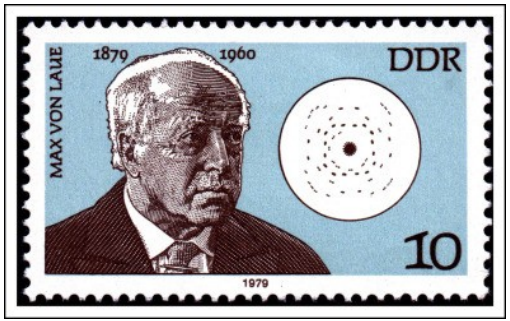
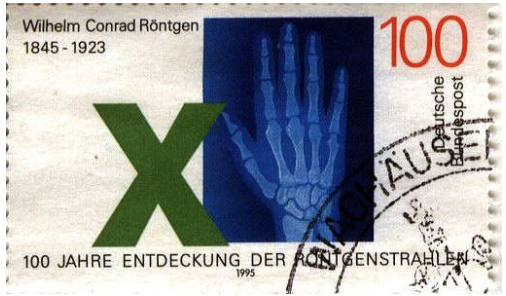
Strukturaufklärung in der molekularen anorganischen Chemie

10. Röntgen- und Neutronendiffraktometrie

Themen

- Röntgenbeugung am Einkristall
- Pulverdiffraktion
- Neutronendiffraktion
- Diffraktion an Flüssigkeiten
- Molekül(e) des Tages





Röntgen- und Neutronenbeugung

γ-ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmw	mm-wave	Micro-wave	Radio-wave	
← < 0.1 Å	5 Å	100 Å 10 nm	2000 Å 200 nm	400 nm	0.7 µm 700 nm	2.5 µm 2500 nm	25 µm		1 mm		10 cm	→	λ
$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400		10		0.1		$\tilde{\nu}$ / cm^{-1}
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8		0.12		1.2×10^{-3}		E / kJ mol^{-1}
120 000	2400	120	6	3	1.7	0.5	0.05		0.001		0.00001		E / eV
3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}		3×10^{11}		3×10^9		ν / Hz

λ ~ **0.5** – **2.5** Å (XRD); ~ **0.5** – **5.0** Å (ND)

XRD, ND

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

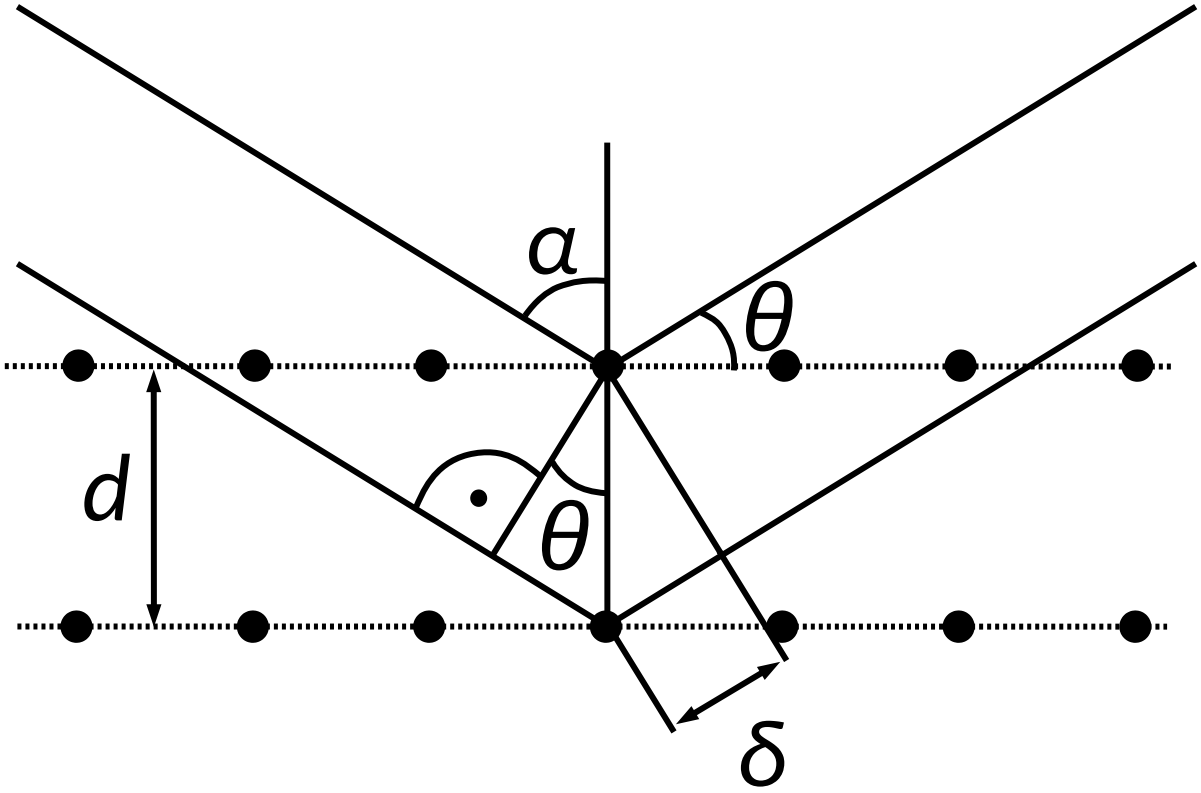
Charakteristische Zeit:

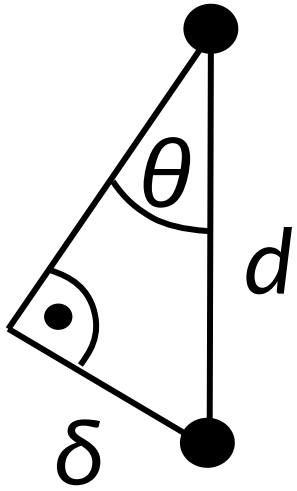
- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

