Christian-Albrechts-Universität zu Kiel

Applications of the Rietveld Method

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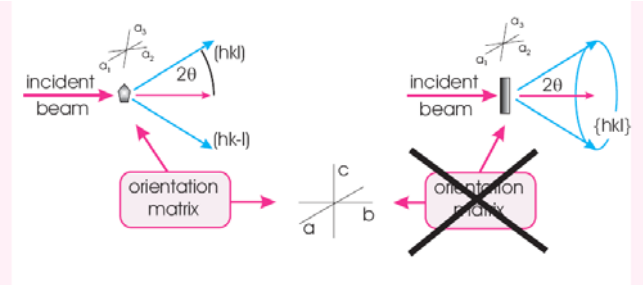
Outline

- General aspects
- low Z elements
  - Protons, $C_4A_3H_3$
- neighboring elements
  - Si/Al order / disorder
  - Co,Mn-cordierite
- extreme conditions
  - high p, NaN_3
  - high pT, Graphite

Powder diffraction: key problem



- totally overlapping reflections
  - $d(h_1, k_1, l_1) = d(h_2, k_2, l_2)$

    cubic: $d = a/(h^2 + k^2 + l^2)^{1/2}$, $d(511) = d(333)$
  - multiplicity of equivalent lattice planes
- partially overlapping reflections, $d(h_1, k_1, l_1) \approx d(h_2, k_2, l_2)$

Neutron diffraction

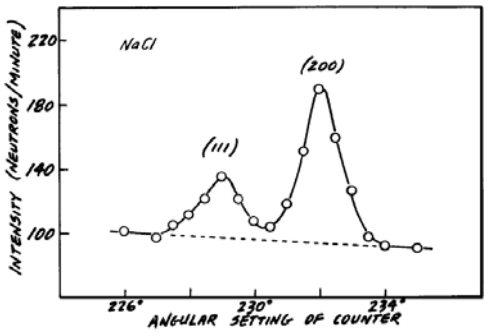
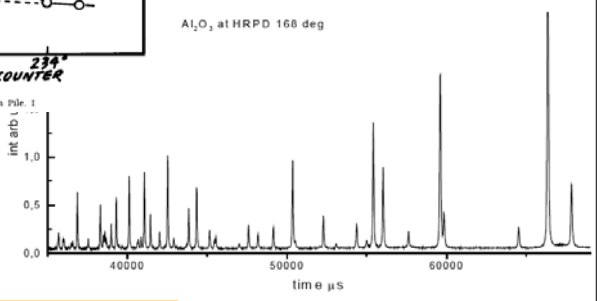


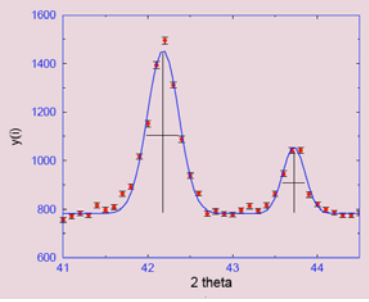
Fig. 4. Portion of the First Powder Diffraction of NaCl taken at the Clinton Pile. 1

NaCl
from Shull: Nobel lecture



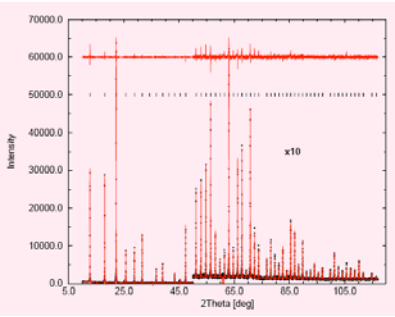
Al_2O_3
HRPD / ISIS

peak-fit



range: single reflections, reflection groups
independent parameters: peak area, position and shape
prior knowledge: none
applications: indexing, cell parameters, $|F|$-determination, line shape analysis

full pattern methods



range: total diffraction pattern,
independent parameters: peak area
dependent parameters:
$2\theta(\text{hkl}) = f(a, b, c, \alpha, \beta, \gamma)$,
$\lambda = 2d\sin(\theta)$, $d = 1/|\vec{H}|$,
$\vec{H} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$
profile parameters $= f(2\theta)$
prior knowledge: approximate unit cell
applications: $|F|$, cell parameters

The Rietveld method

Aim: find best aggreement between measured y_i^o and calculated y_i^c diffraction pattern

$$\sum (y_i^o - y_i^c)^2 \rightarrow \text{Min.}$$

non-linear optimization problem

Method: simultaneous refinement of models for

- diffraction optics, instrumental parameters (resolution function, instrument offsets, ...)
- Background
- phase specific parameters (cell parameters, crystal structure (x,y,z,B,n)
- sample specific parameters (crystallite size, stress, preferred orientation)

