

Chapter 8: Structural Analysis

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<http://www.ifk.rwth-aachen.de>

The „crystal palace“ in Aachen-Burtscheid



<http://www.frm2.tum.de>

Outstation of the IfK at FRM II in Garching

Objectives:

- Discuss Aspects of Structural Analysis specific to **NEUTRONS**
- Advantages / disadvantages compared to X-ray diffraction
- Special properties / experiments that cannot be done with X-rays
- Show that X-ray- and Neutron-diffraction are often complementary
- Typical / advanced experiments and their information content
- Some preparations for the experimental week @FRM-II
(particularly: Single crystals: HEiDi, Powder: SPODI)

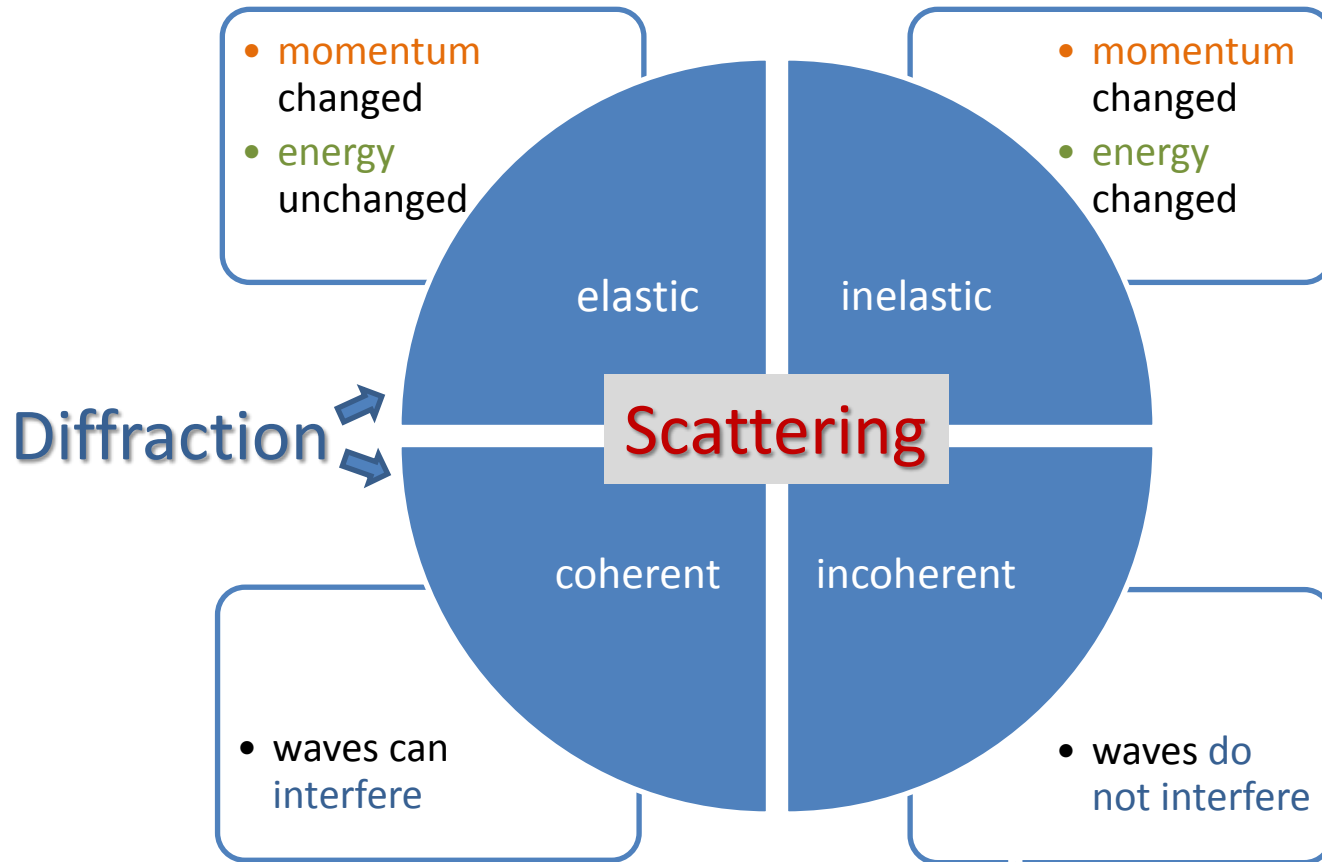
Not covered in this lecture:

- Re-iteration of the fundamentals of neutron diffraction
(see other chapters)
- Equipment, experimental details, machinery etc. in detail
(see experimental week).

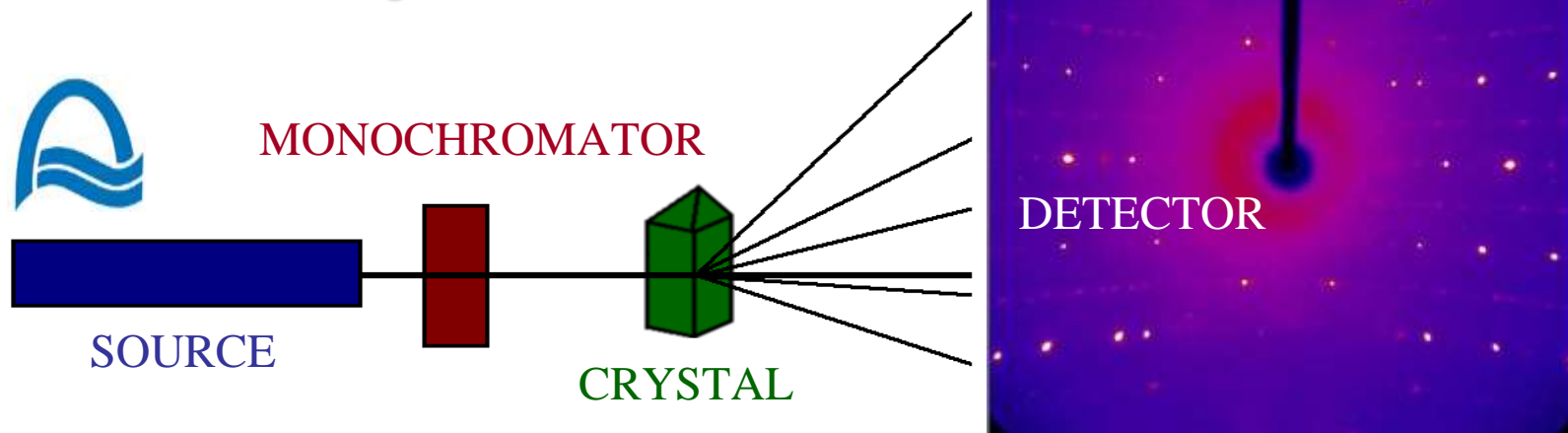
Outline:

- **Diffraction contrast** variation
Site occupation and magnetic phase diagram of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$
- **The hydrogen problem** in structural analysis
H-ordering: Ferroelectric phase transition in RbH_2PO_4 (RDP)
- **Accurate atomic coordinates** and **displacement parameters** from
Neutron diffraction experiments on Co_2SiO_4
- **Magnetic structures** from neutron diffraction: Co_2SiO_4
- **Electron density determination** from combined X-ray and neutron
diffraction: Co_2SiO_4
- **Magnetization density** distribution within the unit cell from neutron
diffraction: Co_2SiO_4 .

