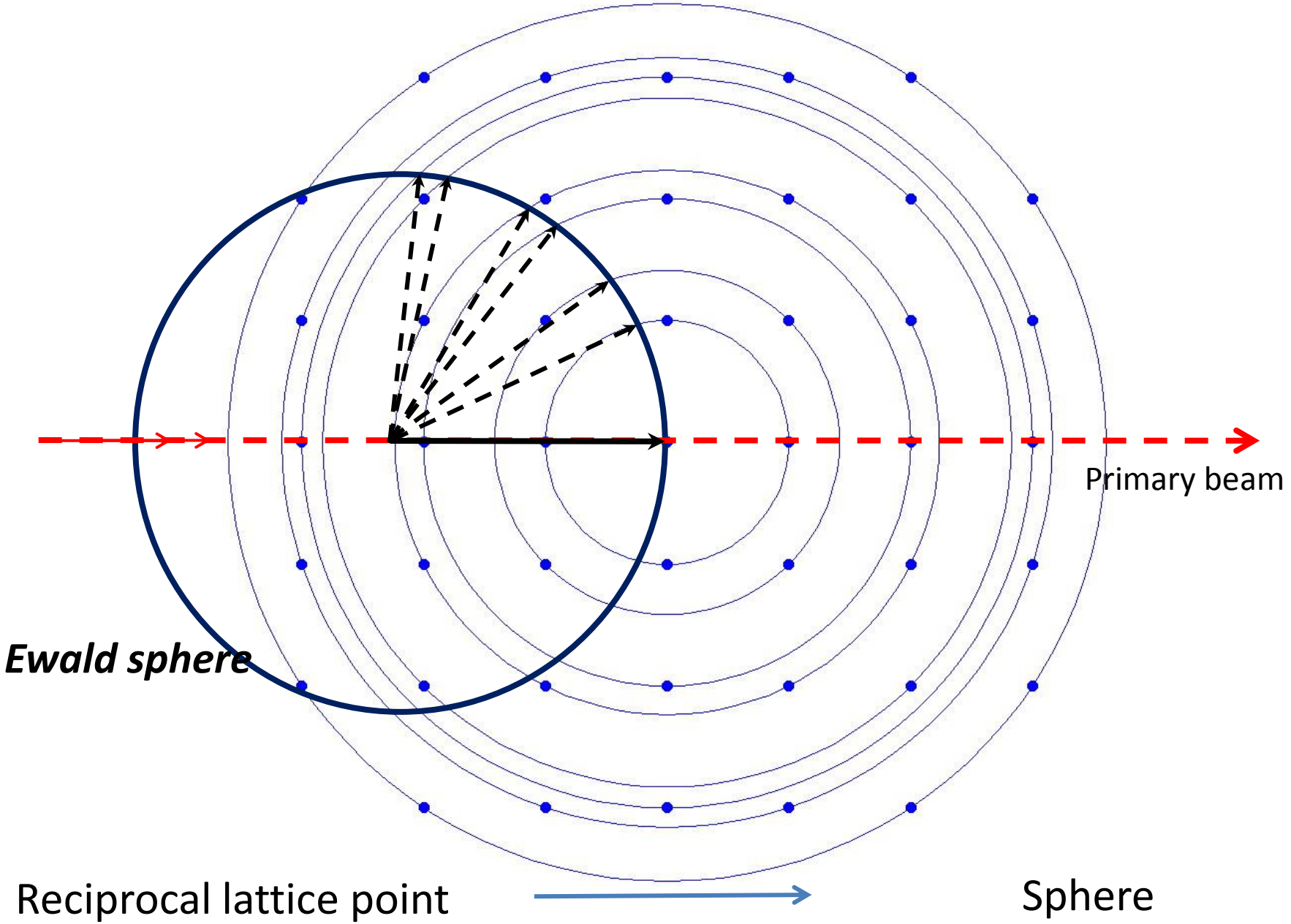
John Helliwell, University of Manchester, UK

Diffraction from the powder

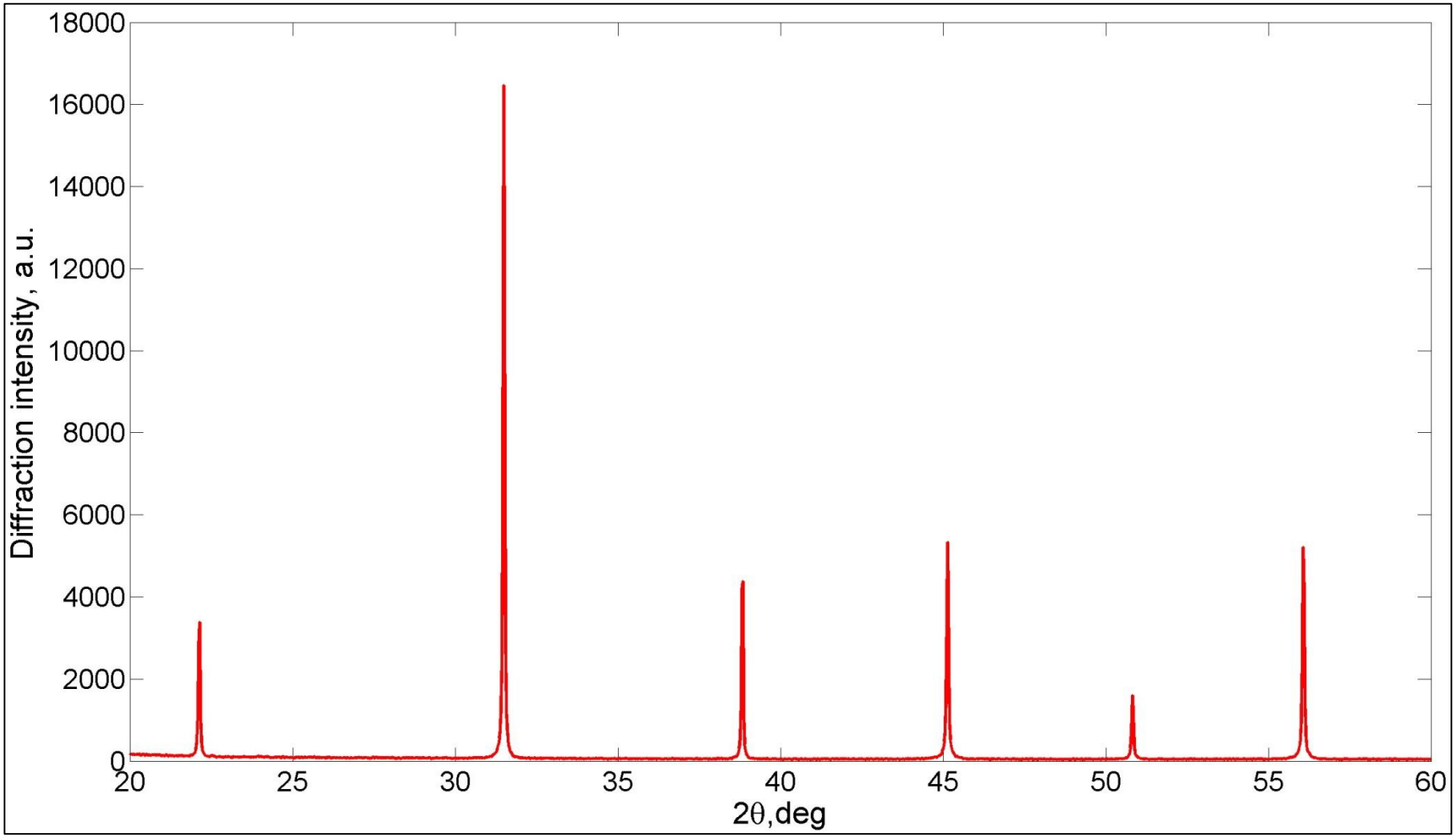
A powder sample is composed of small, single crystalline, randomly oriented grains. Each grain has the same structure, i.e. the same lattice, space group and fractional positions of atoms in the unit cell. As a result each point of the reciprocal lattice is represented by a sphere. Reciprocal space of a powder is the set of concentric spheres