Step intensity

intensity y_i^c at the ith step consists of:

$$y_i^c = y_{bi}^c + \underbrace{S \sum_{k=1}^{n} m_k \, L_k \, |F_k|^2 \, G(\Delta 2\theta_{ik}) \, P_k}_{n \quad \text{overlapping reflections}}$$

y_{bi}^c	...background
S	...scale factor
n	...number of overlapping reflections (hkl)
m_k	...multiplicity of reflection k
L_k	...Lorentz-, polarisation correction
F_k	...structure factor
$G(\Delta 2\theta_{ik})$	...peak shape function
P_k	...preferred orientation correction

Structure factor

The structure factor F_k is given by :

$$
\begin{aligned}
F_k &= T_0 \sum_{r=1}^{n} N_r \, T_r^{\text{iso}} \, f_r \, (A_r + iB_r) \\
A_r &= \sum_{j=1}^{m} T_{rj}^{\text{aniso}} \, \cos\left(2\pi(hx_{rj} + ky_{rj} + lz_{rj})\right) \\
B_r &= \sum_{j=1}^{m} T_{rj}^{\text{aniso}} \, \sin\left(2\pi(hx_{rj} + ky_{rj} + lz_{rj})\right)
\end{aligned}
$$

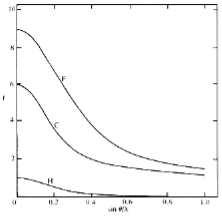
n	...atoms in the asymmetric unit
m	...symmetry equivalent positions
N_r	...site occupancy
T	...temperature factor (T_o - overall, T^{iso} - isotropic and T^{aniso} anisotropic)
f_r	...form factor
x_r, y_r, z_r	...fractional atom coordinates

Peak shape functions

models for the peak shape:

- fundamental parameters approach
- analytical functions (Gauss, Lorentz, pseudo-Voigt, Pearson VII, TCH, split-type, ...)
  - $G(\Delta 2\theta_{ik})^G = \frac{4\ln 2}{\sqrt{\pi} H_k} \exp\left[-4\ln 2 \frac{(2\theta_i - 2\theta_k)^2}{H_k^2}\right]$
    $G(\Delta 2\theta_{ik})^L = \frac{2}{\pi H_k} / \left[1 + \frac{4(2\theta_i - 2\theta_k)^2}{H_k^2}\right]$
    $G(\Delta 2\theta_{ik})^{PV} = \eta G(\Delta 2\theta_{ik})^L + (1-\eta) G(\Delta 2\theta_{ik})^G$
  - asymmetry correction
  - peak half width $H_k = \left[u \tan^2(\theta) + v \tan(\theta) + w\right]^{1/2}$

X-rays vs. neutrons



X-ray: form factor f_j for $j = H, C, F$

$$f_j \propto \sin(\theta)/\lambda$$

structure solution, better with X-ray
phase problem easier to solve for heavy atoms;
mostly good resolution

coherent neutron scattering lengths b_j

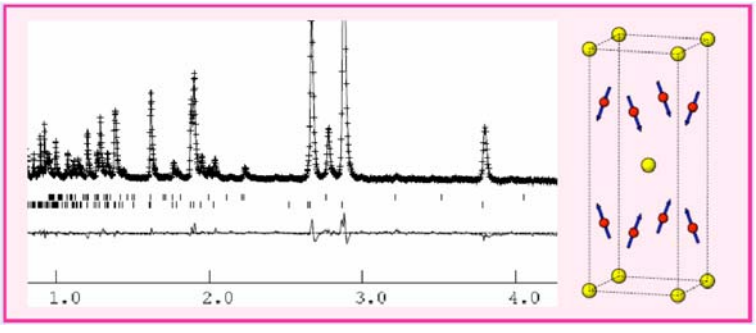
$$\underbrace{H = -3.74, D = 6.67}_{\text{isotopes}}, F = 5.64; \underbrace{Al = 3.45, Si = 4.107}_{\text{neighbouring elements}}; Sn = 6.22$$

refinement, more precise structural parameters from neutrons
intensity at higher θ not influenced by form factor, less systematic errors