Terminology reminder: Scattering of particles / waves



Structural analysis reminder:



```

TITL      KNO3
CELL      .71069  6.449  9.189  5.430  90.000  90.000  90.000
ZERR      4        .005  .005  .005  .005  .005  .005
LATT      1
SYMM      -X,-Y,  .50000+Z
SYMM      .50000+X, .50000-Y, .50000-Z
SYMM      .50000-X, .50000+Y, -Z
SFAC      N  O  K
UNIT      4  12  4
    
```



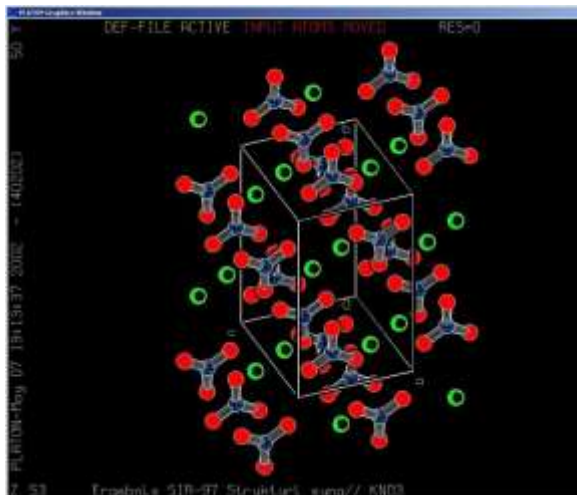
lattice parameters, \uparrow space group, cell content

h	k	l	INT.	SIGMA
-5	-1	3	476.30	12.21
-4	-3	5	418.17	13.60
-4	-3	6	13.75	15.89
-4	-2	3	3.31	7.96
-1	-4	4	1442.42	14.80
...				

integral reflection intensities \uparrow



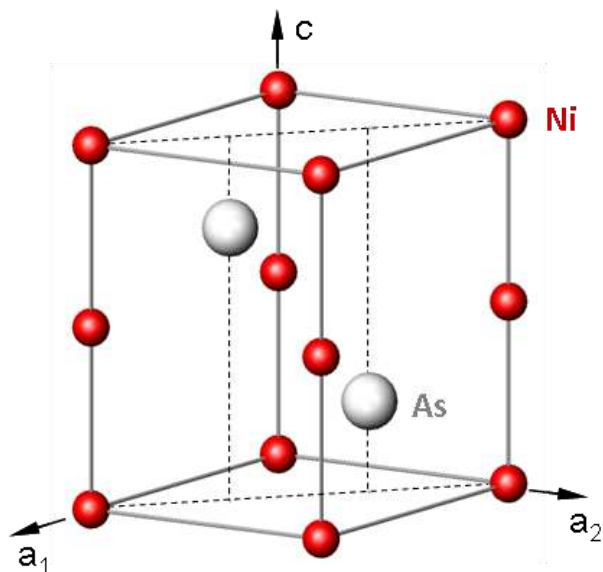
K1	3	.75551	.08365	1.25000	10.50000	.02580
N2	1	.58389	.24479	.75000	10.50000	.02452
O3	2	.58958	.10917	.75000	10.50000	.03636
O4	2	.58483	.31361	.94923	11.00000	.03657



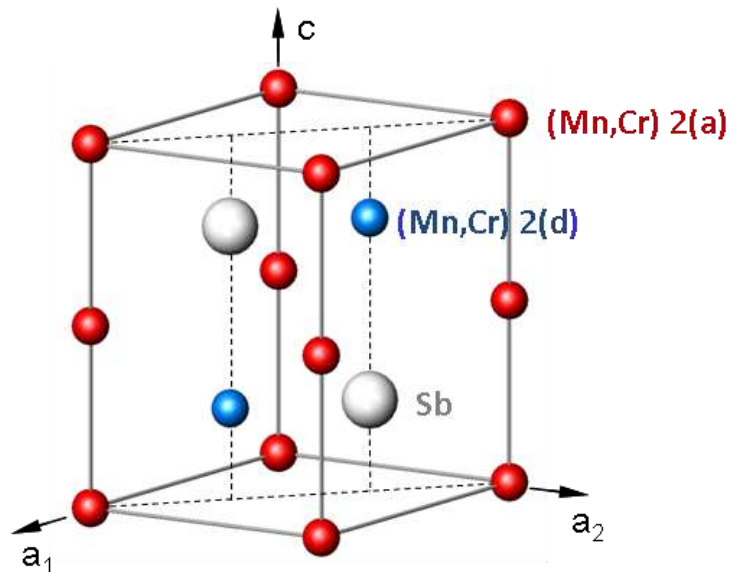
crystal structure of KNO_3

atomic coordinates

Site occupation of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$



NiAs structure

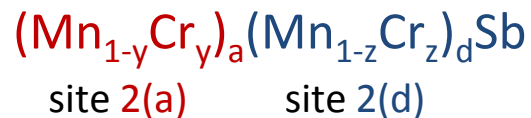


$(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$ structure

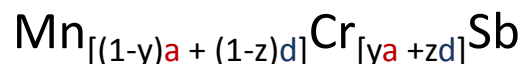
$(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$:

Two different (Mn,Cr) sites: Wykoff positions **2a** and **2d**:

Site-specific formula:



Formula, re-written:



Site occupation of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$

The problem:

Scattering power of Cr and Mn for **X-rays** (no. of electrons) are extremely **similar**:

$$f_{\text{Cr}} = 24 e^- \text{ and } f_{\text{Mn}} = 25 e^- \quad \Rightarrow \text{Very hard to distinguish}$$

Source: Your knowledge of the PSE

The solution:

Nuclear scattering lengths of Cr and Mn for thermal **neutrons** are extremely **different**:

$$b_{\text{Cr}} = +3.52 \text{ fm and } b_{\text{Mn}} = -3.64 \text{ fm} \quad \Rightarrow \text{Easily distinguished}$$

Source: <http://webster.ncnr.nist.gov/resources/n-lengths/>

Take home message: Use *neutron-* instead of *x-ray-diffraction* if *elements with similar atomic numbers* need to be distinguished.

Coherent elastic neutron scattering lengths and cross sections of

Mn:

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Mn	100	-3.73	1.79	1.75	0.4	2.15	13.3

Cr:

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Cr	---	3.635	---	1.66	1.83	3.49	3.05
50Cr	4.35	-4.50	0	2.54	0	2.54	15.8
52Cr	83.79	4.920	0	3.042	0	3.042	0.76
53Cr	9.5	-4.20	6.87	2.22	5.93	8.15	18.1(1.5)
54Cr	2.36	4.55	0	2.6	0	2.6	0.36

All of this data was taken from the Special Feature section of neutron scattering lengths and cross sections of the elements and their isotopes in *Neutron News*, Vol. 3, No. 3, 1992, pp. 29-37.

The contents of the columns are as follows:

Column	Unit	Quantity
1	---	Isotope
2	---	Natural abundance (For radioisotopes the half-life is given instead)
3	fm	bound coherent scattering length
4	fm	bound incoherent scattering length
5	barn	bound coherent scattering cross section
6	barn	bound incoherent scattering cross section
7	barn	total bound scattering cross section
8	barn	absorption cross section for 2200 m/s neutrons

Note: 1fm=1E-15 m, 1barn=1E-24 cm², scattering lengths and cross sections in parenthesis are uncertainties.

Source: <http://webster.ncnr.nist.gov/resources/n-lengths/>

Site occupation of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$

In the structure analysis of the neutron data
site-specific effective scattering lengths $b_{\text{eff}}(2a)$ and $b_{\text{eff}}(2d)$
 are **refined**, which in turn are expressed as:

$$b_{\text{eff}}(2a) = a \cdot [(1-y) \cdot b_{\text{Mn}} + y \cdot b_{\text{Cr}}] \quad \text{and} \quad b_{\text{eff}}(2d) = d \cdot [(1-z) \cdot b_{\text{Mn}} + z \cdot b_{\text{Cr}}]$$

solving for the **unknown** parameters **y** (Cr on 2a) and **z** (Cr on 2d) gives:

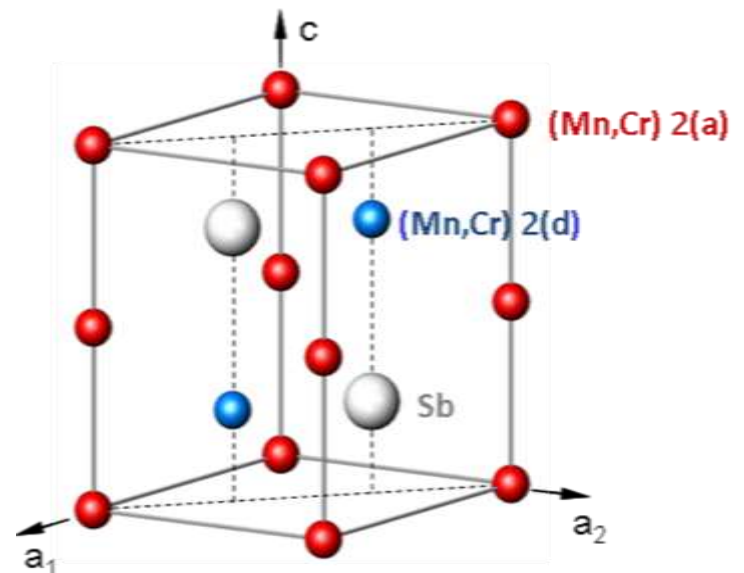
$$y = [b_{\text{eff}}(2a)/a - b_{\text{Mn}}] / [b_{\text{Cr}} - b_{\text{Mn}}] \quad \text{and} \quad z = [b_{\text{eff}}(2d)/d - b_{\text{Mn}}] / [b_{\text{Cr}} - b_{\text{Mn}}]$$

a: overall occupation probability of site 2(a)

d: overall occupation probability of site 2(d)

y: Cr-fractional occupation of site 2(a)

z: Cr-fractional occupation of site 2(d)



Site occupation of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$

Are we done...?...not quite: 4 variables, 2 equations. Still undetermined:

Overall occupation probabilities (Mn plus Cr) **a** and **d** of sites 2(a) and 2(d)

What can we do?

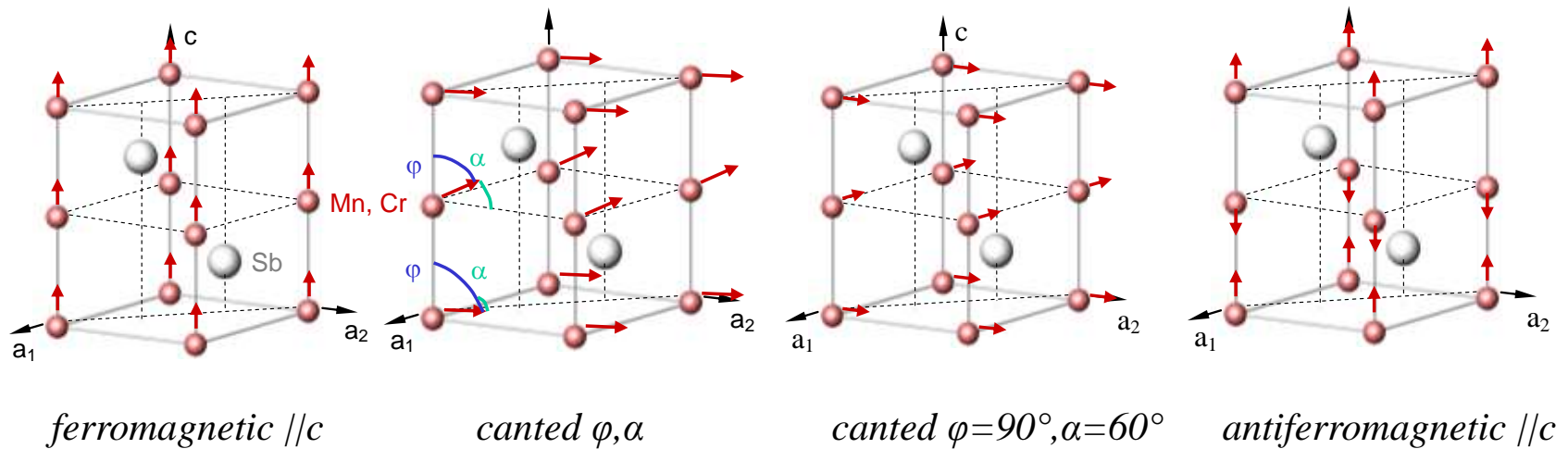
- **Chemical analysis** (like EDX, EPMA, XFA...) can yield δ ,
reminder: $1 + \delta = a + d$
but we need the **two** site specific parameters **a** and **d** separately!
- **Ad hoc assumption:** $a \approx 1.0$ [site 2(a) is the 'regular' cation site in NiAs]
For most of the samples studied, the site 2(a) was indeed found to be fully occupied, but the 2(d)-site is definitely not!So?
- A **second independent diffraction experiment** (with X-rays) is needed if both sites are occupied by more than two species, here: Mn, Cr, vacancy.

Take home message: In general, a statistical occupation of one *crystallographic site* with three kinds of scatterers - e.g. Mn, Cr and "vacancies" - *requires at least two independent experiments* with sufficiently different relative scattering power of the atoms involved to determine the fractional occupancies.

Why bother?

Magnetic ordering in $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$

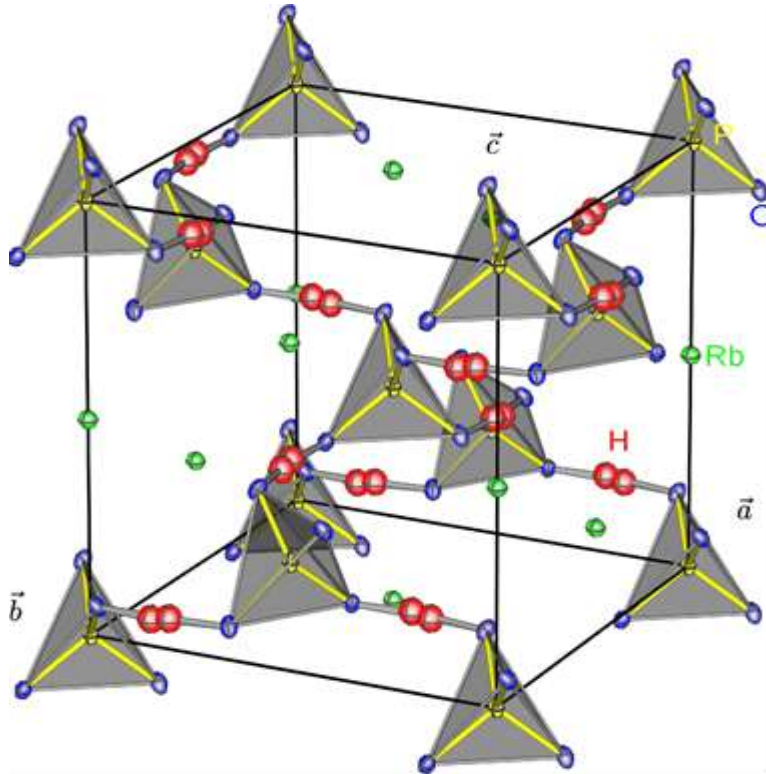
Some of the magnetic structures of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$ derived from magnetic neutron diffraction and susceptibility measurements:



Magnetic structure of $(\text{Mn}_{1-x}\text{Cr}_x)_{1+\delta}\text{Sb}$ depends critically on:

- Mn-Cr-fractions on sites 2a and 2d $\Rightarrow x$
- Vacancy concentrations on 2a and 2d \Rightarrow non-stoichiometry δ
- Temperature T (also pressure p).

H-ordering: Ferroelectric phase transition in RbH_2PO_4 (RDP)



*Paraelectric phase of RDP (RbH_2PO_4)
 PO_4 -tetrahedra, split-model representation of the **hydrogen disorder***

*Ph.D. thesis S. Mattauch
RWTH-Aachen 1997*

Member of the KH_2PO_4 (KDP) group of **hydrogen-bonded ferroelectrics**.