Powder diffraction is an important technique for the structure determination. The solution of a structure from powder diffraction is known as Rietveld refinement

Ewald construction for the powder diffraction



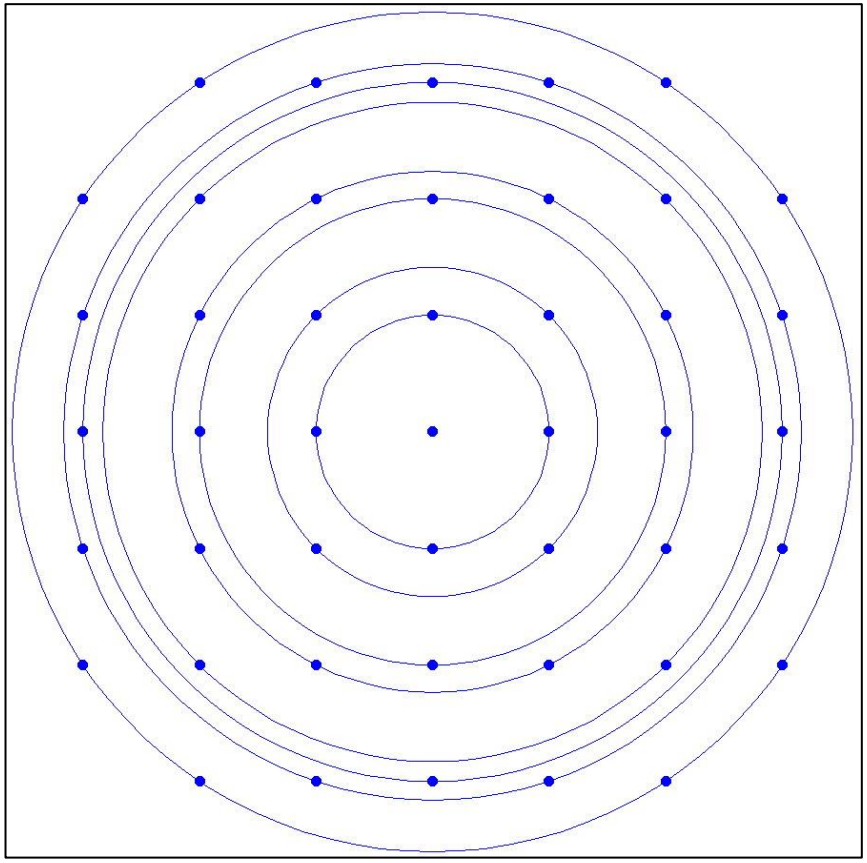
Typical powder diffraction pattern



Powder diffraction is one dimensional data representing the spherically averaged reciprocal lattice of a crystal. The position of each peak corresponds to the LENGTH of a reciprocal lattice vector.

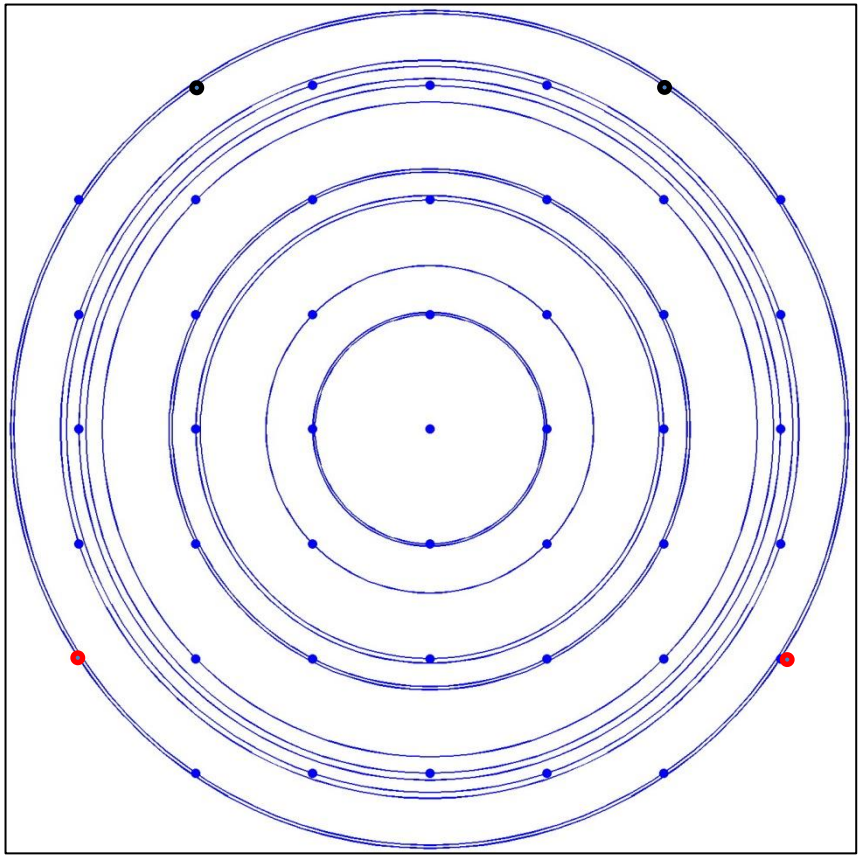
Splitting of the peak positions: example 1