Magnetic structures

magnetic neutron form factor $\langle j_0 \rangle \propto (\sin\theta)/\lambda$

rietveld refinement $\rightarrow$ spin arangement, magnetic moments



$LaMn_2Si_2$: canted AF

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Weak X-ray scatterer

- Hydrogen
  - OH: boehmit AlOOH, goethite FeOOH, bucite $Mg(OH)_2$, hydoxylapatite, hydrogarnets, ...
  - H_2O: gypsum, bassanite, zeolites, ...
  - Ammonia, e.g. nitrammite ND_4NO_3
  - Organics in zeolites
  - clathrates, ice → cf. Kuhs & Hansen
- Lithium
  - strong neutron absorber
  - several minerals
  - microporous litiosilicates (RUB-#)
- Beryllium
  - rare minerals, Be-phosphate/arsenate microporous materials

Proton positions

- H weak X-ray but strong neutron scatterer,
  b_c(H) = -3.74, b_i(H) = 25.22
  b(D) = 6.67 fm
- example: NaH / NaD
  (C. Shull / Nobel lecture)

- here: $C_4A_3H_3$ = $4CaO•3Al_2O_3•3H_2O$
- motivation: Portland cement phase,
  high temperature dehydration
  and mechanism of transformation
  to SOD-type,
  role of the protons,
  H positions unknown

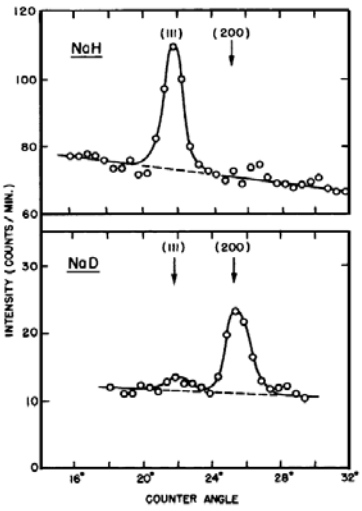


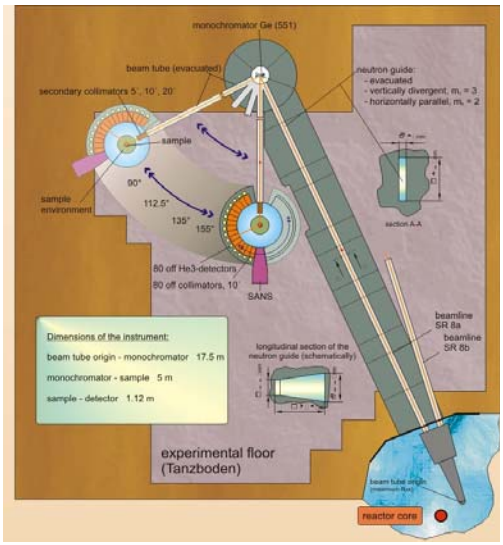
Fig. 5: Patterns for NaH an NaD Showing that Hydrogen Contributes Normally to the Pattern.

experiment: Munich FRM-2

graphics: http://www.frm2.tum.de

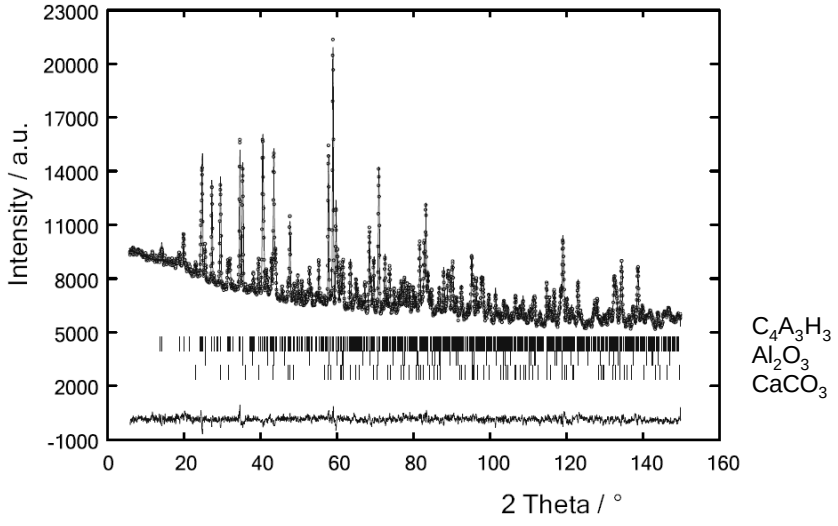
The powder diffractometer: SPODI

- operated by LMU and TU Darmstadt
- monochromator:
  - Ge (551)
  - different take-off angles
  - vertically focussing
- Detectors:
  - multi detector 80 ^{3}He tubes with 10‘ collimators
  - SANS option (MAR IP)