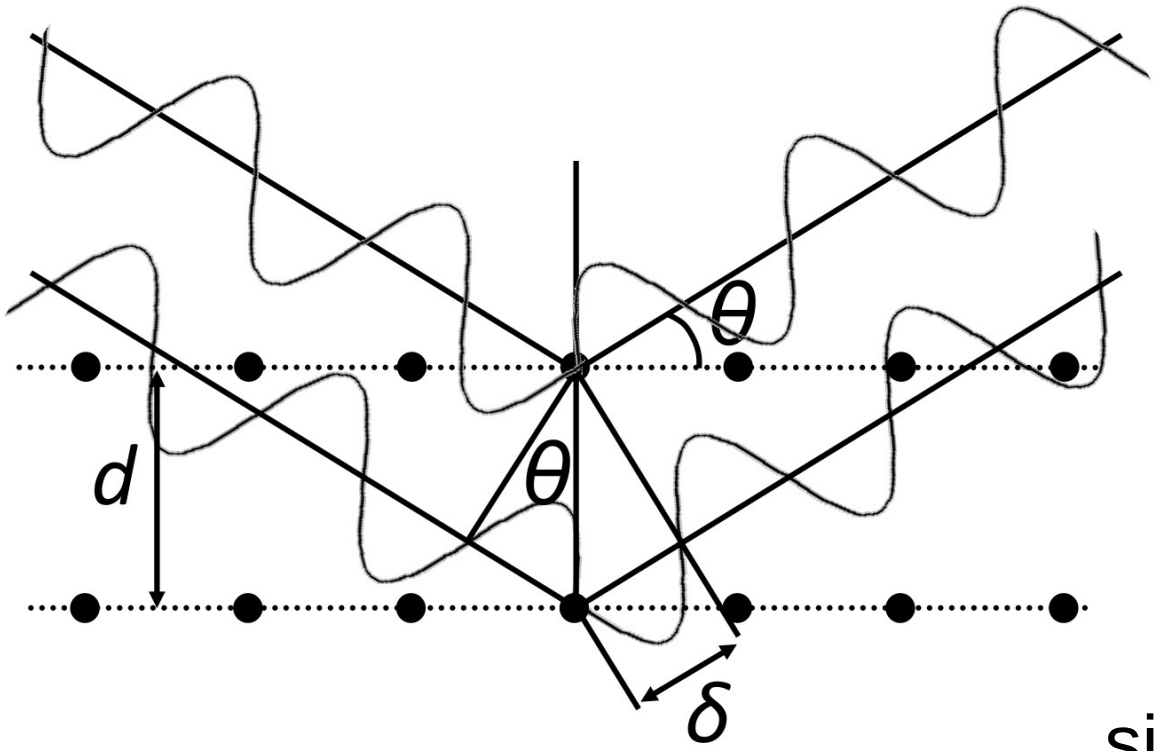
- Gas
- Flüssigkeit
- Feststoff

Beugung: die Bragg‘sche Gleichung





Beugung: die Bragg‘sche Gleichung



Laufunterschied: 2δ

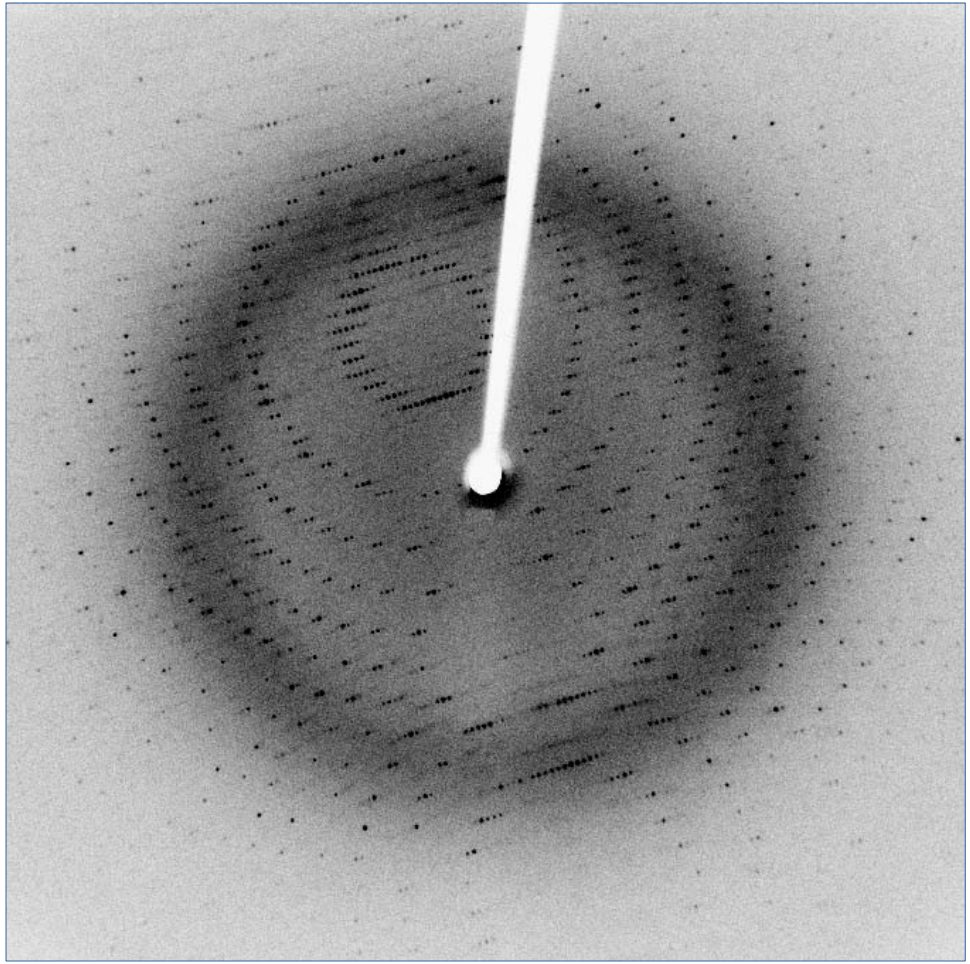
Für konstruktive Interferenz:

$\lambda = 2\delta = 2d \sin(\theta)$

$$\boxed{n\lambda = 2d \sin(\theta)}$$

$\sin(\theta) \leq 1 \rightarrow \lambda \leq 2d/n$

XRD Beugungsbild

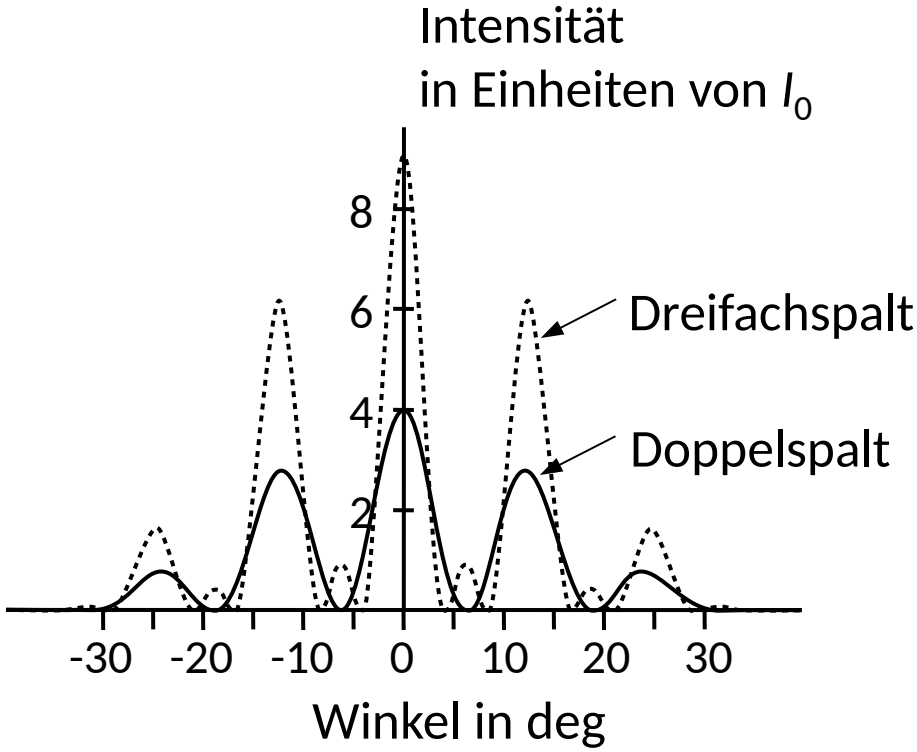


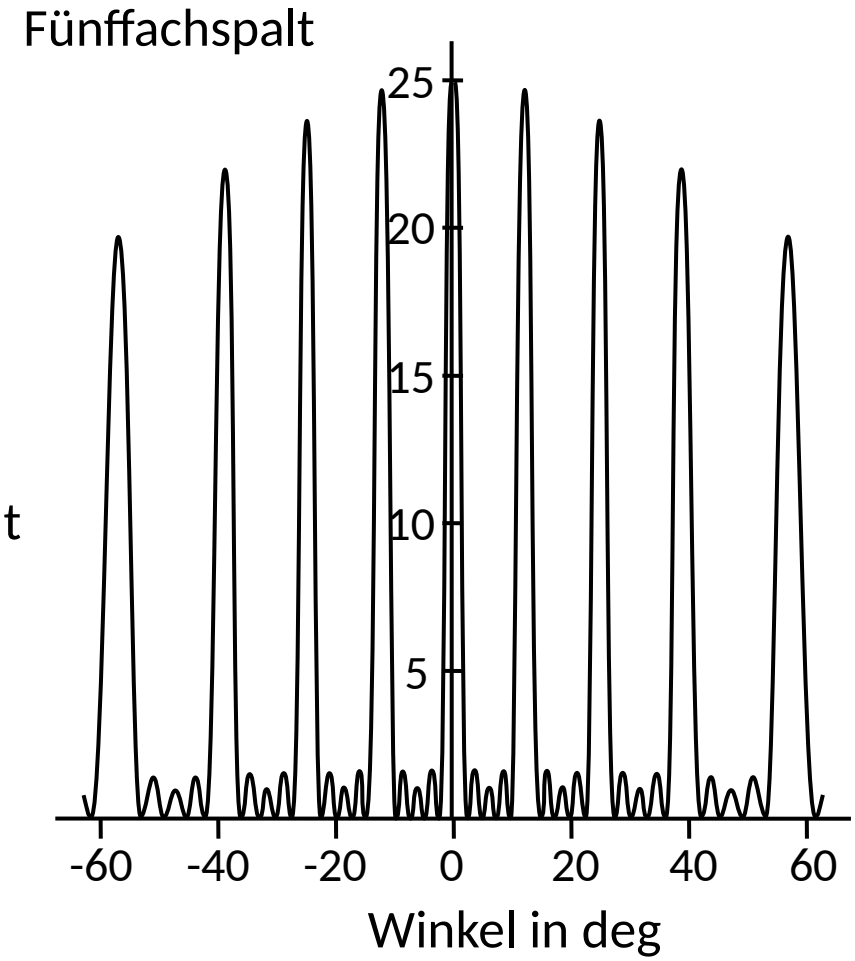
Schwarze Punkte: Reflexe (Beugung am Einkristall wegen passender Bedingungen λ, d, θ)

Diffuser Hintergrund: Beugung an amorphen Phasen, inelastische Beugung, ungleichmäßige Absorption