a*=1 b*=1 α=90 deg



Cubic crystal system

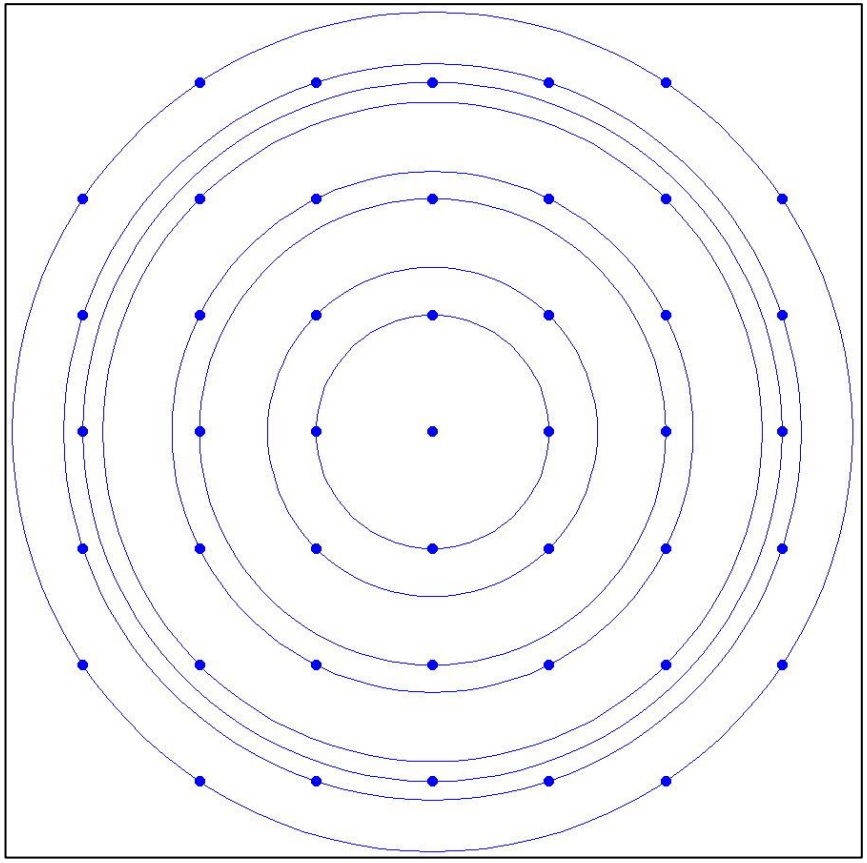
a*=1.02 b*=1 α=90 deg



Tetragonal crystal system

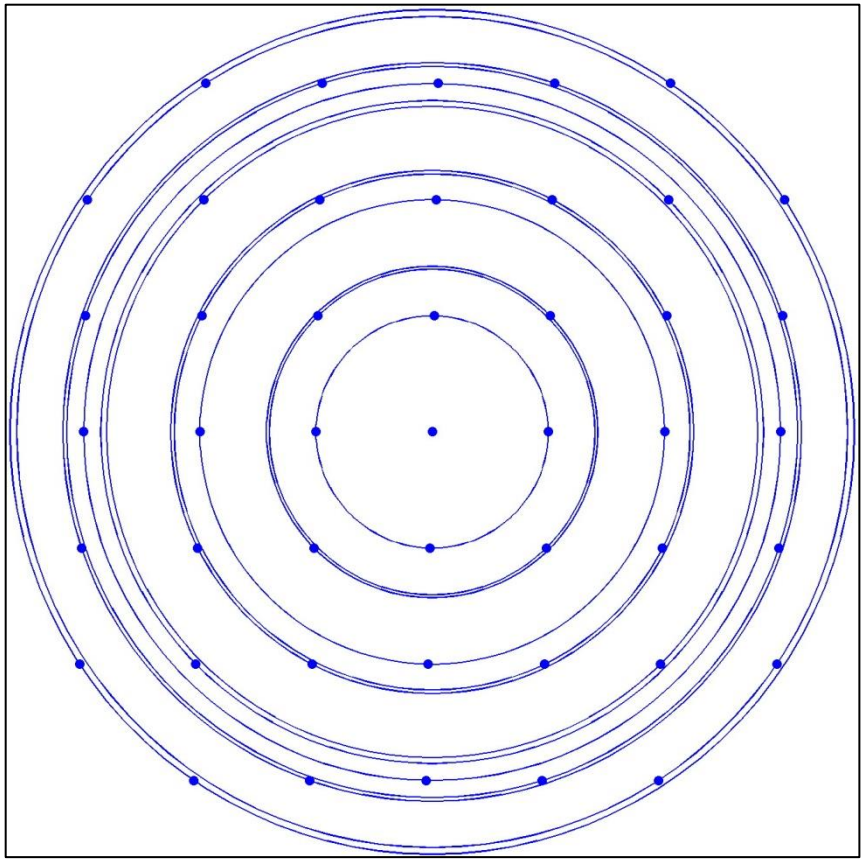
Splitting of the peak positions: example 2