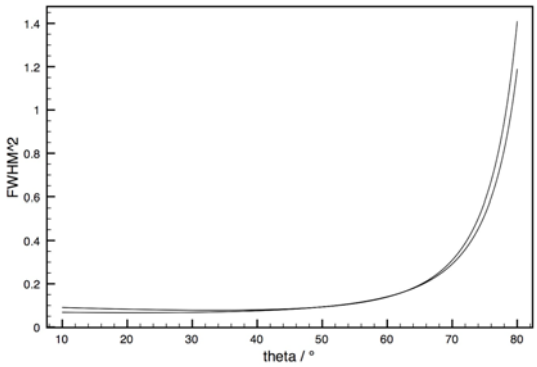


graphics: http://www.frm2.tum.de

Structure refinement, 5K



Results



Rp: 2.37 Rwp: 3.53

a: 12.42764 0.00039
b: 12.80914 0.00038
c: 8.86485 0.00026
space group *Abma*

11 atoms
>35 structural parameters (XYZ, Biso)

typical coordinates 0.3659(3)

6 global parameters

>700 reflections

Quantitative phase analysis

step intensity y_i of k overlapping reflections from a multiphase mixture of p phases

$$|^2 G_{ikp} P_{kp}$$

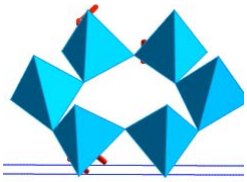
the scale facto

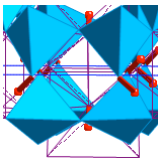
- $C_4A_3H_3$ 88.5 wt-%
- Al_2O_3 7.5(2) wt%
- $CaCO_3$ 4.0(1) wt%

M_p ...mass per formula unit
Z_p ...number of formula units per unit cell
V_p ...volume of the unit cell

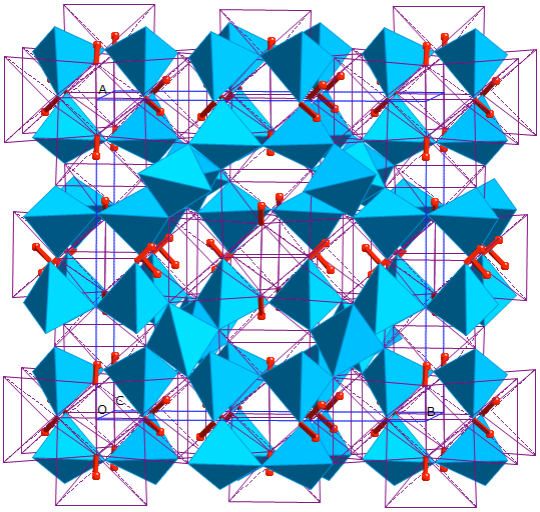
Structure

6-membered ring





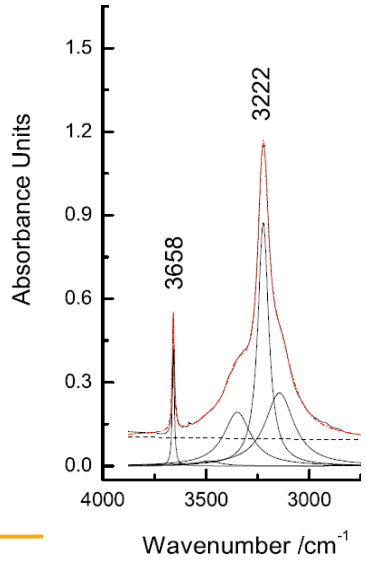
broken 4-membered ring



$C_4A_3H_3$: protons

- IR spectroscopy
- OH group
  3658 cm^{-1} = O5-H2
  d(OH)n 0.88(1)Å
  d(OH)IR 0.9 Å
- Hydrogen bond
  3222 cm^{-1} = O3-H1...O1