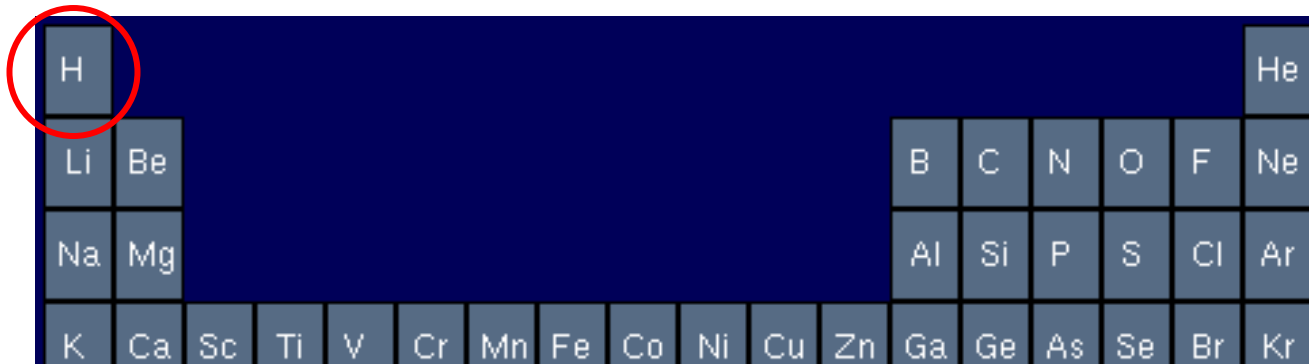
Technical application:
Nonlinear optics:
Laser frequency doubling



*KDP-crystal for optical applications
Source: Lawrence Livermore Natl. Labs.*

Reminder: Neutron-scattering lengths of hydrogen isotopes

<http://webster.ncnr.nist.gov/resources/n-lengths/>



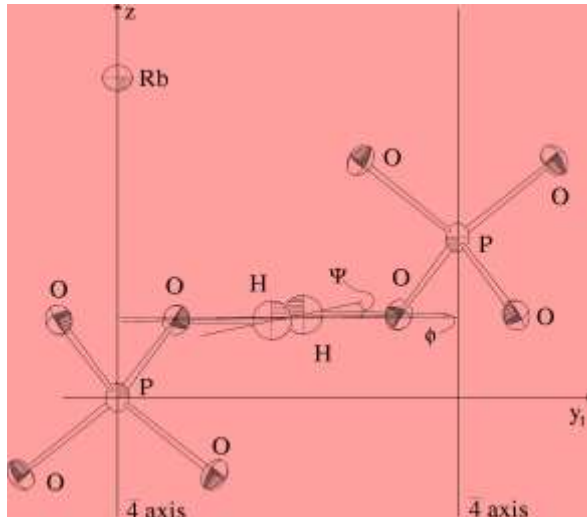
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Neutron scattering lengths and cross sections of hydrogen

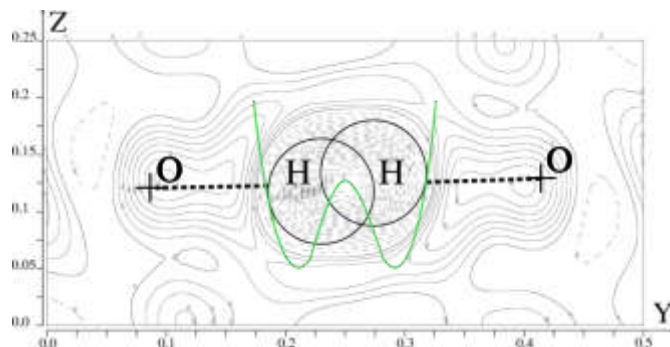
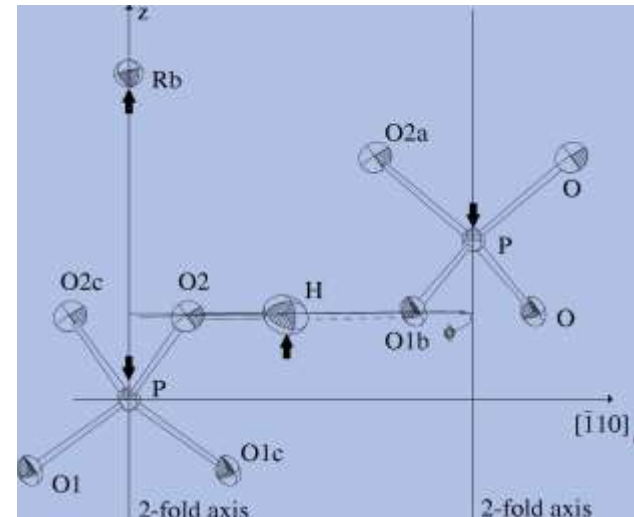
Isotope	concentration	coh b [10 ⁻¹⁵ m]	inc b [10 ⁻¹⁵ m]	coh σ [10 ⁻²⁴ cm ²]	inc σ [10 ⁻²⁴ cm ²]	total scatt σ [10 ⁻²⁴ cm ²]	scattabs σ [10 ⁻²⁴ cm ²]
H (natural)	---	- 3.7390	---	1.7568	80.26	82.02	0.3326
¹ H	99.985	- 3.7406	25.274	1.7583	80.27	82.03	0.3326
² H ≡ D	0.015	+ 6.671	4.04	5.592	2.05	7.64	0.000519
³ H ≡ T	(12.32 a)	+ 4.792	-1.04	2.89	0.14	3.03	0

H/D ordering: Ferroelectric phase transition in RbH_2PO_4 (RDP)

High temperature, $T > 147$ K: *Disordered*
 $\text{PO}_4 \cdots \text{H}-\text{H} \cdots \text{PO}_4$ hydrogen bond
 \Rightarrow *paraelectric*



Low temperature, $T < 147$ K: *Ordered*
 $\text{PO}_4 \cdots \text{H}-\text{H} \cdots \text{PO}_4$ hydrogen bond
 \Rightarrow *ferroelectric*



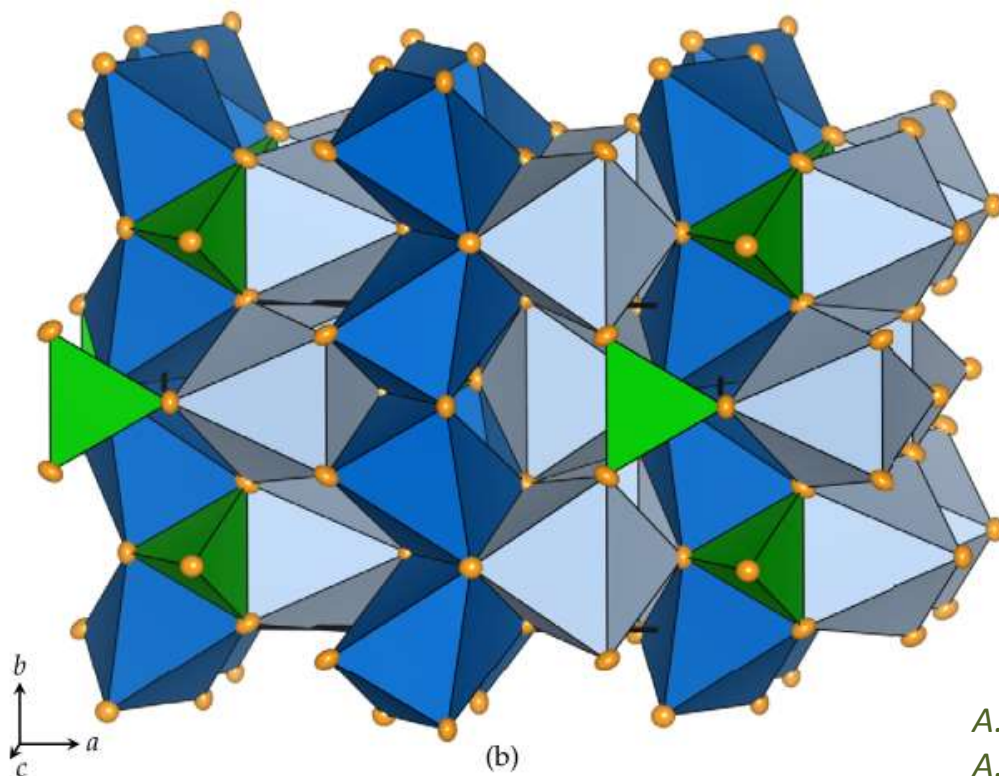
model: dynamic H-disorder according to a double-well potential

Difference-Fourier-plot of the negative proton density in the hydrogen bond of paraelectric RDP indicated by broken contour lines.