a*=1 b*=1 α=90 deg



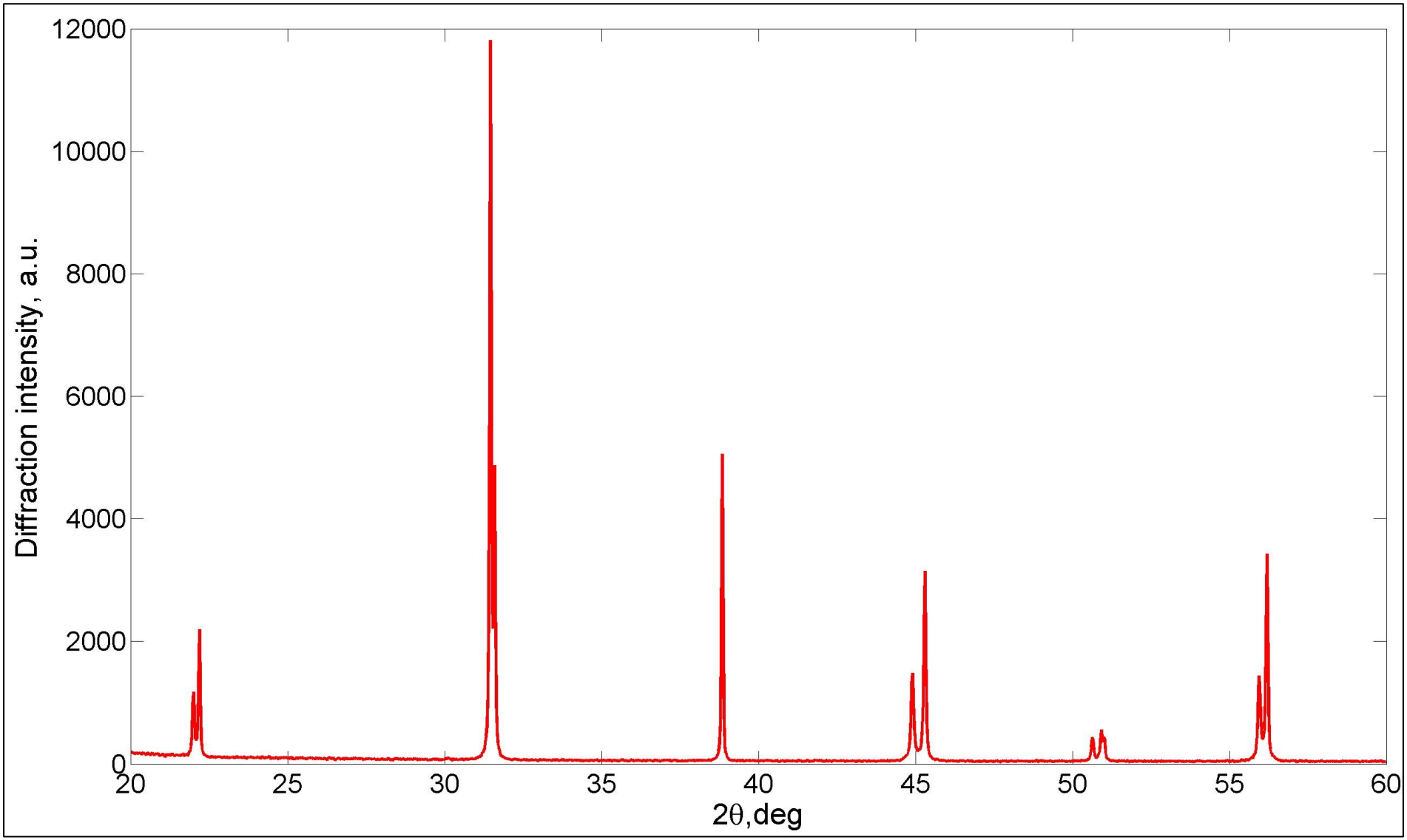
Cubic crystal system

a*=1 b*=1 α=89 deg

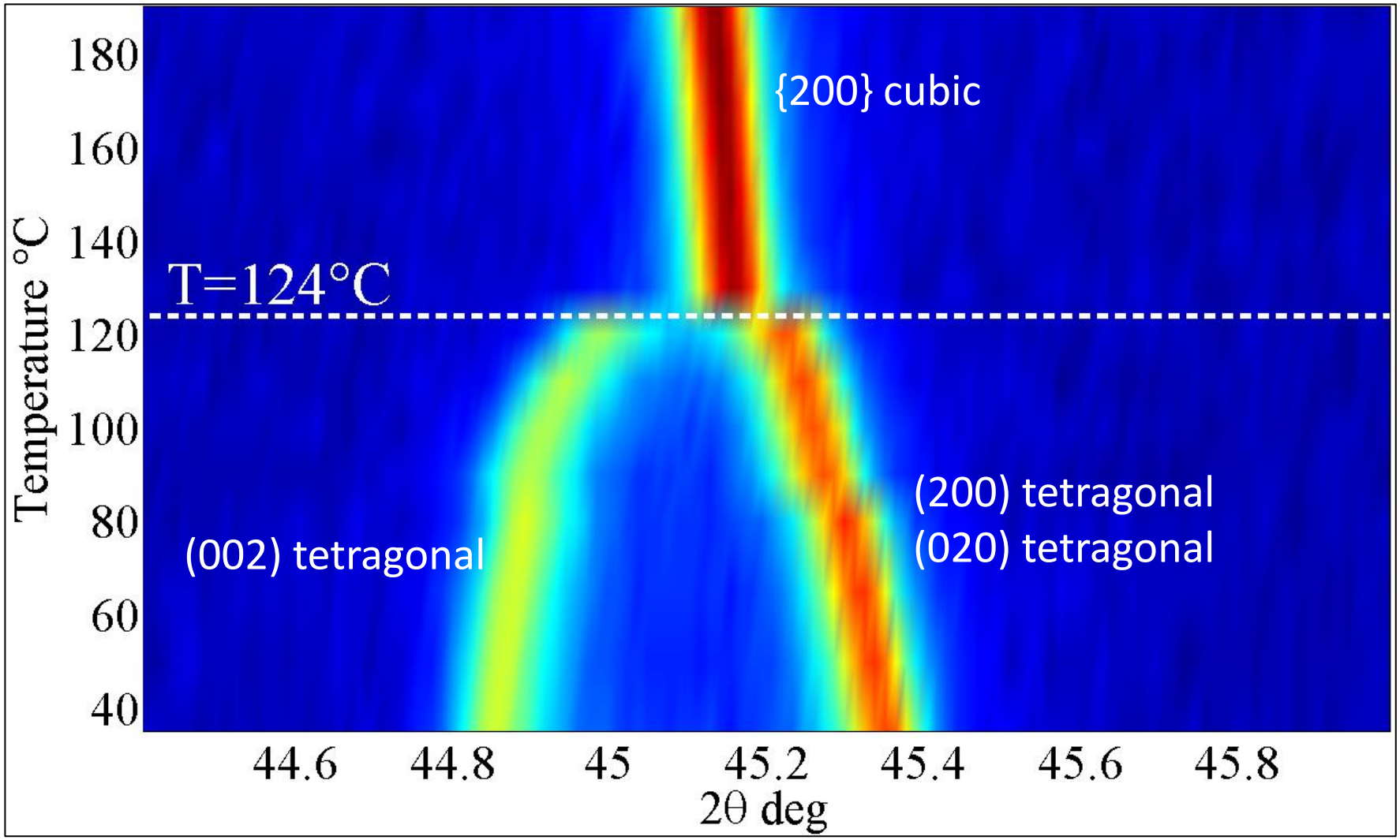


‘Rhombohedral’ crystal system

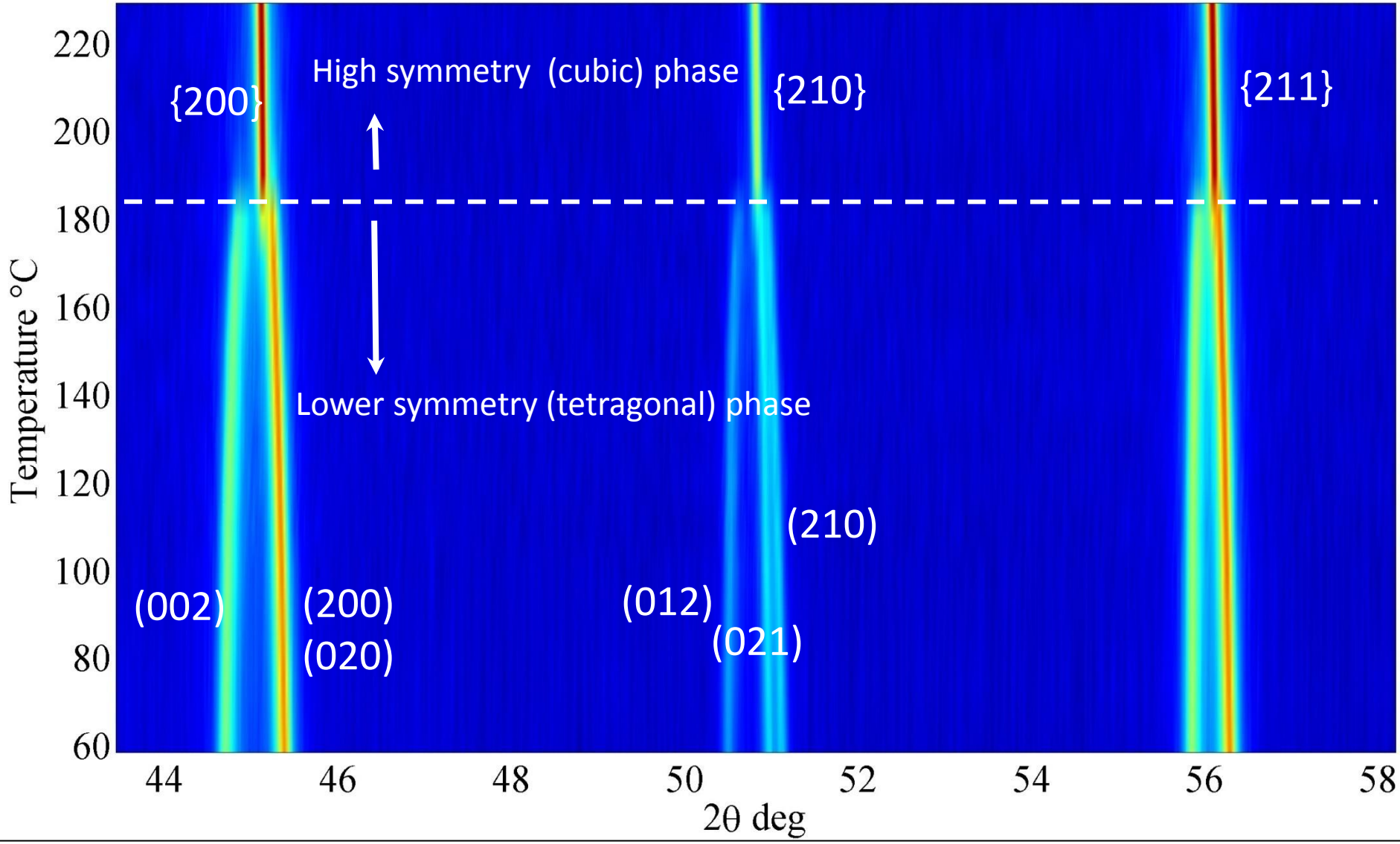
Powder diffraction showing splitting of peaks



Cubic to tetragonal (paraelectric to ferroelectric) phase transition in $BaTiO_3$.
The temperature of the phase transition is known as Curie temperature