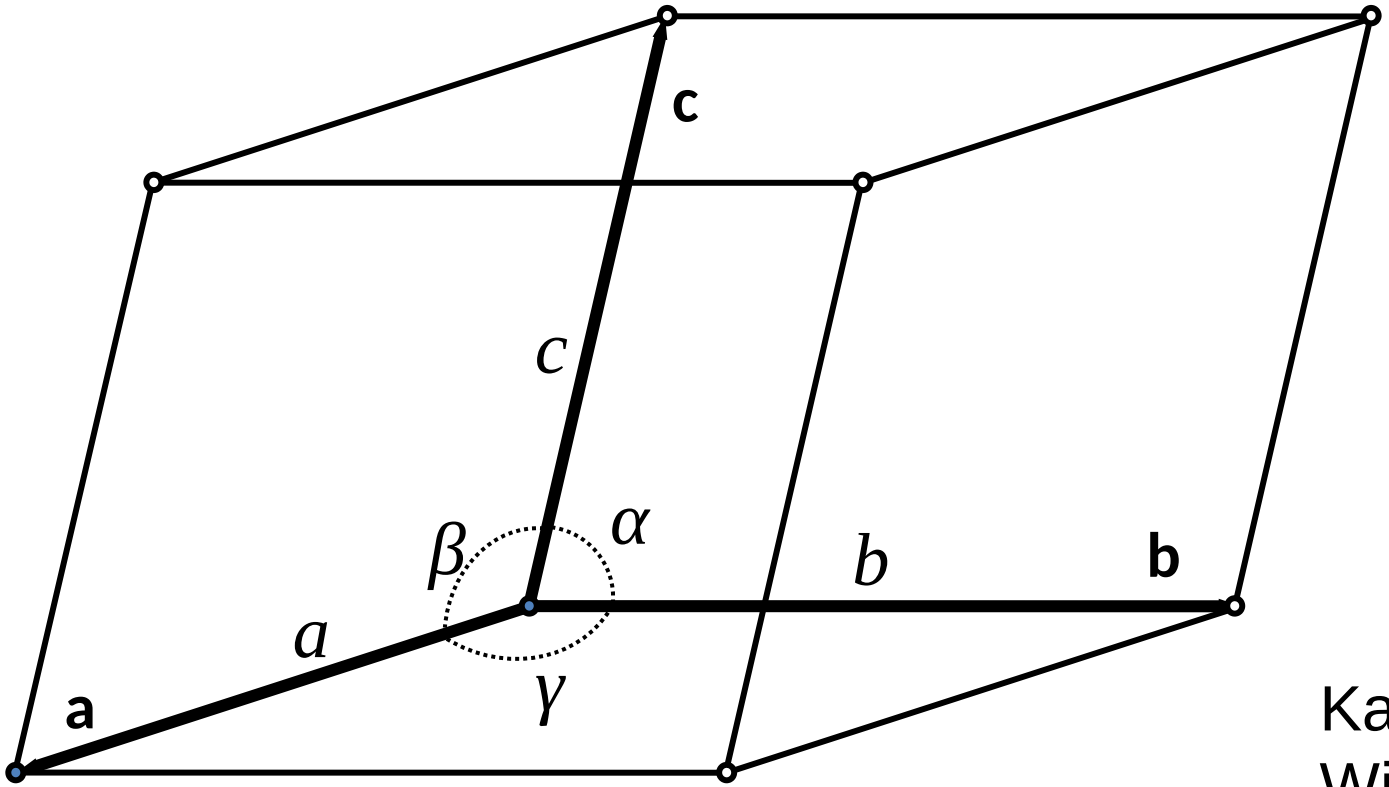
Weiße Figur: Schatten vom Beamstop

Vom Doppelspalt zum Gitter



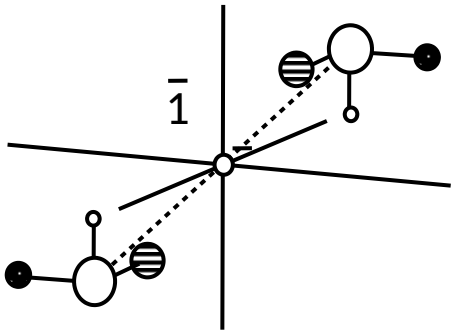


Aufbau von Kristallen: die Einheitszelle

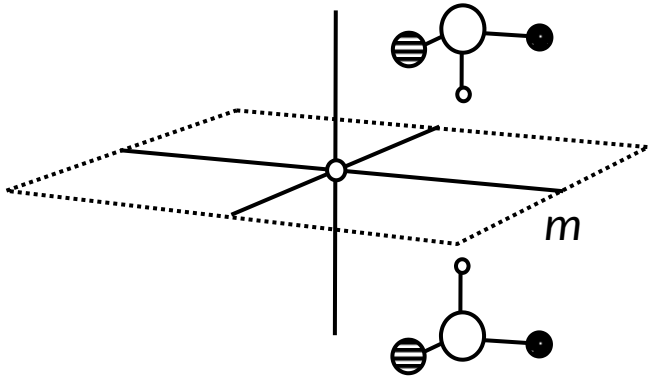


Kantenlängen a, b, c
Winkel α, β, γ
Gittervektoren **a**, **b**, **c**

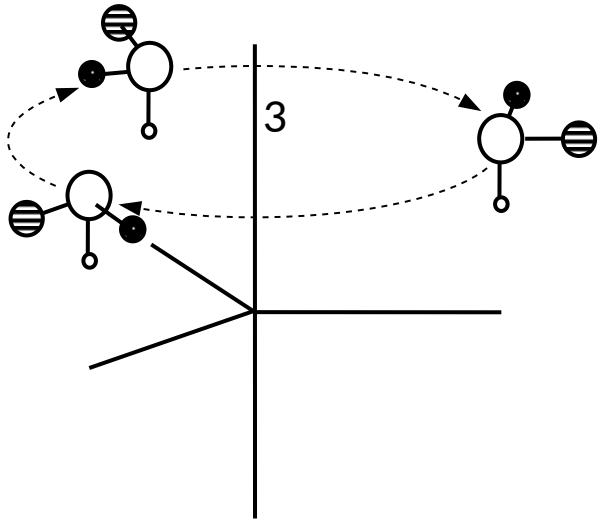
Einfache Symmetrielemente



Inversionszentrum
$\bar{1}$ (i)



Spiegelebenen
m (σ)

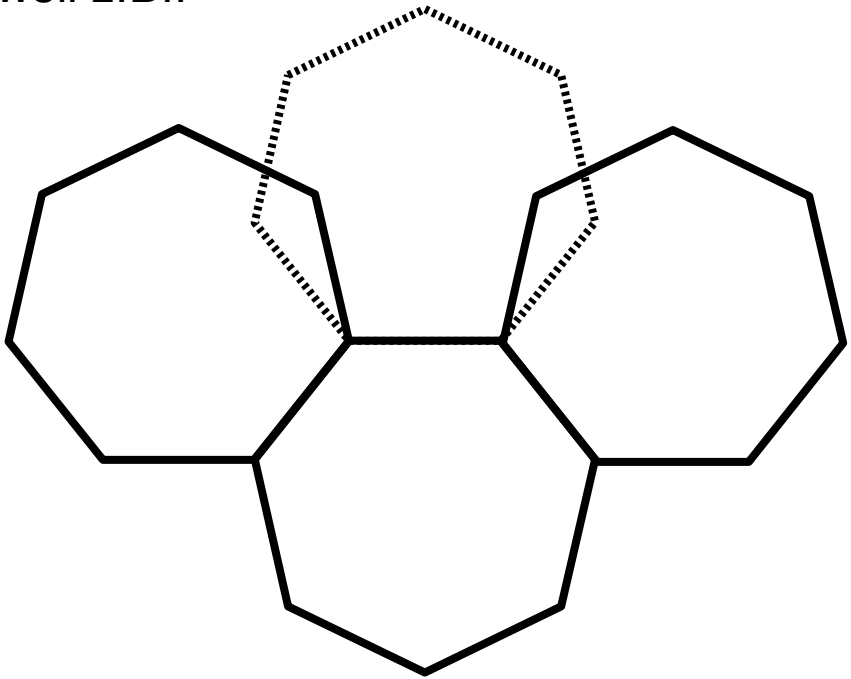


Drehachsen
2, 3, 4, 6 (C_n)

Herrmann-Mauguin-Nomenklatur
(Schöfließ-N. in Klammern)