  d(OH)n 0.97(1) Å
  d(OH)IR 0.96-..0.92 Å



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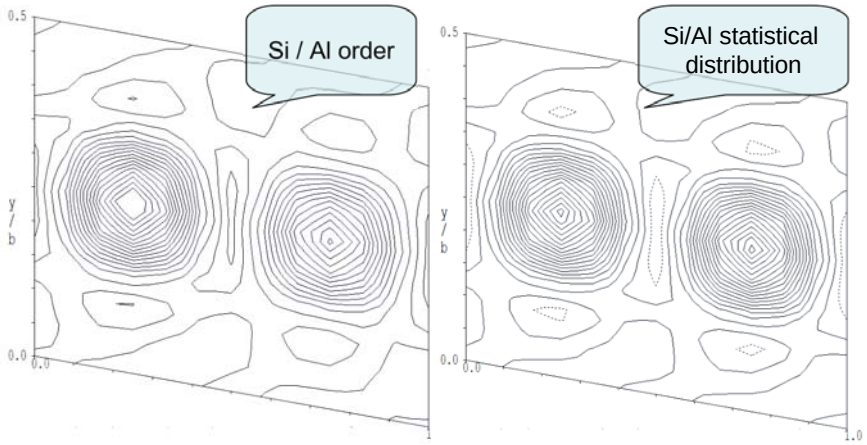
Neighboring elements

- ions with same or similar number of electrons typical for minerals
  - Ti^{4+}, Ca^{2+}, K^{+}, Cl^{-}
  - Na^{+}, Mg^{2+}, Al^{3+}, Si^{4+}
  - Fe^{2+}, Mn^{2+}
- distances diffrent: Al-O = 1.74, Si-O = 1.61 Å
- linear ratio d(T-O) = Al/Si
- direct determination → refine site occupancy from neutron data
- scattering length (fm):

Si	Al	Mn	Fe
4.15	3.45	-3.73	9.54

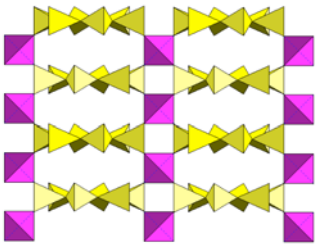
Si/Al Order

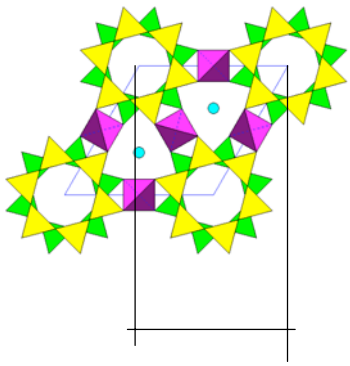


model calculation in $P\bar{1}$

Cordierite

$Mn_2Al_4Si_5O_{18}$	
$P6/mcc$	Ccm
a=9.841(2) Å	a=17.128(1) Å
c=9.372(2) Å	b= 9.764(1) Å
	c= 9.147(1) Å