Ph.D. thesis S. Mattauch
RWTH-Aachen 1997

Take home message: Such studies can only be done with neutrons! Lots of other applications to H-bonded crystals:
...Proteins...!

Accurate atomic coordinates and displacement parameters from neutron diffraction: Co_2SiO_4



Structure of Co_2SiO_4 olivine at room temperature, projected along c.

Green: SiO_4 -tetrahedra

Dark blue: $\text{Co}(1)\text{O}_6$ -octahedra

Light blue: $\text{Co}(2)\text{O}_6$ -octahedra

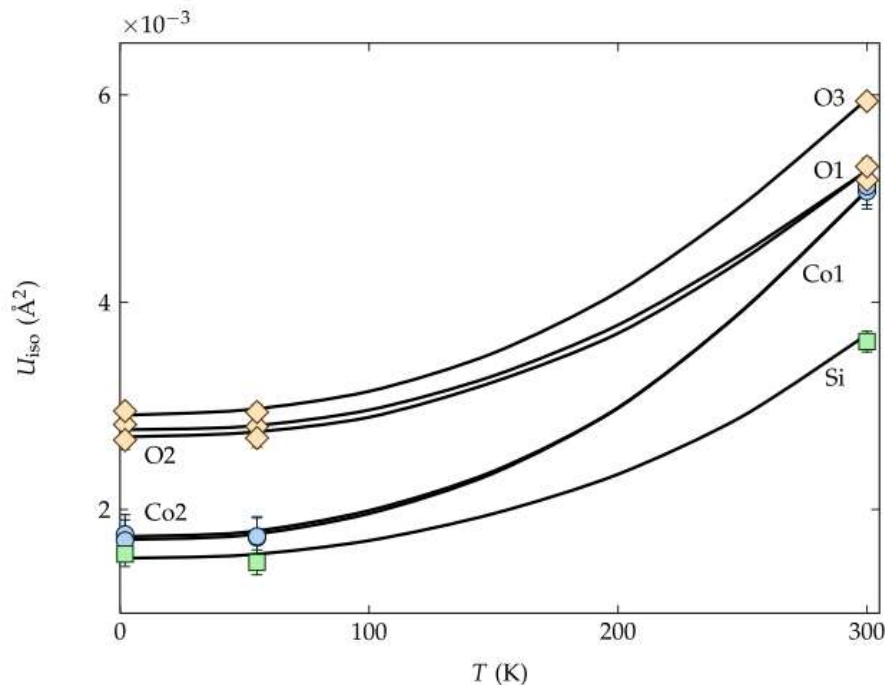
Displacement ellipsoids are plotted at the 95% probability level

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

A. Sazonov et al., Acta Cryst. B65, 664-675 (2009)

Take home message: *Neutron diffraction* allows *improved accuracy/precision* compared to X-ray diffraction with respect to: Fractional atomic coordinates x, y, z and displacement parameters U_{ij} .

Accurate atomic coordinates and displacement parameters from neutron diffraction: Co_2SiO_4

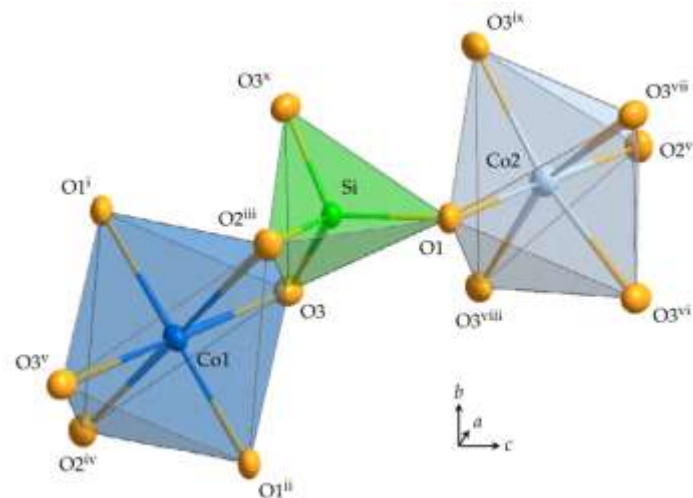


Temperature dependence of the isotropic displacement parameters of Co_2SiO_4

Reminder: “Thermal” Displacements:
 Snapshot of instantaneous deviations
 from average atomic positions
 Time & space average

U_{iso} vs. U_{ij}

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)
 measured on HEiDi@FRM II



Clinographic view of the CoO_6 and SiO_4 polyhedra in Co_2SiO_4 at room temperature

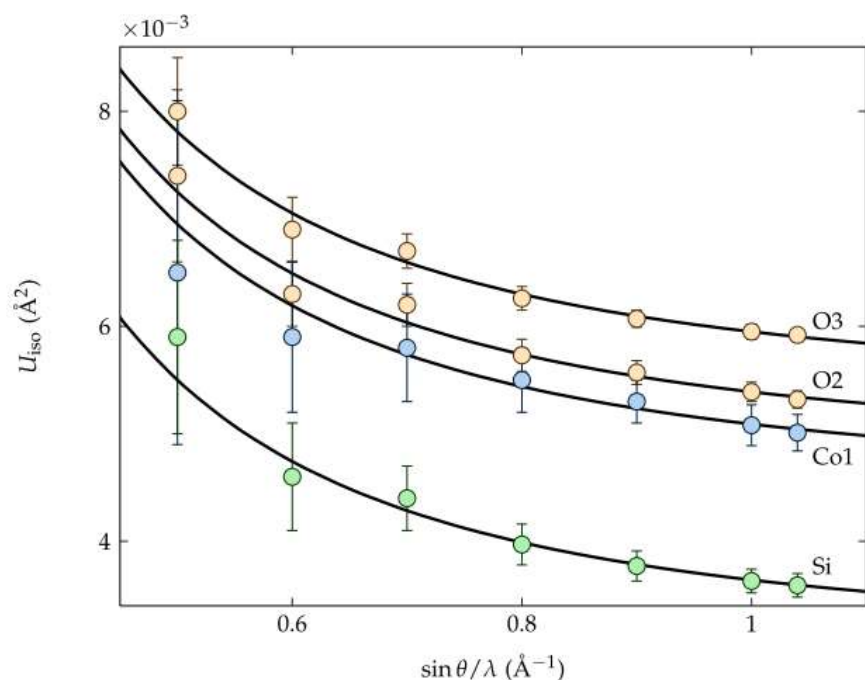
Why:

Levelling off of U_{iso} at low temps?
 Displacements larger for oxygen?

Why does neutron diffraction allow improved accuracy/precision?

Major factor: No atomic form factor fall-off

- Constant (Q-independent) scattering power.
- More reflections at high Q-values measurable
- Better spatial resolution, higher accuracy



Statistical (error bars) and systematic errors of *isotropic displacement parameters* in Co_2SiO_4 as a function of measured $\sin \theta / \lambda$ range from single-crystal neutron diffraction data at room temperature

Observation:

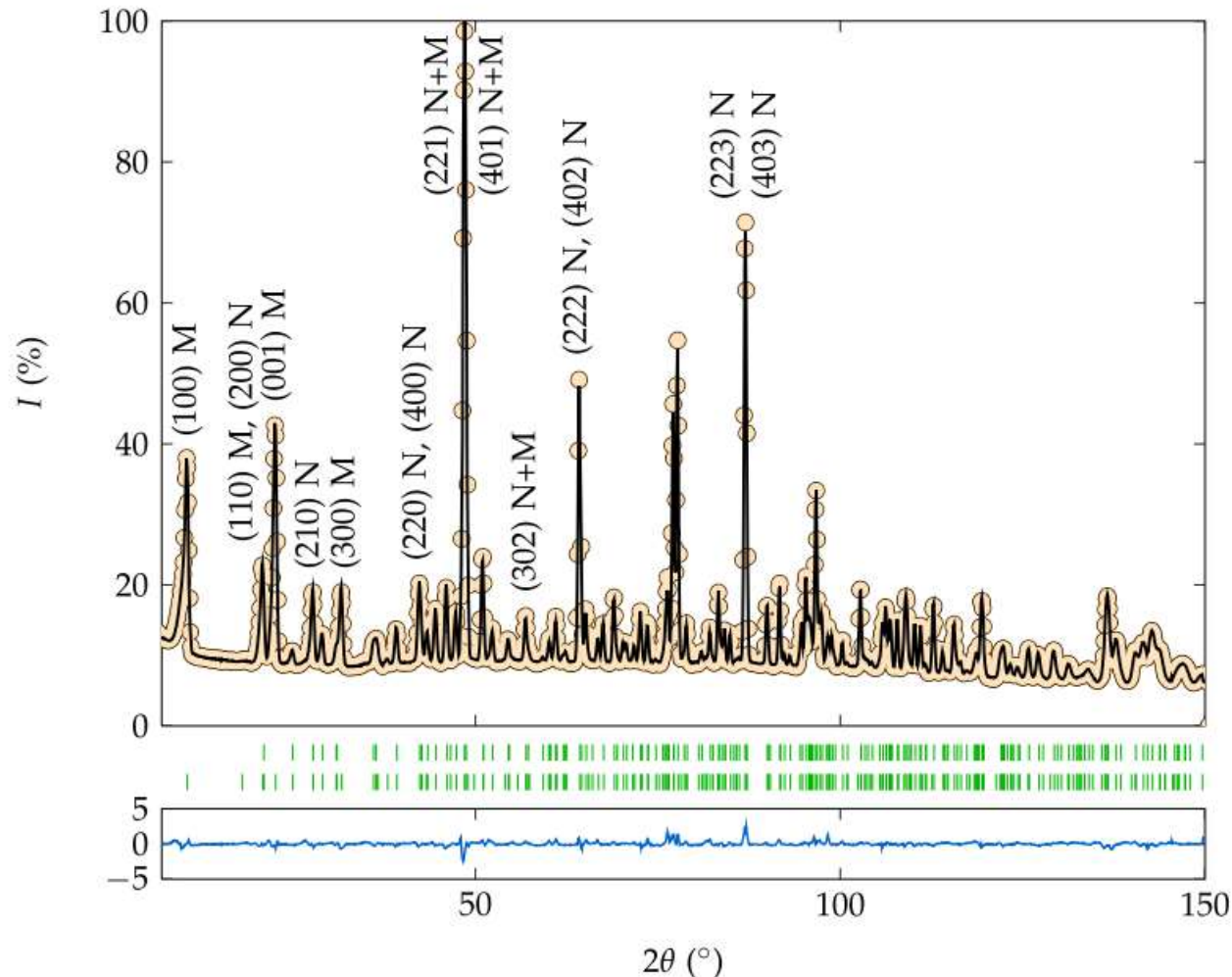
Statistical error (bars) decreases with increasing $\sin \theta / \lambda$ range

But also:

Systematic decrease of the absolute values of U_{iso} ...
...decreasing systematic errors...?

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)
measured on HEiDi@FRM II.

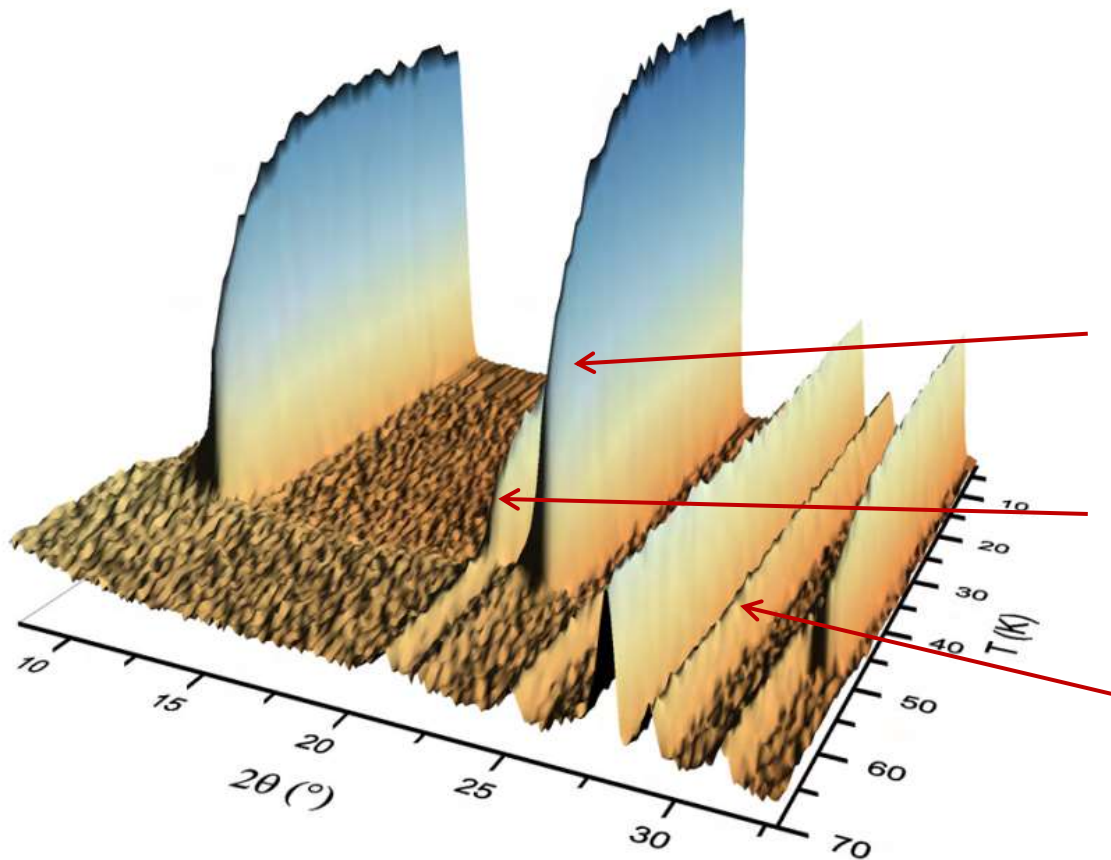
Magnetic structures from neutron diffraction: Co_2SiO_4



*A. Sazonov, Ph.D.-thesis,
RWTH Aachen (2009),
measured on SPODI@FRM II*

Neutron powder diffraction pattern (dots), Rietveld fit (black line) and allowed Bragg reflections (green marks) at 5 K of Co_2SiO_4 .
N: nuclear, M: magnetic reflection, blue: $I_{\text{obs}} - I_{\text{calc}}$.

Magnetic structures from neutron diffraction: Co_2SiO_4



Purely **magnetic** reflections appear below 50 K

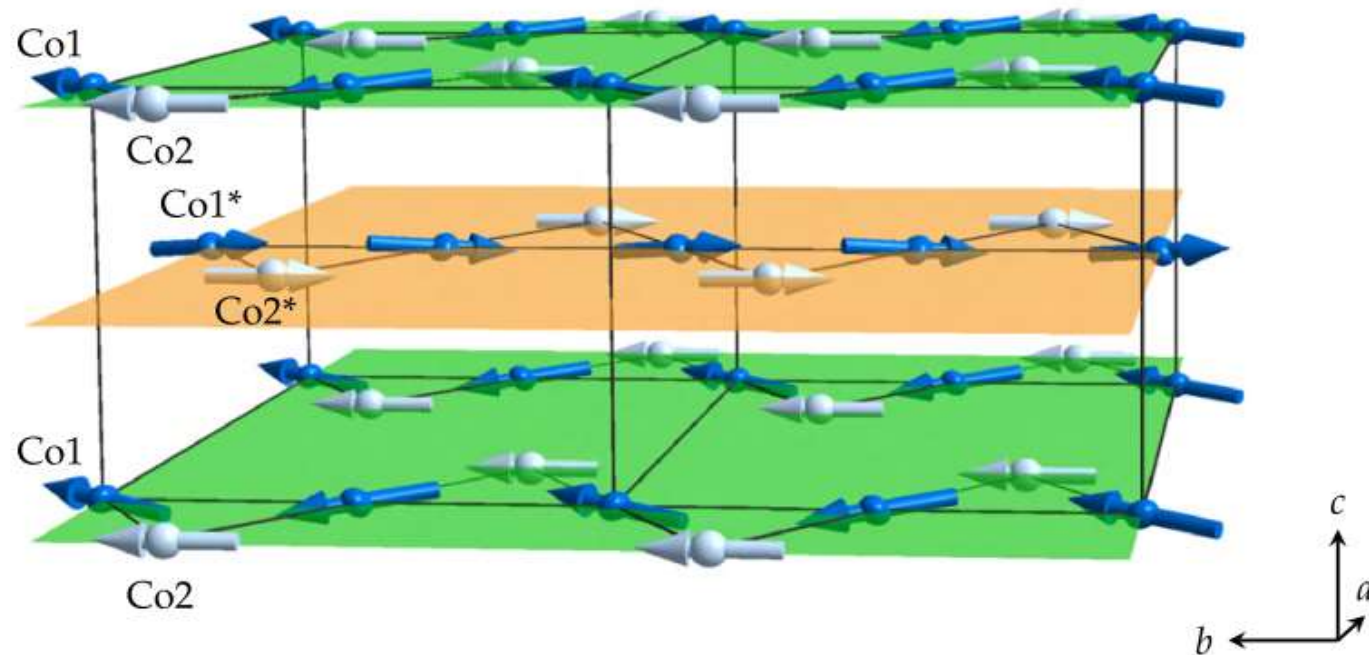
Some **nuclear** reflections gain intensity below 50 K