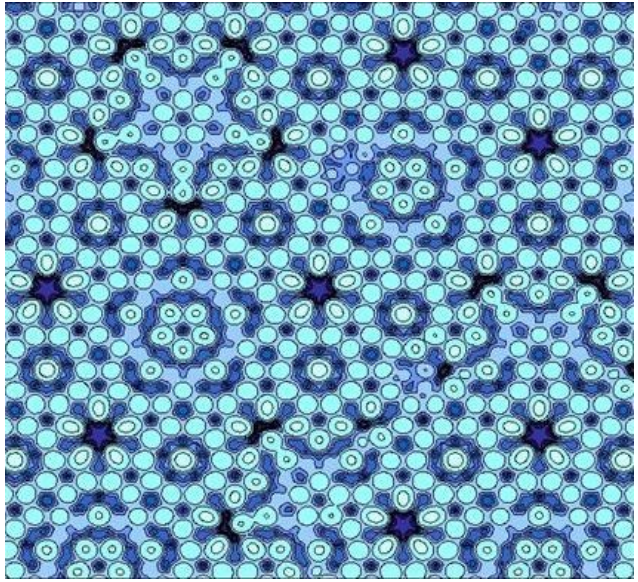
Fünf- und siebenzählige Achsen

Nicht möglich in normalen Kristallen,
weil z.B.:



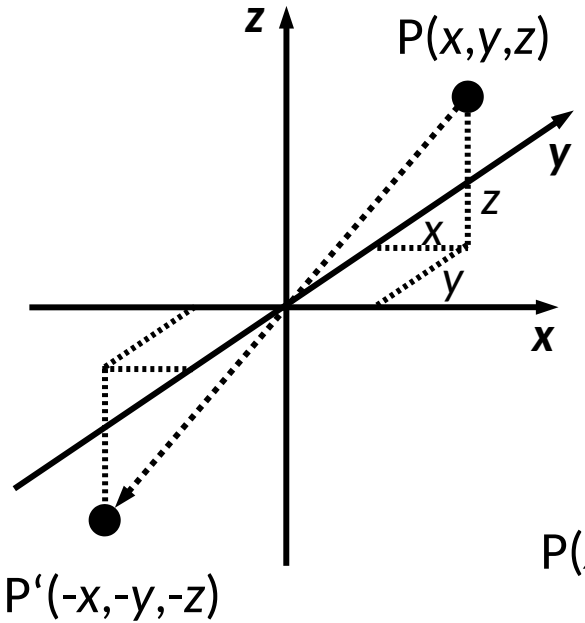
(s. Parkettierung von euklidischen Ebenen in Mat.)

Aber möglich in Quasikristallen!
(Dan Shechtman, Chemie-Nobelpreis, 2011)

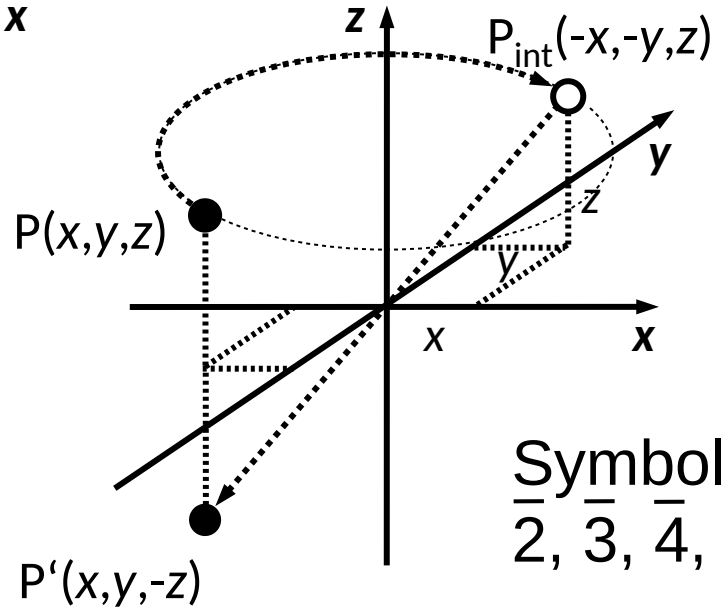


Kombinierte Symmetrielemente

Inversion

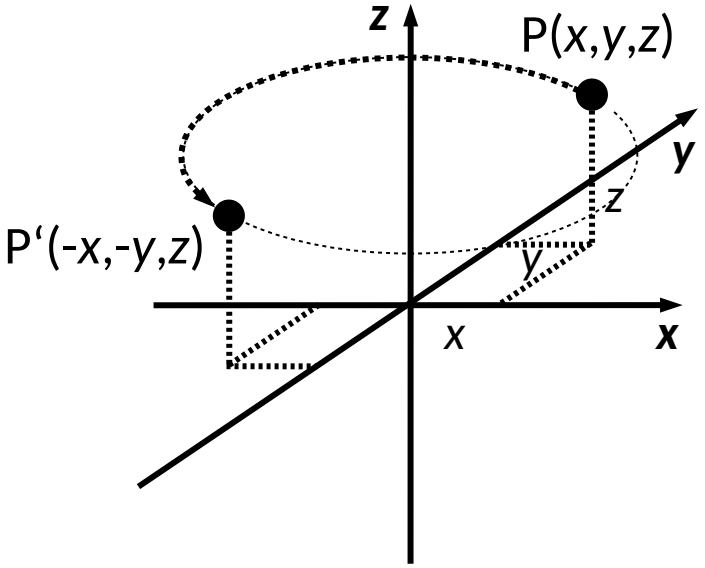


Inversion-Rotation



Rotation

(z. B. um ½ von 360°)



Symbol:

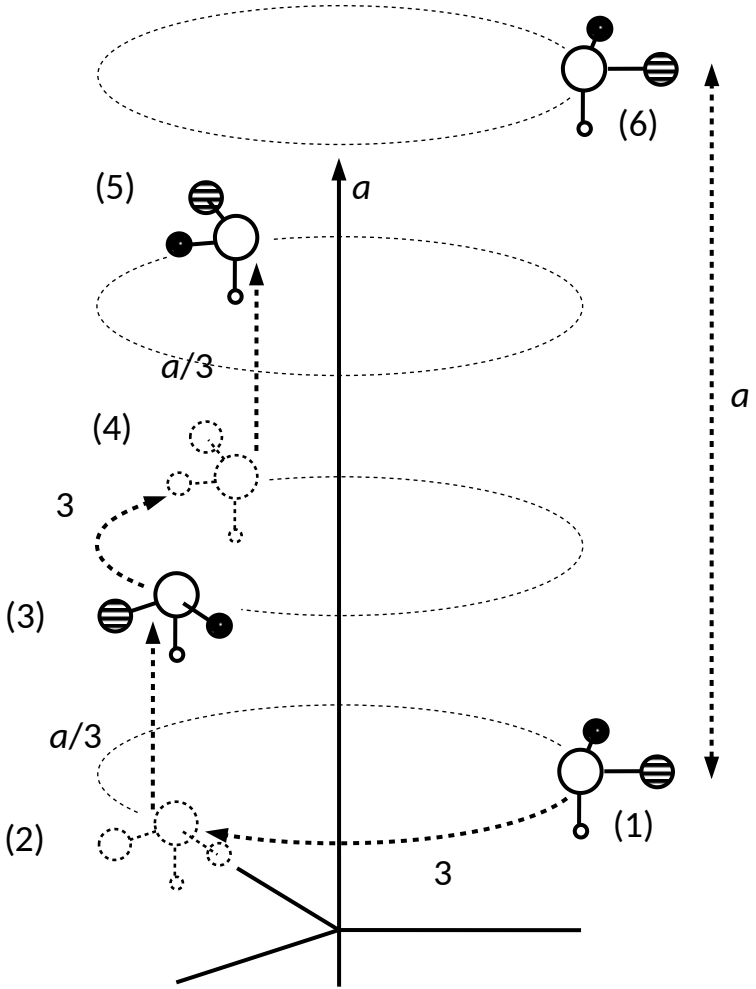
$\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$

P_{int} = intermediäre, nicht realisierte Position

Achsenabschnitte

Transformation

Kombinierte Symmetrielemente



Schraubenachse

Kombination aus
n-facher Rotation mit Translationselement

Nomenklatur n_m
m Translation entlang
einer Achse um *m*/*n*

← Beispiel
3_1 : nächstes Objekt
gedreht um 120°
translatiert um ⅓ des Gittervektors

Mögliche Schraubenachsen:
2_1, 3_1, 4_1, 4_2, 6_1, 6_2, 6_3.