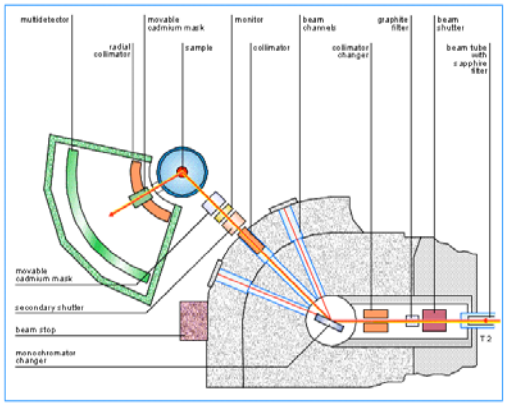




Figs.: socrates.berkeley.edu

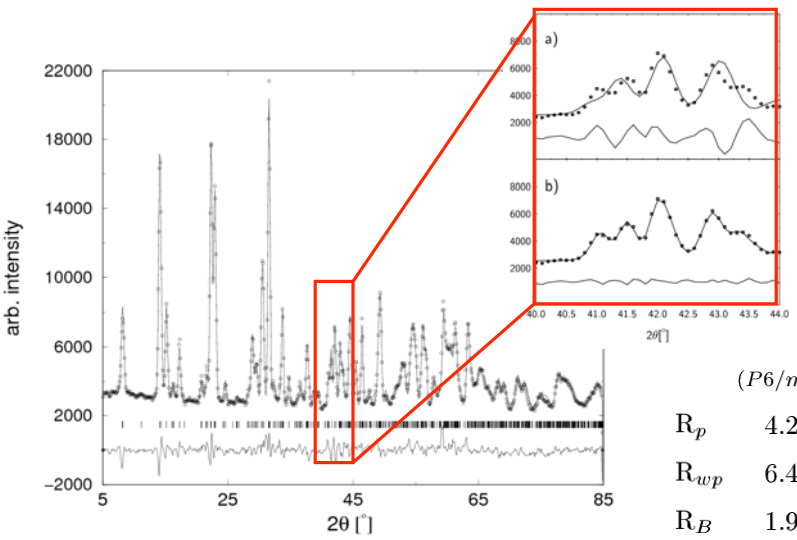
Cordierite: Experiment

- Hahn-Meitner-Institute
  BENSC Berlin



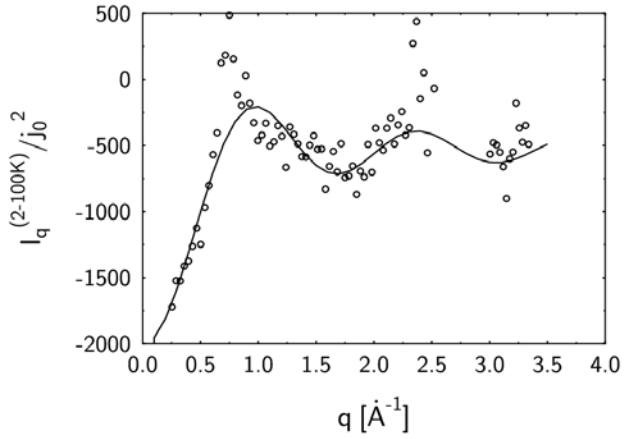
- E3
- Ge monochromator
- λ = 1.2 Å

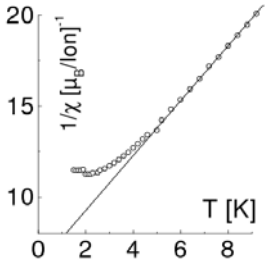
Mn-Cordierit: structure refinement



	$(P6/mcc\ /\ Cccm)$
R_p	4.27 / 2.16
R_{wp}	6.46 / 3.84
R_B	1.97 / 1.23

Mn-Cordierite: background





$$\frac{I_q^{(2-100K)}}{j_0^2} = \sum_i A_i \frac{\sin(d_i q)}{d_i q} + B_i \left[\frac{\sin(d_i q)}{d_i^3 q^3} - \frac{\cos(d_i q)}{d_i^2 q^2} \right]$$

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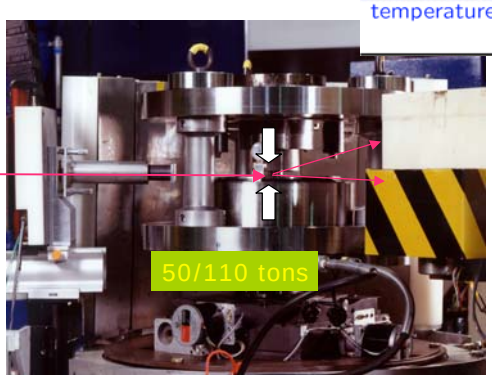
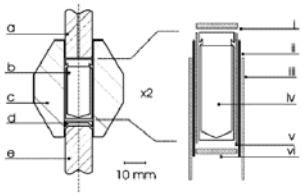
Kiel-Berlin cells

- piston/cylinder
- large volume
- simultaneous **pT**

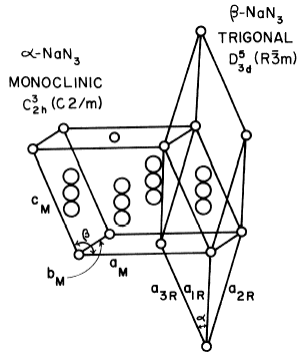
		Cell–I	Cell–II
sample volume	[cm^3]	0.7	1.5
max. pressure	[GPa]		
with Ti/Zr cylinder		2.2	1.2
with Al_2O_3 cylinder		(2.5)	(3.5)
temperature range	[K]	300 – 700 (±10)	
		(1.5 – 300)	

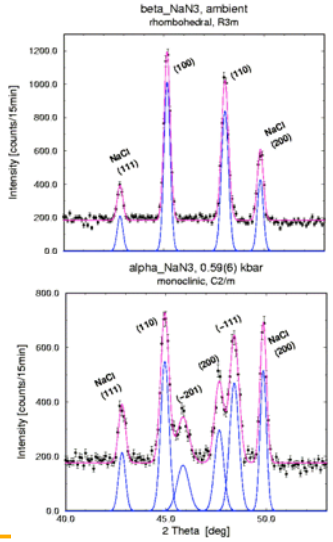




Rev. Sci. Instrum. 68(1997)3817
Rev. Sci. Instrum. 70(1999)1501
JAC 32(1999)373

NaN_3





- Sodium azide, NaN_3
- distorted rocksalt type
- phase transition at ca. 290 K
  β: **R-3m** α: **C2/m**

Polaris

ISIS, gas pressure cell
Ti/Zr- cylinder b(Ti) = -3.44, b(Zr)=7.16, zero-scatter alloy