Change of the symmetry as a phase transition



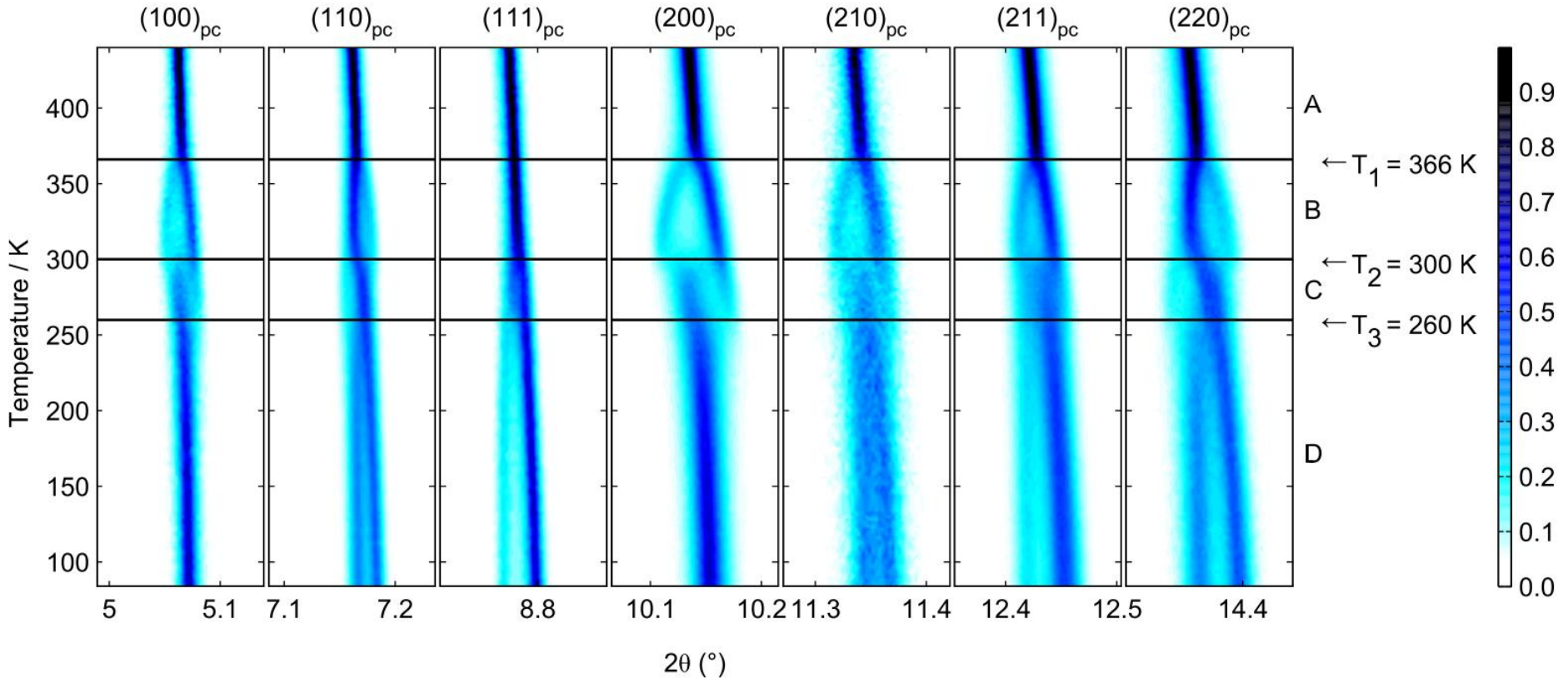
Example 2: Following phase transitions

Revised structural phase diagram of $(Ba_{0.7}Ca_{0.3}TiO_3)$-$(BaZr_{0.2}Ti_{0.8}O_3)$

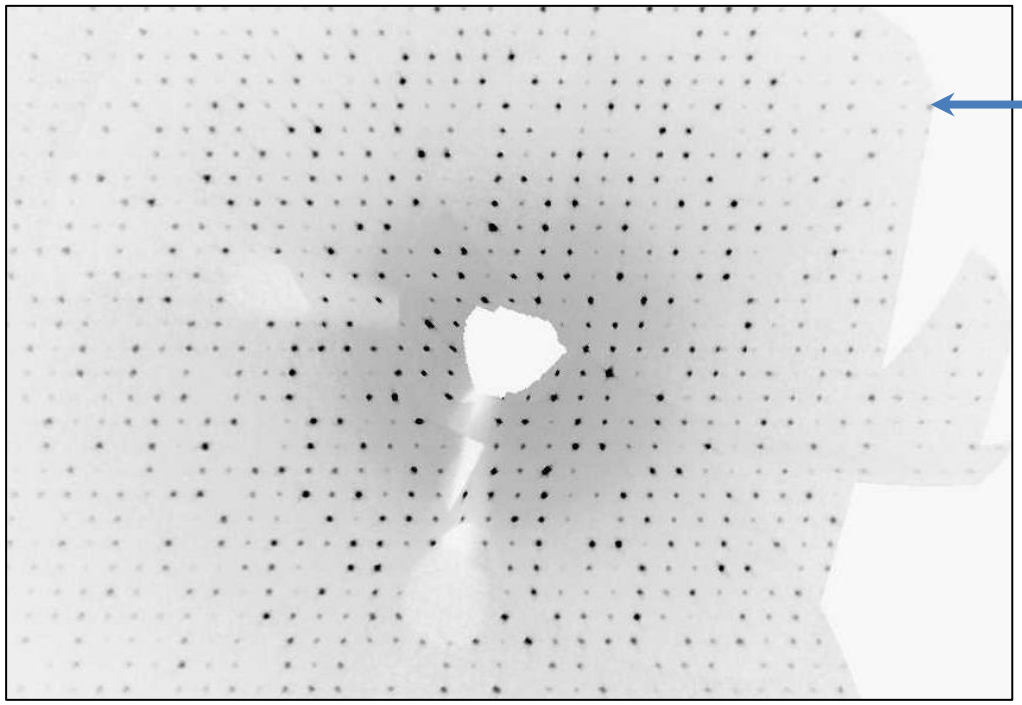
Dean S. Keeble,[1] Feres Benabdallah,[2] Pam A. Thomas,[1] Mario Maglione,[2] and Jens Kreisel[1,3]

[1]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*
[2]*ICMCB, Université de Bordeaux, CNRS, 33600 Pessac, France*
[3]*Department of Science and Analysis of Materials, CRP Gabriel Lippmann, Belvaux, Luxembourg*

(Received 11 December 2012; accepted 7 February 2013; published online 7 March 2013)



Single crystal structure refinement



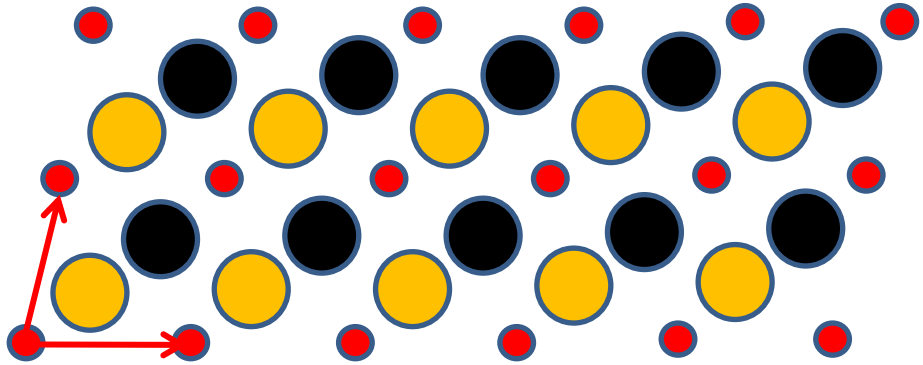
NB! Remember that reflection intensities are $I(hkl) = |F(hkl)|^2$

$$F(hkl) = \sum_{\mu=1}^{n} f_\mu(\mathbf{H}) \exp\left(2\pi i(hx_\mu + ky_\mu + lz_\mu)\right)$$