Kombinierte Symmetrielemente

Gleitspiegelebene

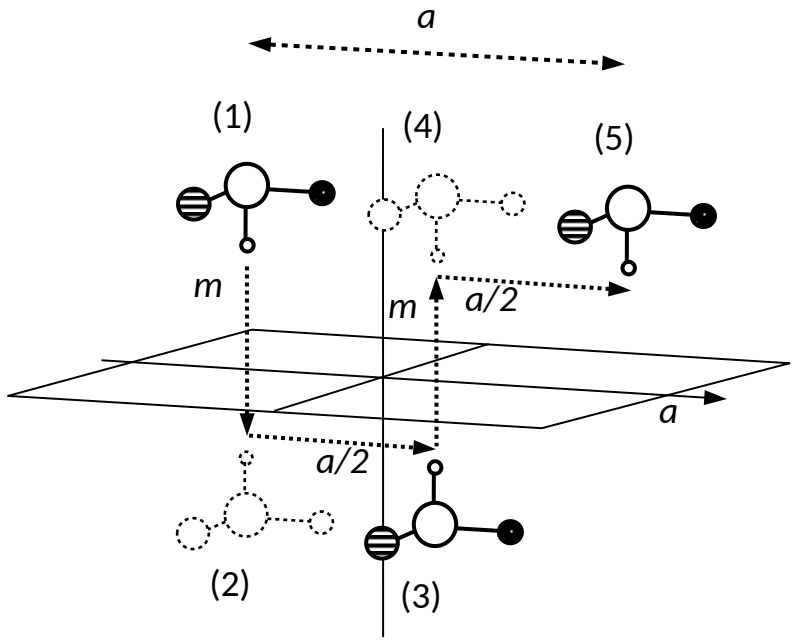
Kombination aus
Spiegelung *m* mit Translationselement

Nomenklatur *a, b, c*
Spiegelung und Translation um ½ des Gittervektors

Bei Wiederholung:
Resultat nur Translation

n : Gleiten entlang der Flächendiagonale
d : ¼ … der Flächendiagonale
e : ½ … der Flächendiagonale

Beispiel: *a*



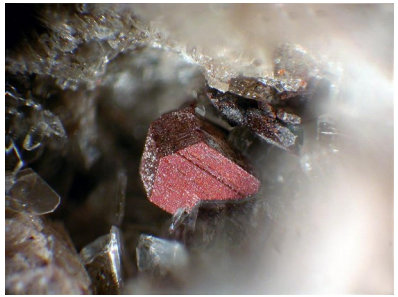
7 Kristallsysteme

Kristallsystem	Achsen- und Winkel-Dimensionen	Minimale Symmetrie	Laue Gruppe (Symmetrie des Beugungsbilds)	Bravais-Gitter	Kristallographische Punktgruppen	Übliche Raumgruppen
Triklin	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	–	$\bar{1}$	P	$1, \bar{1}$ (C_1, C_i)	$P\bar{1}$
Monoklin	$a \neq b \neq c$ $\alpha = \gamma = 90°, \beta \neq 90°$	$2 \parallel b$ oder $m \perp b$	$2/m$	P, C	$2, m, 2/m$ (C_2, C_s, C_{2h})	$P2_1$, $C2/c$, $P2_1/c$
Ortho-rhombisch	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	2,2,2 oder mmm	mmm	P, C, I, F	$222, mm2, mmm$ (D_2, C_{2v}, D_{2h})	$P2_12_12_1$, $Pbca$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$4 \parallel c$	4/mmm	P, I	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$ $(C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h})$	$I4/mmm$
Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$	$3 \parallel c$	$\bar{3}$m	P, I, F	$3, \bar{3}, 32, 3m, \bar{3}m$ $(C_3, S_6, D_3, C_{3v}, D_{3d})$	$R\bar{3}m$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	$6 \parallel c$	6/mmm	R	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$ $(C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h})$	$Pm3m$, $Fm3m$, $Fd3m$
Kubisch	$a = b = c$ $\alpha = \beta = \gamma = 90°$	$3 \parallel [111]$	$m3m$	P	$23, m3, 432, 43m, m3m$ (T, T_h, O, T_d, O_h)	$P6_3/mmc$

Kristalle und Kristallsysteme

trikliner Rhodonit
$Mn^{2+}SiO_3$

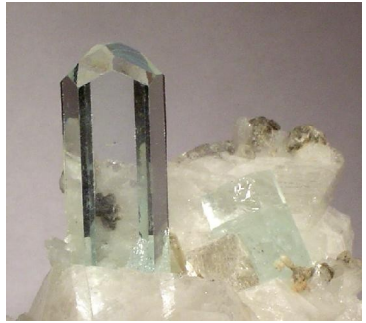
monokliner Vivianit
$Fe^{2+}{}_3[PO_4]_2 \cdot 8H_2O$



orthorhombischer
Fayalit $Fe_2{}^{2+}[SiO_4]$

tetragonaler
Anatas TiO_2

trigonaler Hämatit Fe_2O_3



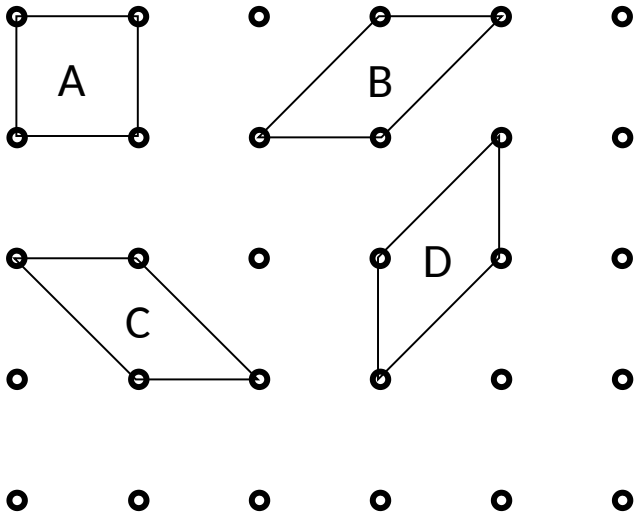
hexagonaler Beryll $Al_2Be_3[Si_6O_{18}]$

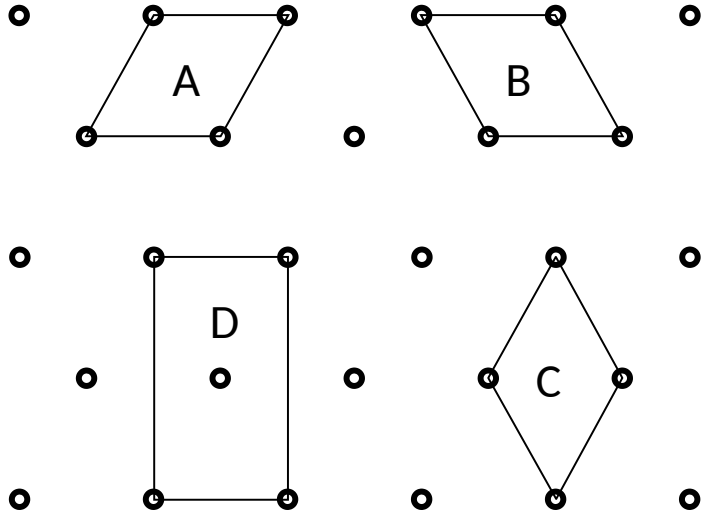
kubischer Spessartin
$Mn_3Al_2[SiO_4]_3$