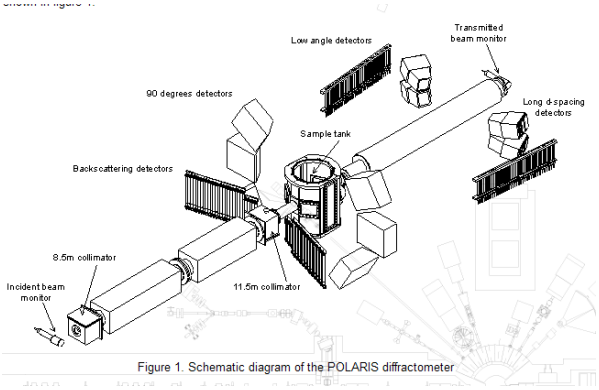


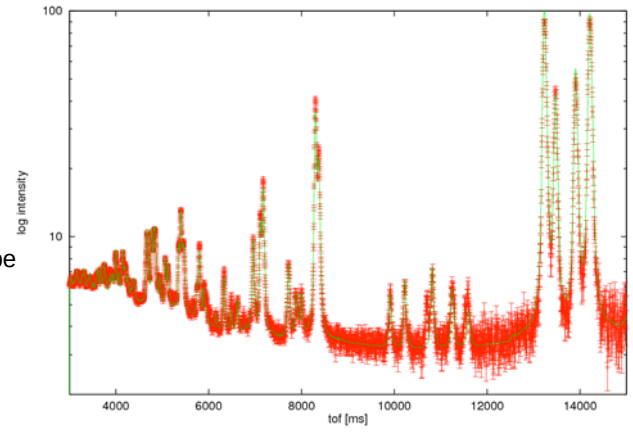
Figure 1. Schematic diagram of the POLARIS diffractometer

Structure refinement

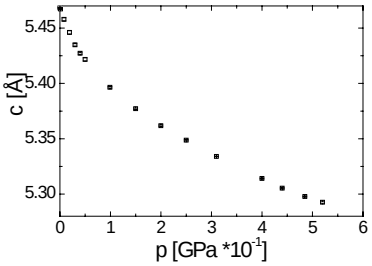
TF14LS

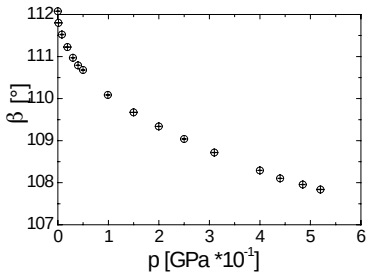
Cambridge Crystallographic Subroutine Library