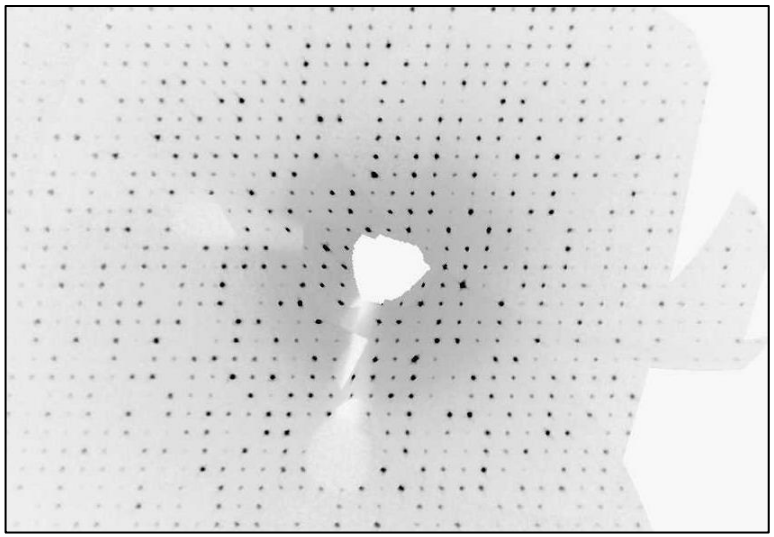
CRYSTAL STRUCTURE

Additional factors to be taken into account:

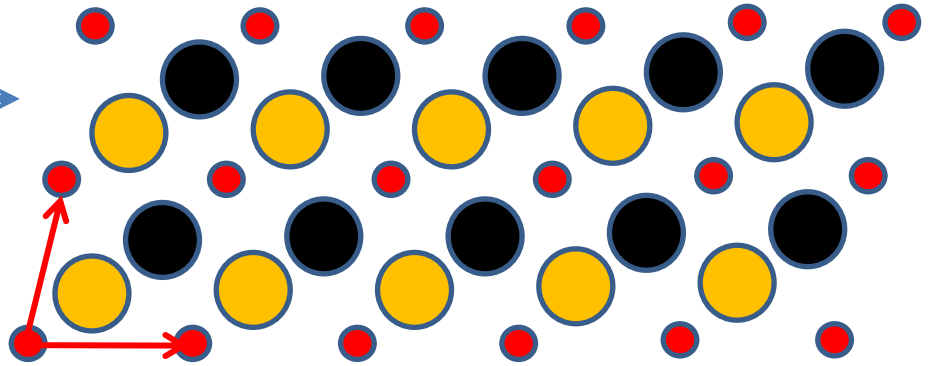
- Thermal motion (Debye-Waller factors)
- Anomalous scattering
- Structural disorder (Static Debye-Waller factors)
- Anharmonic motion



Reliability (R) factor



CRYSTAL STRUCTURE



OBSERVED STRUCTURE FACTOR

Weight of each reflection

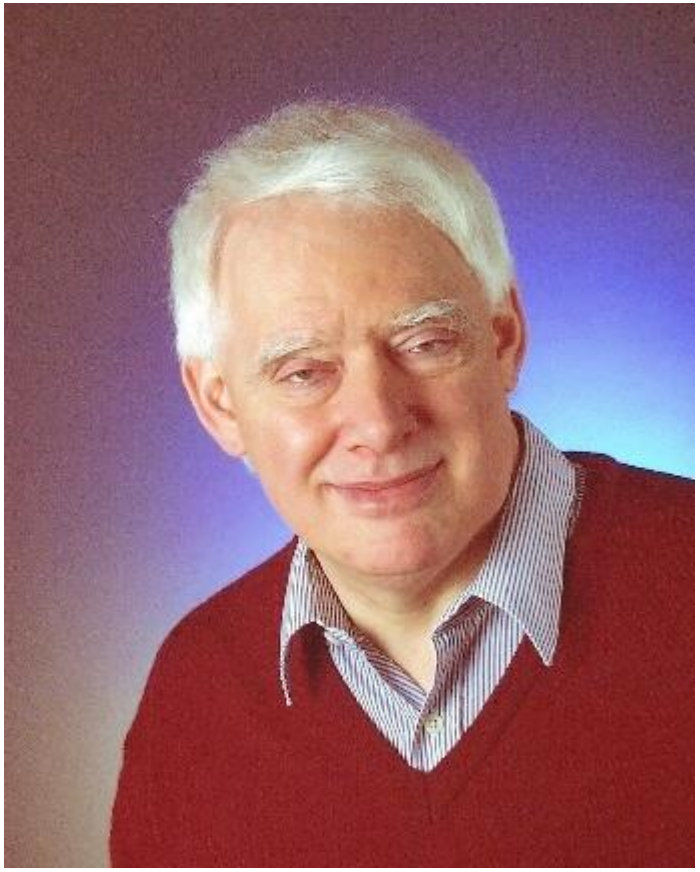
$$R_w = \frac{\sum_{hkl} w_{hkl} \cdot [|F_{OBS}|^2 - |F_{SIM}|^2]^2}{\sum_{hkl} w_{hkl} \cdot [|F_{OBS}|^2]^2}$$

SIMULATED STRUCTURE FACTOR

Modern software for single crystal X-ray diffraction

SHELX at UCSF

MSG | Index | Contents | SHELX Homepage



Developed by George Sheldrick: University of Goettingen

feature articles

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A short history of *SHELX*

George M. Sheldrick

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An account is given of the development of the *SHELX* system of computer programs from *SHELX*-76 to the present day. In addition to identifying useful innovations that have come into general use through their implementation in *SHELX*, a critical analysis is presented of the less-successful features, missed opportunities and desirable improvements for future releases of the software. An attempt is made to understand how a program originally designed for photographic intensity data, punched cards and computers over 10000 times slower than an average modern personal computer has managed to survive for so long. *SHELXL* is the most widely used program for small-molecule refinement and *SHELXS* and *SHELXD* are often employed for structure solution despite the availability of objectively superior programs. *SHELXL* also finds a niche for the refinement of macromolecules against high-resolution or twinned data; *SHELXPRO* acts as an interface for macromolecular applications. *SHELXC*, *SHELXD* and *SHELXE* are proving useful for the experimental phasing of macromolecules, especially because they are fast and robust and so are often employed in pipelines for *high-throughput* phasing. This paper could serve as a general literature citation when one or more of the open-source *SHELX* programs (and the Bruker AXS version *SHELXTL*) are employed in the course of a crystal-structure determination.