Some purely **nuclear** reflections remain unchanged below 50 K.

Thermal evolution of the neutron powder diffraction pattern (low angle part) of Co_2SiO_4

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

Magnetic structures from neutron diffraction: Co_2SiO_4



Graphical representation of the magnetic structure of Co_2SiO_4 below 50 K. The non-magnetic atoms (Si and O) are excluded for simplicity. The figure shows the zigzag chains of Co(1) and Co(2) in layers perpendicular to the c axis

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

Magnetic structures from neutron diffraction: Co_2SiO_4

Quantitative information from magnetic neutron diffraction:

Site specific magnetizations M_x , M_y , M_z along x, y, z

Magnitude M and direction angles ϕ , θ of the magnetization vector

	Co1 (0,0,0)	Co2 (x,1/4,z)
$M_x (\mu_B)$	1.18 ± 0.05	—
$M_y (\mu_B)$	3.61 ± 0.04	3.37 ± 0.04
$M_z (\mu_B)$	0.66 ± 0.18	—
$M (\mu_B)$	3.86 ± 0.05	3.37 ± 0.04
$\phi (^\circ)$	71.9 ± 0.7	90
$\theta (^\circ)$	80.2 ± 2.7	90

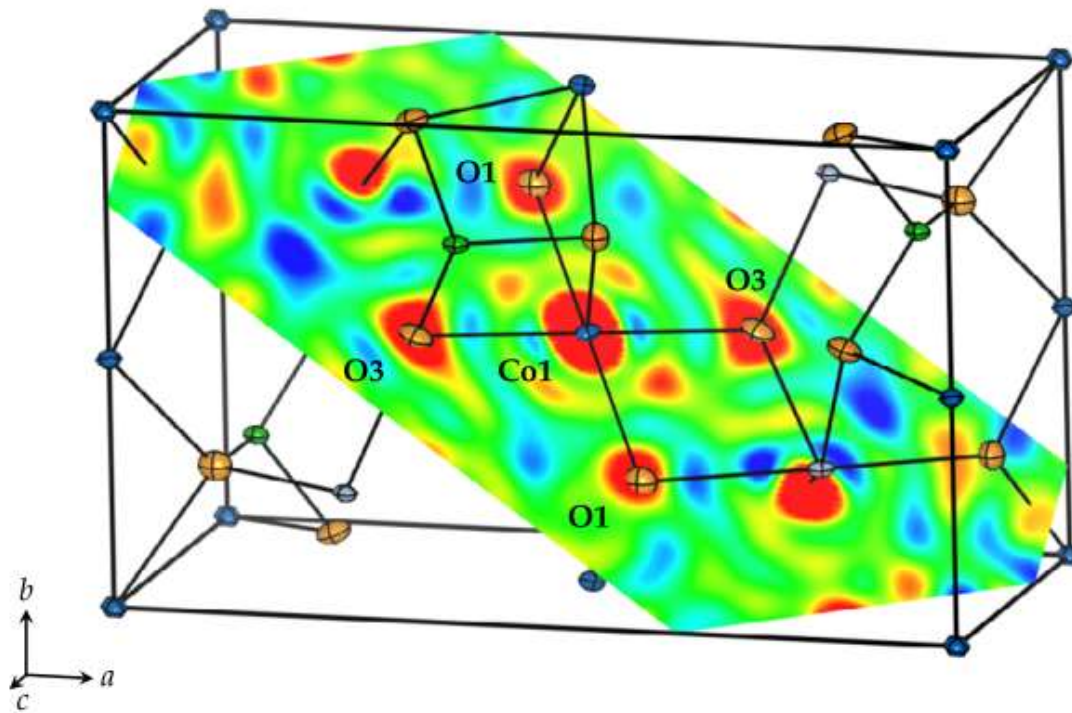
A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

$$\chi^2 = 2.23, R[F^2 > 2\sigma(F^2)] = 0.033, wR(F^2) = 0.044.$$

Take home message: *Neutron diffraction* is THE method to determine **magnetic structures**: Qualitative: Arrangement of magnetic moments in the unit cell, Quantitative: Orientation and absolute magnetic moment on the magnetic atoms.

Electron density determination from X-ray and neutron diffraction: Co_2SiO_4

Single crystal X-ray-diffraction experiment:



This is the **total electron density** (incl. inner shells)

How to get infos on the **bonding electron density**?

*A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)
measured at synchrotron source*

Electron density distribution $\rho(\mathbf{r})$ of Co_2SiO_4 at 12 K from Fourier synthesis of X-ray data. Contours range from $-8 \text{ e}/\text{\AA}^3$ (blue) to $10 \text{ e}/\text{\AA}^3$ (red). A plane which intersects the CoO_6 octahedron and contains the Co1, O1 and O3 atoms is shown together with a sketch of the crystal structure .

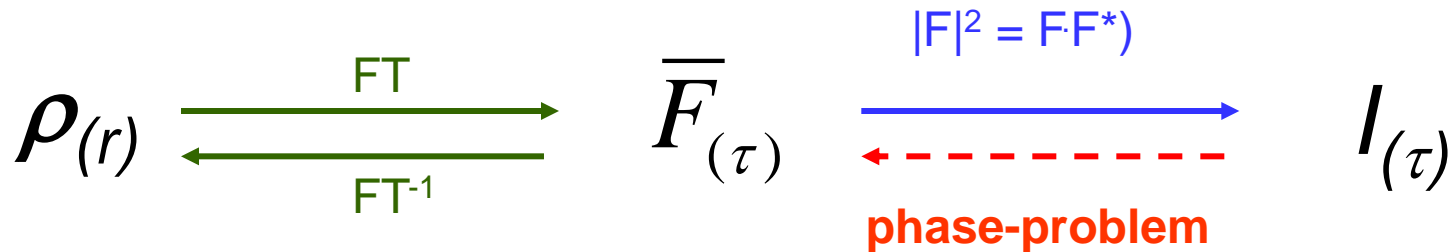
Reminder:

The diffraction experiment – at a glance:

Object:
direct space
crystal

Fourier-transform:
reciprocal space
structure factor

Intensity: (observable)
reciprocal space
squared structure factor



FT: fourier-transform
FT⁻¹: inverse FT

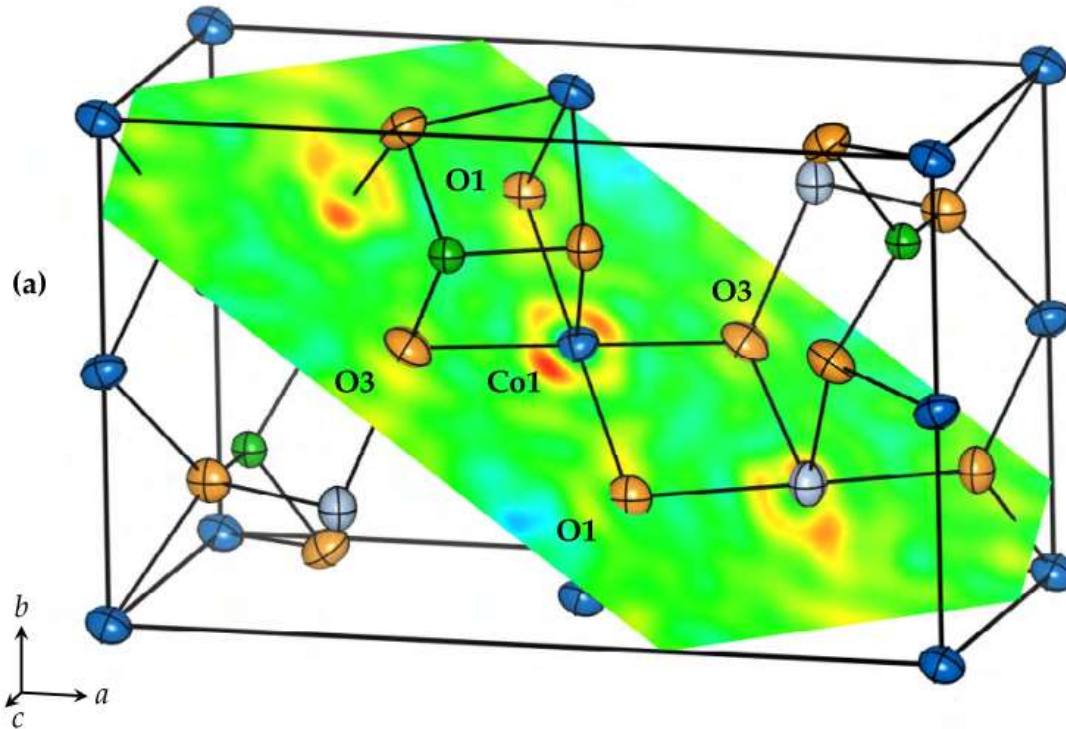
r: vector of x,y,z
 τ : vector of h,k,l

The experiment involves:

$\rho(r)$: electron density in the unit cell
 $F(\tau)$: structure factor (complex)
 $I(\tau)$: integral reflection intensity

Electron density determination from X-ray and neutron diffraction: Co_2SiO_4

X-N (X-ray minus Neutron) difference Fourier map:



Deformation density from the X-N-difference Fourier map of Co_2SiO_4 at 300 K: Section through the O1–Co1–O3 plane. The difference density varies from $-1.25 \text{ e}/\text{\AA}^3$ (blue) to $1.15 \text{ e}/\text{\AA}^3$ (red).

A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

X-N map:

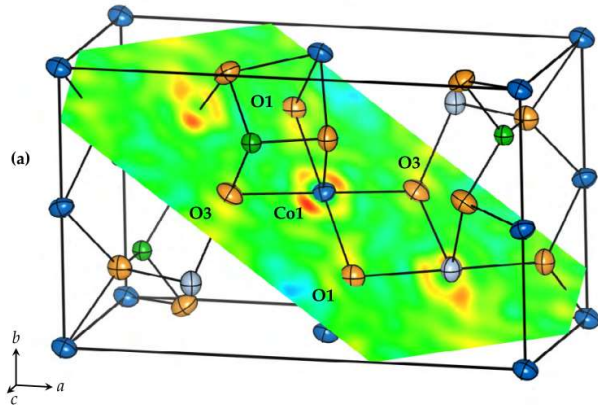
Combination of single crystal X-ray (synchrotron) and neutron diffraction experiment to obtain the **bonding electron density**

Needed:

VERY accurate single crystal X-ray and neutron diffraction data.

Electron density determination from X-ray and neutron diffraction: Co_2SiO_4

X-N (X-ray minus Neutron) difference Fourier map:



Deformation density from the X-N-difference Fourier map of Co_2SiO_4 at 300 K: Section through the O1–Co1–O3 plane. The difference density varies from $-1.25 \text{ e}/\text{\AA}^3$ (blue) to $1.15 \text{ e}/\text{\AA}^3$ (red).

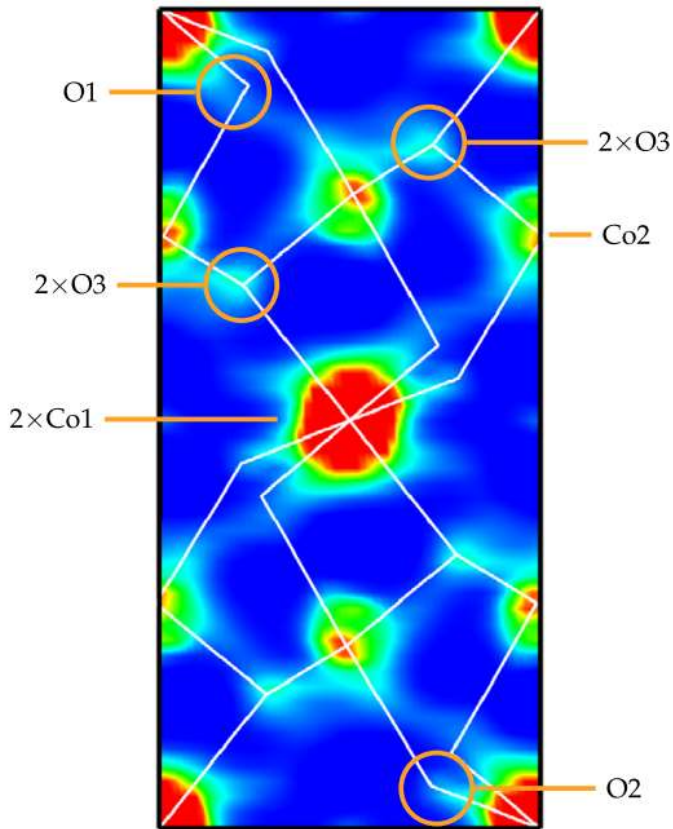
A. Sazonov, Ph.D.-thesis, RWTH Aachen (2009)

Calculation of X-N maps:

- Take accurate x, y, z and U_{ij} from neutron diffraction experiment
 - Decorate point atoms with spherical electron density from quantum mechanical calculations for the free atom (without bonding)
 - Calculate the difference to the total electron density from the X-ray experiment
- => **Deformation density:** $\rho(r)_{\text{deform}} = \rho(r)_{\text{X-ray}} - \sum \rho(r)_{\text{spherical}}$

Take home message: Combined *single crystal neutron and x-ray diffraction* allows to study the spatial distribution of the bonding electron density in solids.

Magnetization density distribution from neutron diffraction: Co_2SiO_4



Reconstruction of the density (proj. along **b**) corresponding to the observed magnetization distribution of Co_2SiO_4 at 70 K with contours ranging from $0 \mu_B/\text{\AA}^3$ (blue) to $2 \mu_B/\text{\AA}^3$ (red)

Experiment:

Polarized neutron diffraction on a single crystal using the flipping ratio method (*see other chapters*)

Interpretation:

This is the density of the **unpaired electrons** responsible for the magnetic properties

It is again only a fraction of the bonding electron density discussed above.

It tells, where (in the unit cell) the magnetization is located...

...magnetization on oxygen atoms (O3)...

...YES: **Transferred magnetic moments!**

Take home message: Polarized neutron diffraction allows to determine the magnetization density distribution in the unit cell.

Summary:

Strengths of neutrons for structural analysis: (vs. X-rays)

- Large **contrast** between neighboring elements (even bw. isotopes)
- **H/D** is a strong scatterer
- Nuclear scattering **without form factor-falloff**
- Lots of **data at high Q** measurable => superior precision
- Almost **no absorption** => improved accuracy
- **Magnetic scattering** from unpaired electrons
- Magnetic scattering length comparable to nuclear scattering

Weaknesses of neutrons for structural analysis:

- **Extinction** often the major source of systematic errors
- Notoriously **too few of them** available => **need large crystals**
- **Production expensive**

Thank you for your attention!