Quelle: https://de.wikipedia.org/wiki/Kristallsystem

Wahl der Einheitszelle

Hypothetische Beispiele in 2 Dimensionen

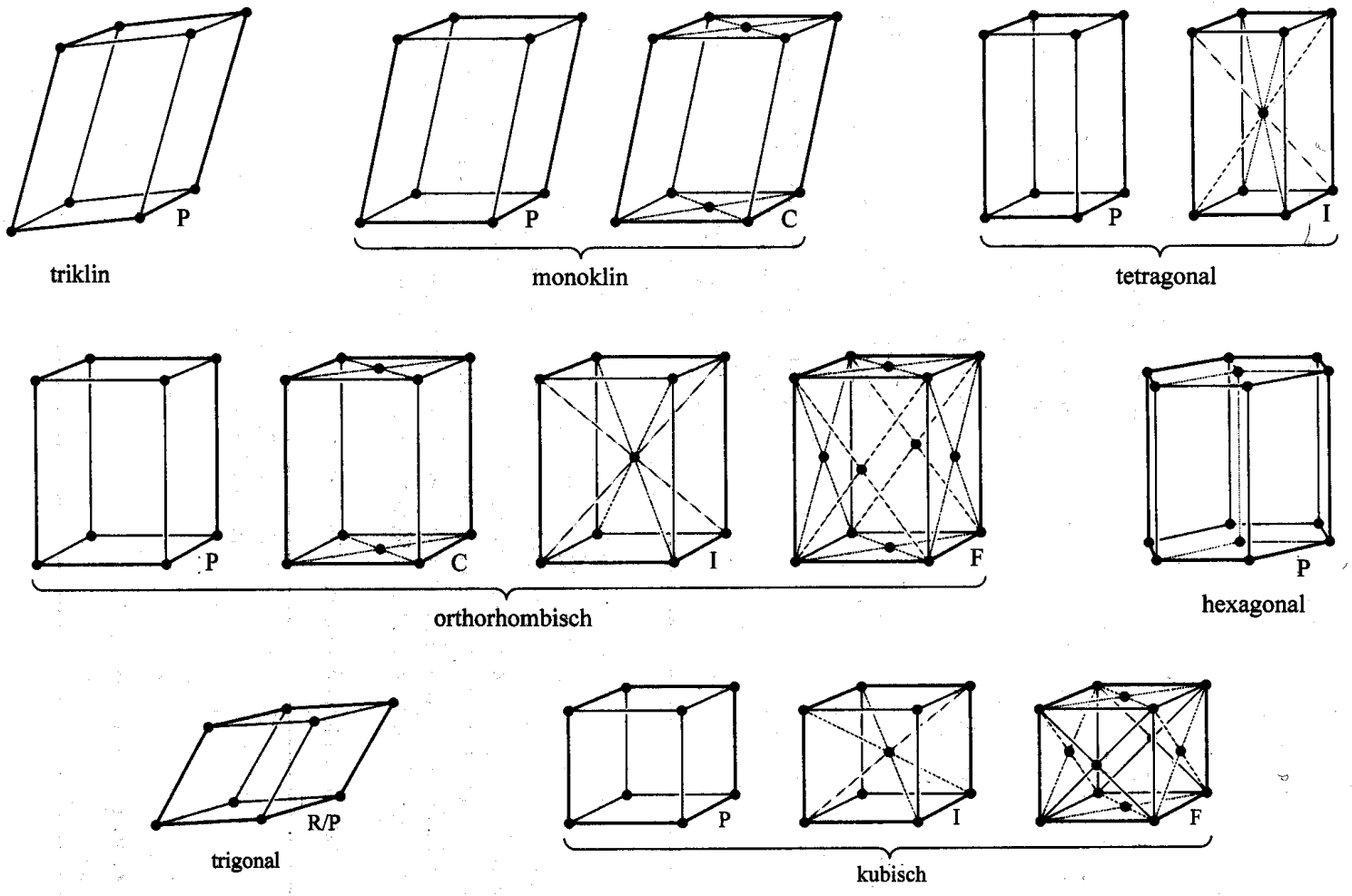




Die am besten geeignete primitive Zelle (A)

Hier wird eine zentrierte Zelle (D) Bevorzugt, da sie die Symmetrie am besten widergibt

Die 14 Bravais-Gitter



7 Kristallsysteme

+

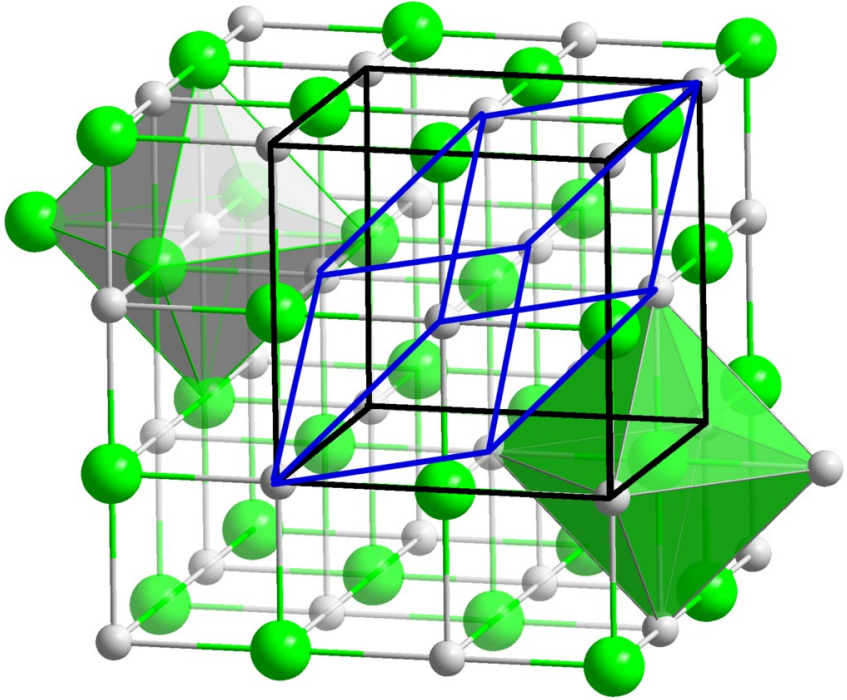
Translationen
(Zentrierungen)

14 Bravais-Gitter

P – primitiv
C – basiszentriert
I – raumzentriert
F – flächenzentriert

Bravais-Gitter

Halit (NaCl)



Rhomboeder (blau): kleinstmögliche Zelle

Elementarzelle (schwarz): kubisch F

Kristallsystem: kubisch
Raumgruppe: $Fm\bar{3}m$

Symmetrie: Zusammenfassung

7 Kristallsysteme

+ Translationen
(Zentrierungen)

14 Bravais-Gitter

Nicht-translative Symmetrieoperationen
(Rotationen, Spiegelungen, ...)

32 kristallographische Punktgruppen

+ Gleitspiegelebenen,
+ Schraubenachsen

230 kristallographische Raumgruppen

Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Pnma

eine Abkürzung für $\boldsymbol{P}\ \frac{\mathbf{2_1}}{\boldsymbol{n}}\ \frac{\mathbf{2_1}}{\boldsymbol{m}}\ \frac{\mathbf{2_1}}{\boldsymbol{a}}$

Bedeutet:

- Einheitszelle ist primitive Zelle *P* (ohne Zentrierung)
- 2_1 Schraubenachsen entlang aller drei Vektoren ***a***, ***b*** und ***c***
- Diagonale Gleitspiegelebene *n* senkrecht zu ***a***
  mit Gleitrichtung entlang des Vektors (***b***+***c***)
- Spiegelebene senkrecht zu ***b***
- Gleitspiegelebene senkrecht zu ***c*** mit Translationskomponente entlang ***a***.