specialised peak shape function

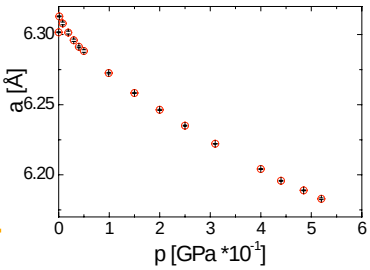


NaN_3 cell parameters

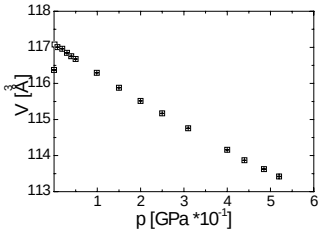




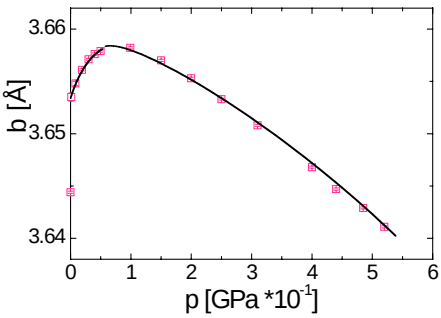
monoclinic plane,
shear



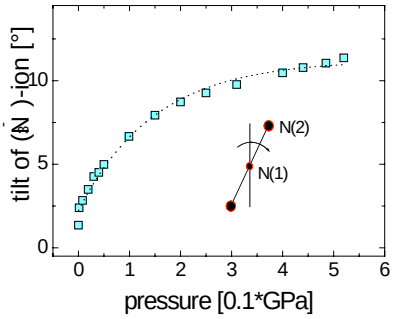
NaN_3 cell parameters

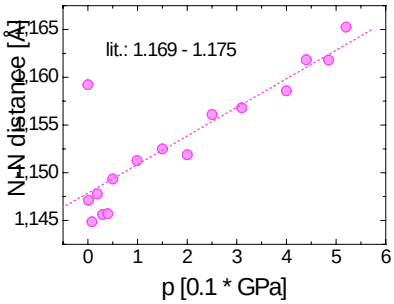


equation of state,
elastic anomaly in b



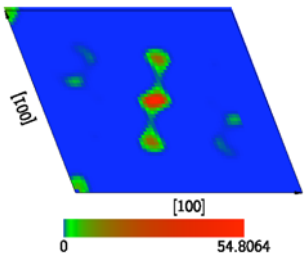
NaN_3 structure

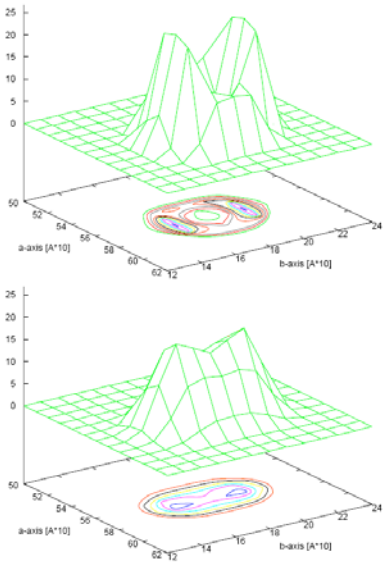




- tilt of the N_3 from its vertical orientation
- N-N distances short
  unusual ADP's ! disorder of N_3

N_3- disorder





- scattering density maps
- calculated from neutron powder data (POLARIS)

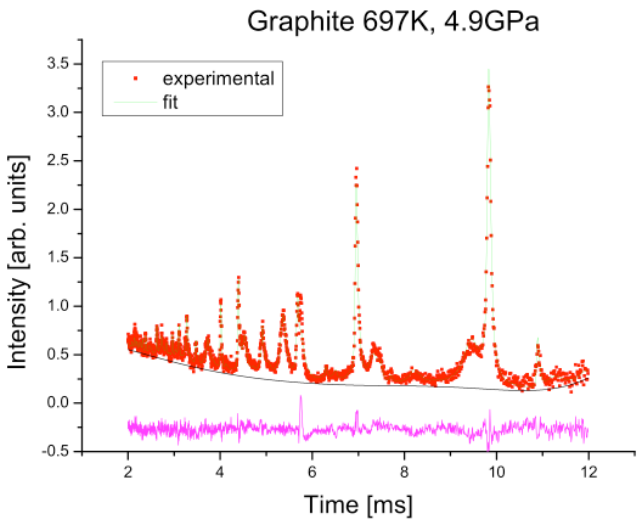
- ***p***-dependent out of monoclinic ***ac***-plane displacement of N_3

Outline

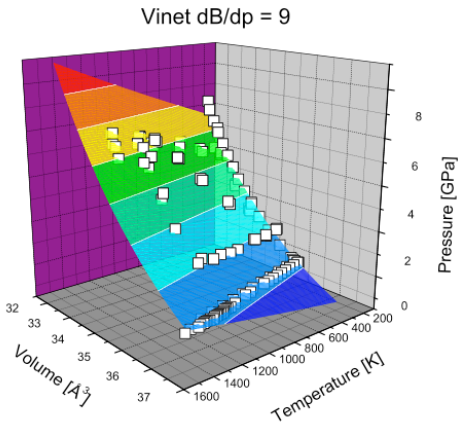
- General aspects
- low Z elements
  - Protons, $C_4A_3H_3$
- neighboring elements
  - Si/Al order / disorder
  - Co,Mn-cordierite
- extreme conditions
  - high p, NaN_3
  - high pT, Graphite

High PT EOS

- PE cell
- ISIS Pearl
- LANSCE
- Smarts / HT



Graphite



Parameter	HTBMAG
Volume (Å^3)	74.76(0.01)
B_0 (GPa)	159.9(3.0)
$(\partial B_{0T}/\partial T)_P$ (GPa K^{-1})	-
$(\partial B/\partial P)$	3.0(1.0)
a (10^{-5} K^{-1})	4.16(0.05)
b (10^{-9} K^{-2})	5.0(1.0)
δ_T	3.8(0.3)
γ	2.02(0.08)

Lowitzer, Winkler, Tucker (2006) PRB

Take home message

- neutrons are good for minerals containing:
  - light / neighboring elements
  - heavy next to light elements
  - high-pressure / high-temperature
- Rietveld (full pattern) for cell parameters, precise crystal structure, quant. phase analysis, orientational disorder
- complimentary to other methods

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