38320 citations

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Modern software for single crystal X-ray diffraction

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Department of Structure Analysis
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Czech Republic

CRYSTALLOGRAPHIC COMPUTING SYSTEM FOR STANDARD AND MODULATED STRUCTURES

Vaclav Petricek, Michal Dusek & Lukas Palatinus

Jana2006 is a crystallographic program focused to solution, refinement and interpretation of difficult, especially modulated structures. It calculates structures having up to three modulation vectors from powder as well as single crystal data measured with X-ray or neutron diffraction. The input diffraction data can be unlimitedly combined, the combination of powder neutron data with single crystal X-ray data being a typical example. The structure solution can be done using the built-in charge flipping algorithm or by calling an external direct methods program. Jana can handle multiphase structures (for both powder and single crystal data), merohedric twins as well as twins with partial overlap of diffraction spots, commensurate and composite structures. It contains powerful transformation tools for symmetry (group-subgroup relations), cell parameters and commensurate-supercell relations. Wide scale of constrains and restrains is available including a powerful rigid body approach and possibility to define a local symmetry affecting only part of the structure. The latest development of Jana concerns magnetic structures.

News

May 01, 2014 **New reference for Jana2006**: Petricek, V., Dusek, M. & Palatinus, L. (2014). Z. Kristallogr. 229(5), 345-352. DOI 10.1515/zkri-2014-1737

March 12, 2014 Zeitschrift fuer Kristallographie offers free online access to the journal's present and previous issues until June 30,2014.

February 14, 2014 **Postal stamp with crenel function** has been issued in Slovakia at the occassion of the IYCr2014. The stamp and e-shop

August 14-16, 2014 **Magnetic Workshop in Hamilton, Canada.** Satellite workshop of the IUCr congress on the Role of Magnetic Symmetry in the Description & Determination of Magnetic Structures.

March 15, 2013 **Maintenance release of Jana2006 for Windows** can be obtained in Download area. It cumulates many improvements, supports better magnetic structures and electron diffraction.

November 25 - December 3, 2012 **Workshop in Uberlandia, Brazil.** Workshop on Jana2006 at the International School on Fundamental Crystallography.

June 11-14, 2012 **Workshop in Klatovy, Czech Republic.** Workshop on Jana2006 at the Colloquium of the Czech Crystallographic Association.

June 7-9, 2012 **Workshop in Izmir, Turkey.** Workshop on Jana2006 at the 3rd Turkish Crystallographic Meeting.

May 7-12, 2012 **3rd Shanghai Workshop of X-Ray Crystallography, China.**

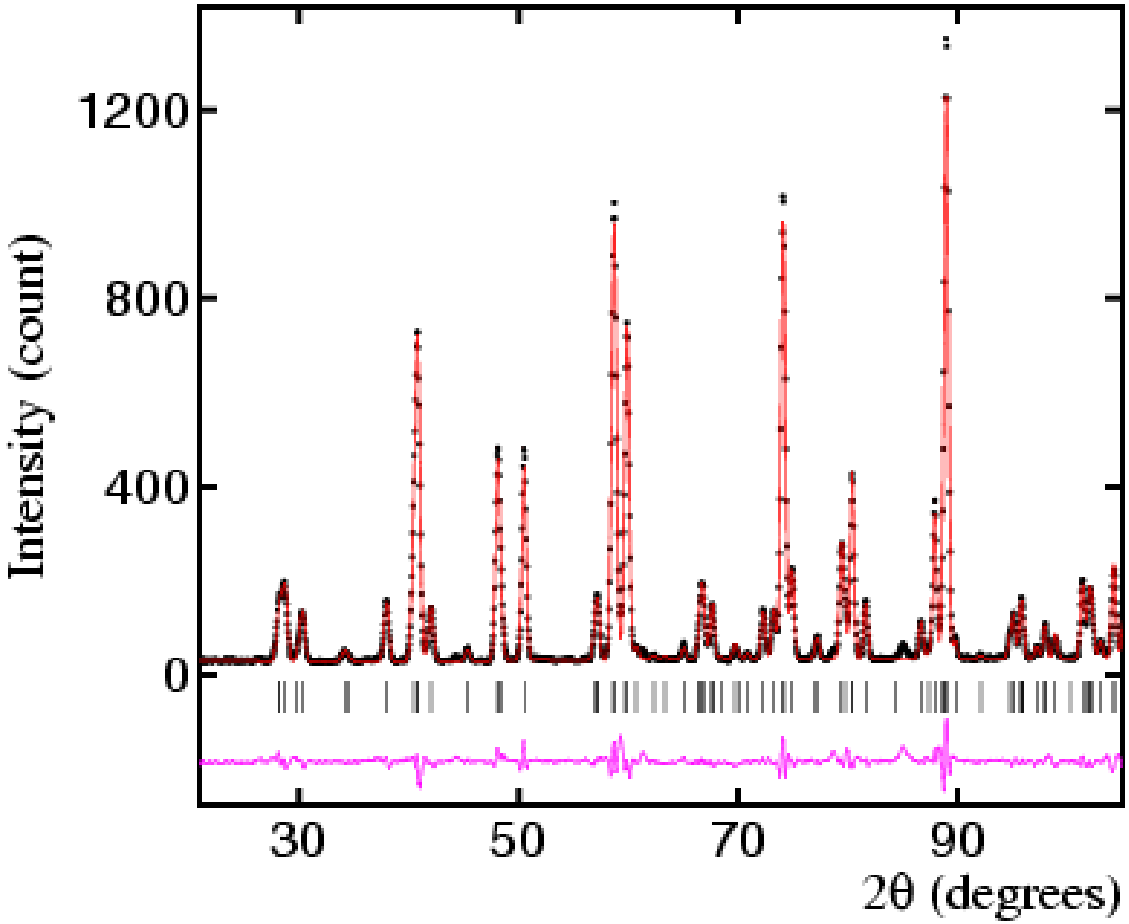
February 23 - March 08, 2012 **Workshops in Kosice, Slovakia.** Four half-day workshops about solution of 3d structures in Jana2006, in Czech language. Dates: 23.2., 1.3., 6.3., 8.3. Contact: dusek@fzu.cz.

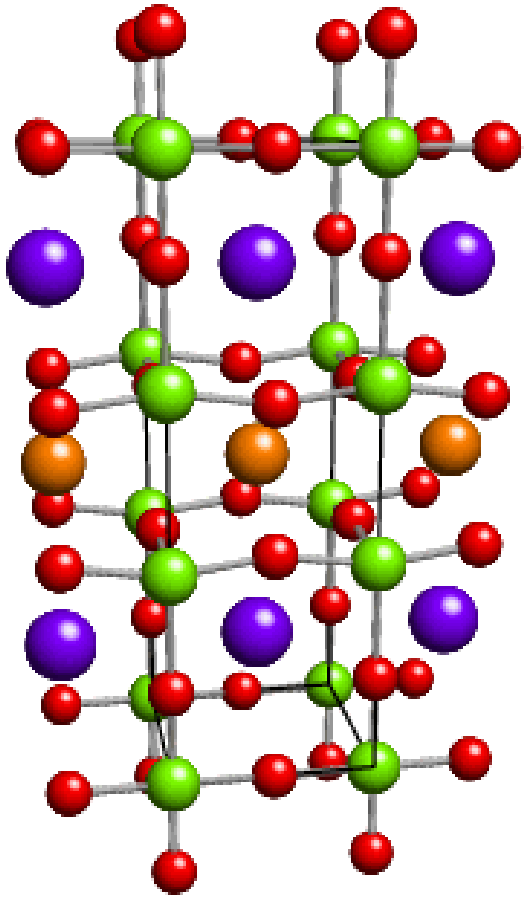
July 01, 2011 **Maintenance release of Jana2006 for Windows** can be obtained in Download area. It cumulates small improvements before larger changes planned for the summer 2011.