Selbst hier nicht alle Symmetrielelemte gezeigt

Vollständig: International Tables for Crystallography, Vol. A

Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

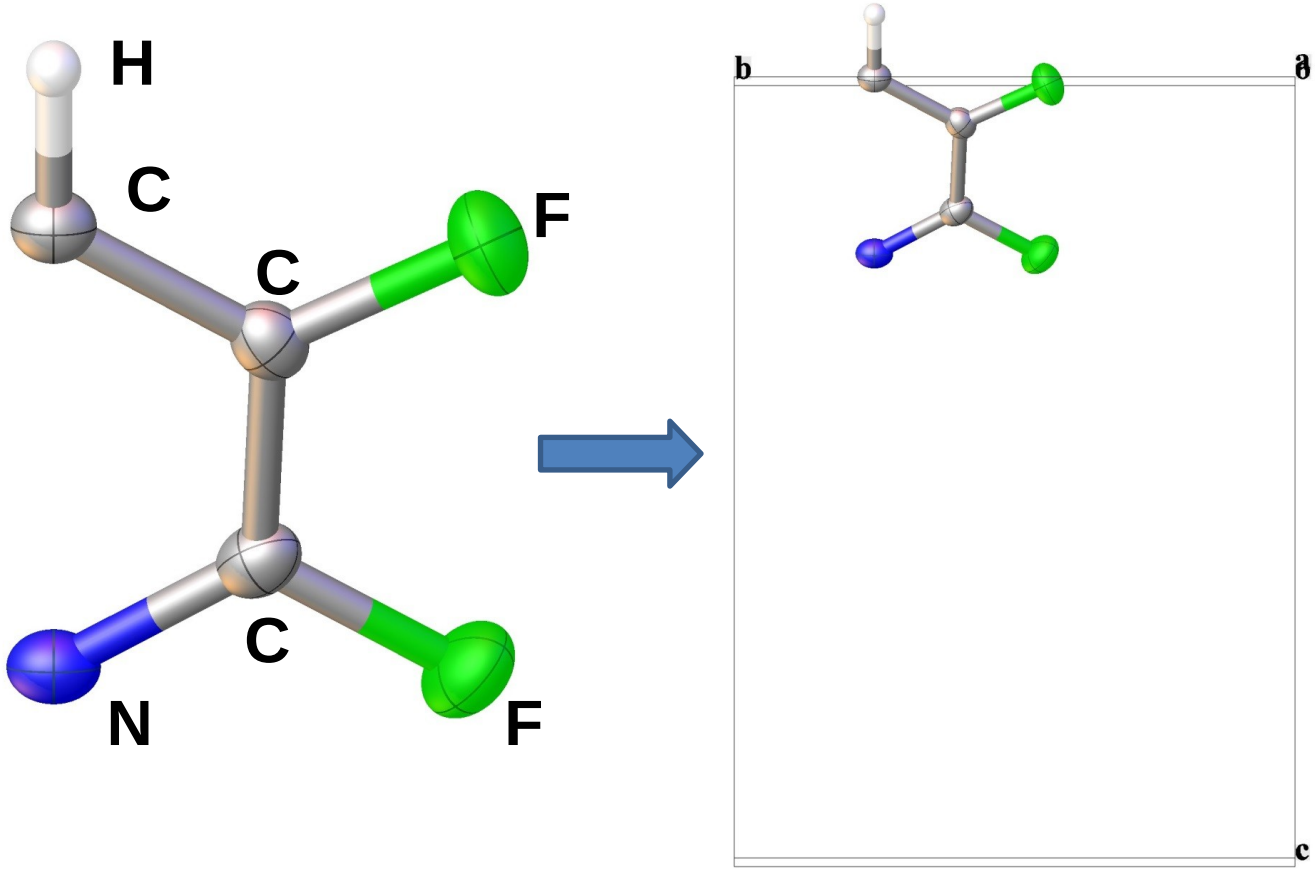
Pnma No. 62

Symmetry Operators			Reflection Conditions
1 x, y, z	1		(general)
2 $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$	n	$(\frac{1}{4}, y, z)$ $[0, \frac{1}{2}, \frac{1}{2}]$	$0kl: \; k+l=2n$
3 $x, \frac{1}{2}-y, z$	m	$(x, \frac{1}{4}, z)$	$hk0: \; h=2n$
4 $\frac{1}{2}+x, y, \frac{1}{2}-z$	a	$(x, y, \frac{1}{4})$ $[\frac{1}{2}, 0, 0]$	$h00: \; h=2n$
5 $\bar{x}, \bar{y}, \bar{z}$	$\bar{1}$	$(0, 0, 0)$	$0k0: \; k=2n$
6 $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$	2_1	$(x, \frac{1}{4}, \frac{1}{4})$ $[\frac{1}{2}, 0, 0]$	$00l: \; l=2n$
7 $\bar{x}, \frac{1}{2}+y, \bar{z}$	2_1	$(0, y, 0)$ $[0, \frac{1}{2}, 0]$	
8 $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	2_1	$(\frac{1}{4}, 0, z)$ $[0, 0, \frac{1}{2}]$	

International Tables

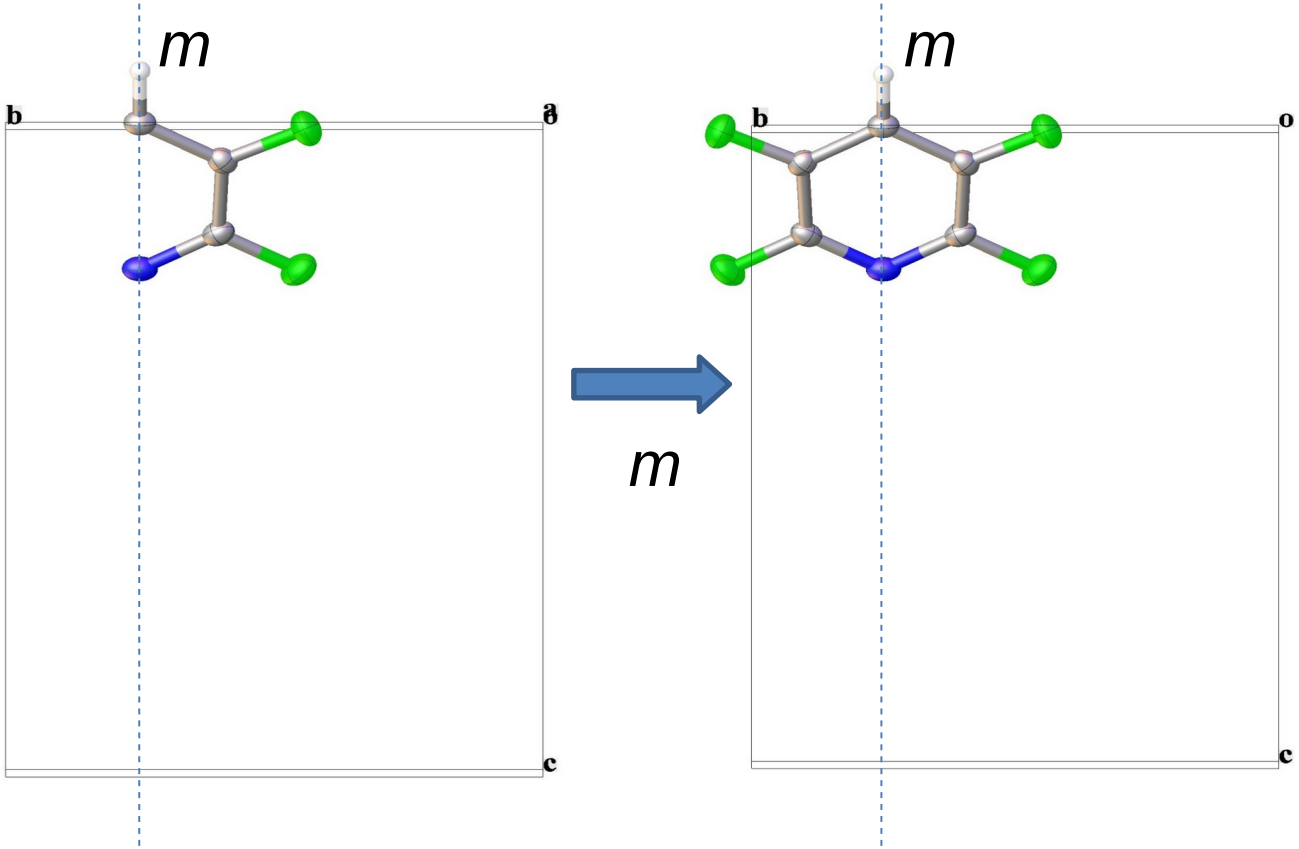
Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Asymmetrische Einheit (Blick entlang a)



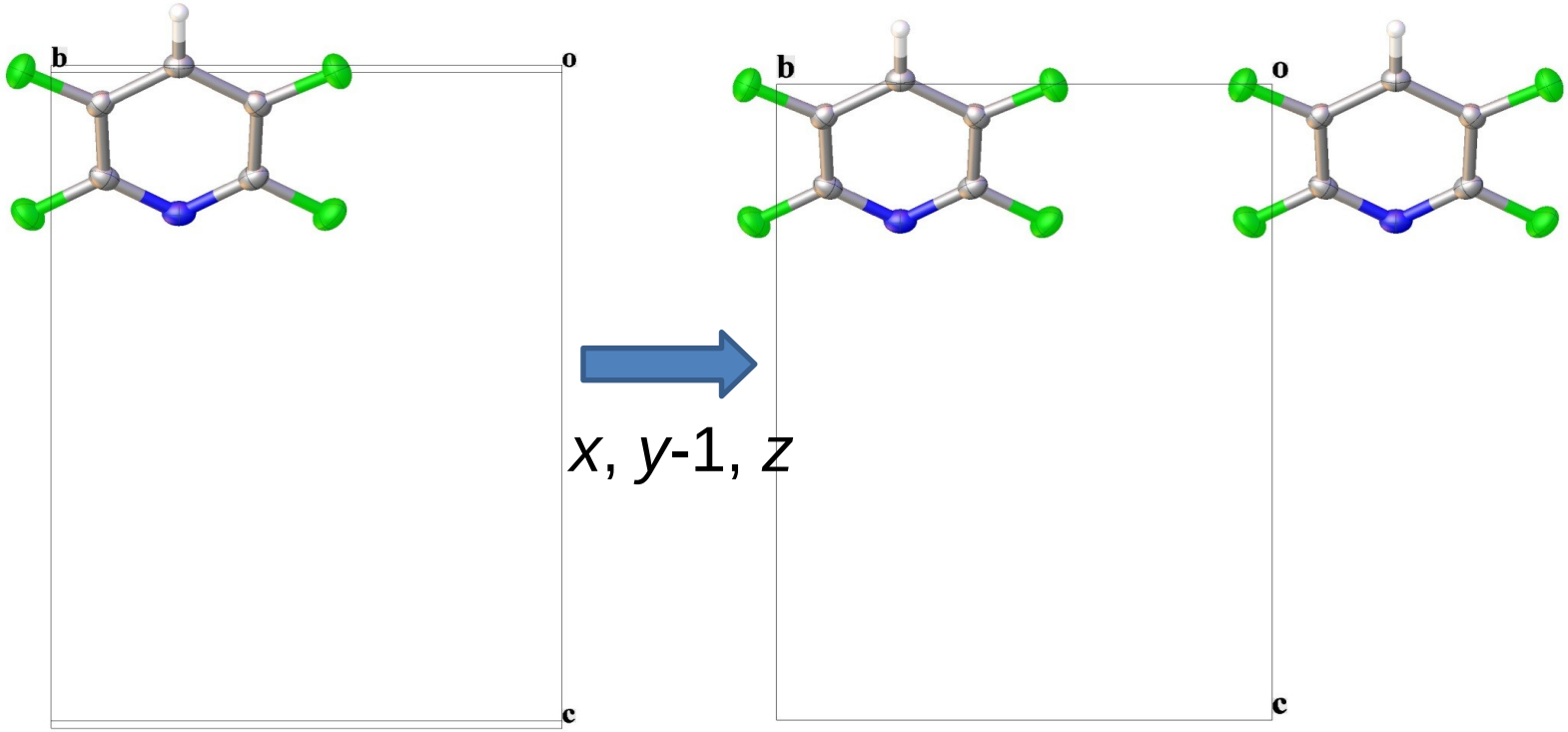
Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Anwendung eines Symmetrieelementes