May 03, 2011 **Maintenance release of Jana2006 for Windows** can be obtained in

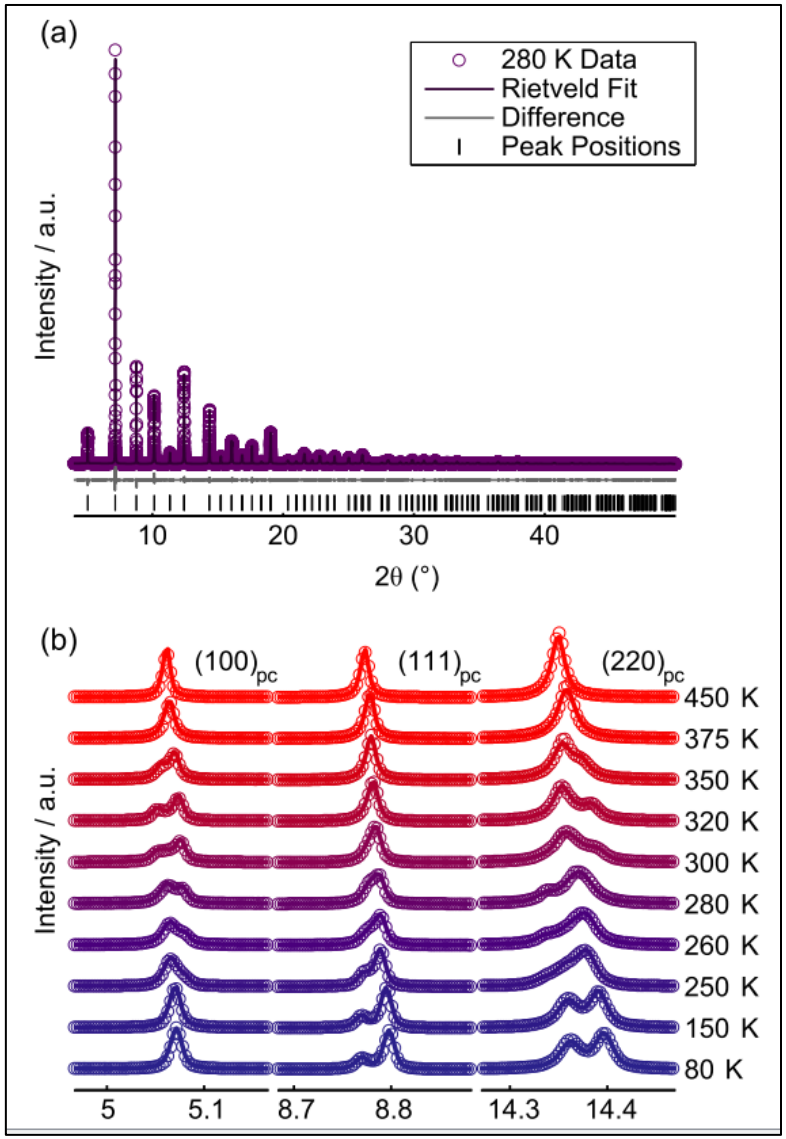
Powder diffraction (Rietveld) refinement

Determination and refinement of crystal structures using powder diffraction profiles is known as Rietveld refinement! It is named after Hugo Rietveld who developed the mathematical algorithms and prescribed the procedure of refinement.



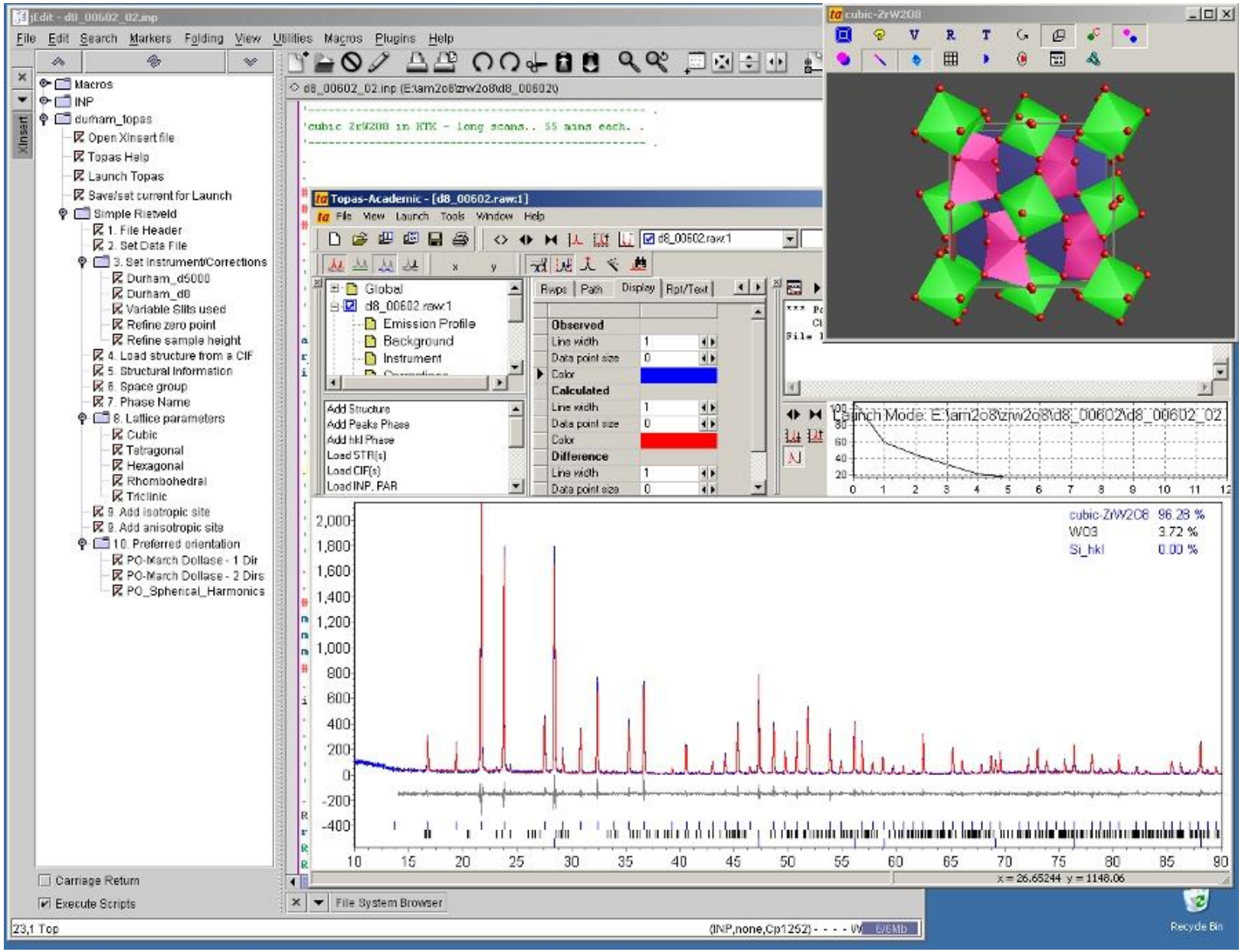


Rietveld refinement includes:



- Locating powder peaks
- Indexing of reflections (assigning hkl to each individual peak) (mind the peak overlap)
- Determination of lattice constants
- Deducing the shape of the peaks, separating overlapping profiles
- Refinement of peak shape parameters
- Refinement of atomic positions
- Refinement of thermal displacement parameters

Modern software for Rietveld Refinement: TOPAS



Modern software for Rietveld Refinement: FULLPROF