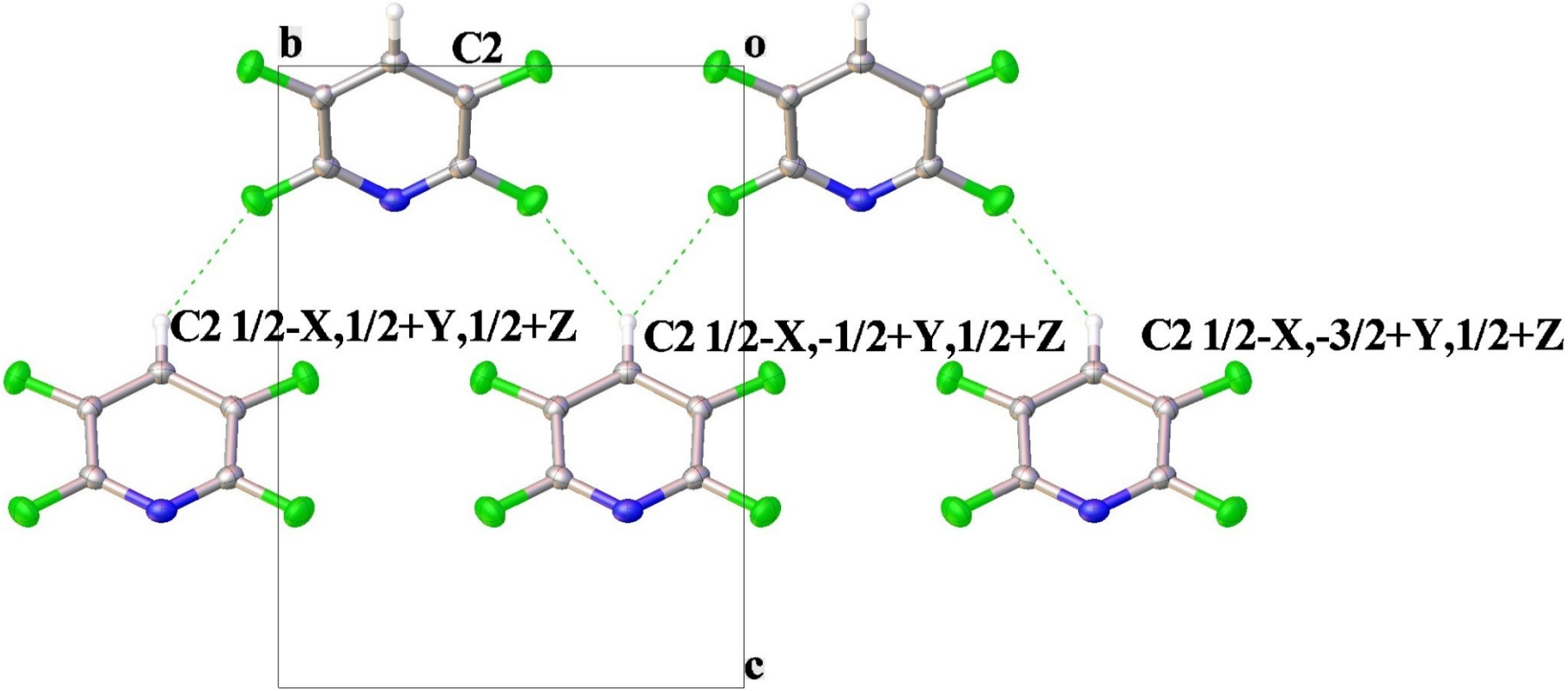
Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Anwendung der Translation



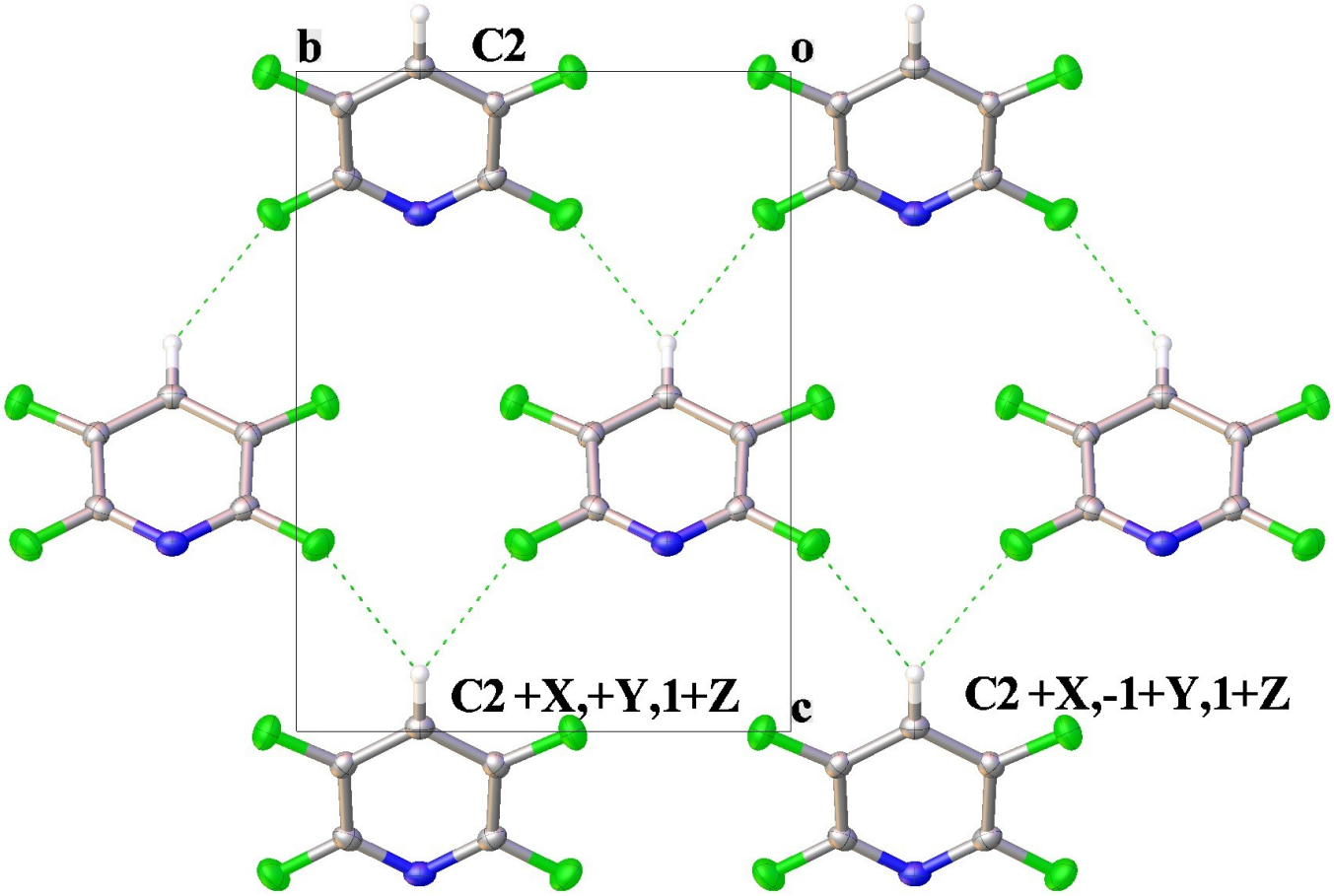
Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Weitere Symmetrieoperationen



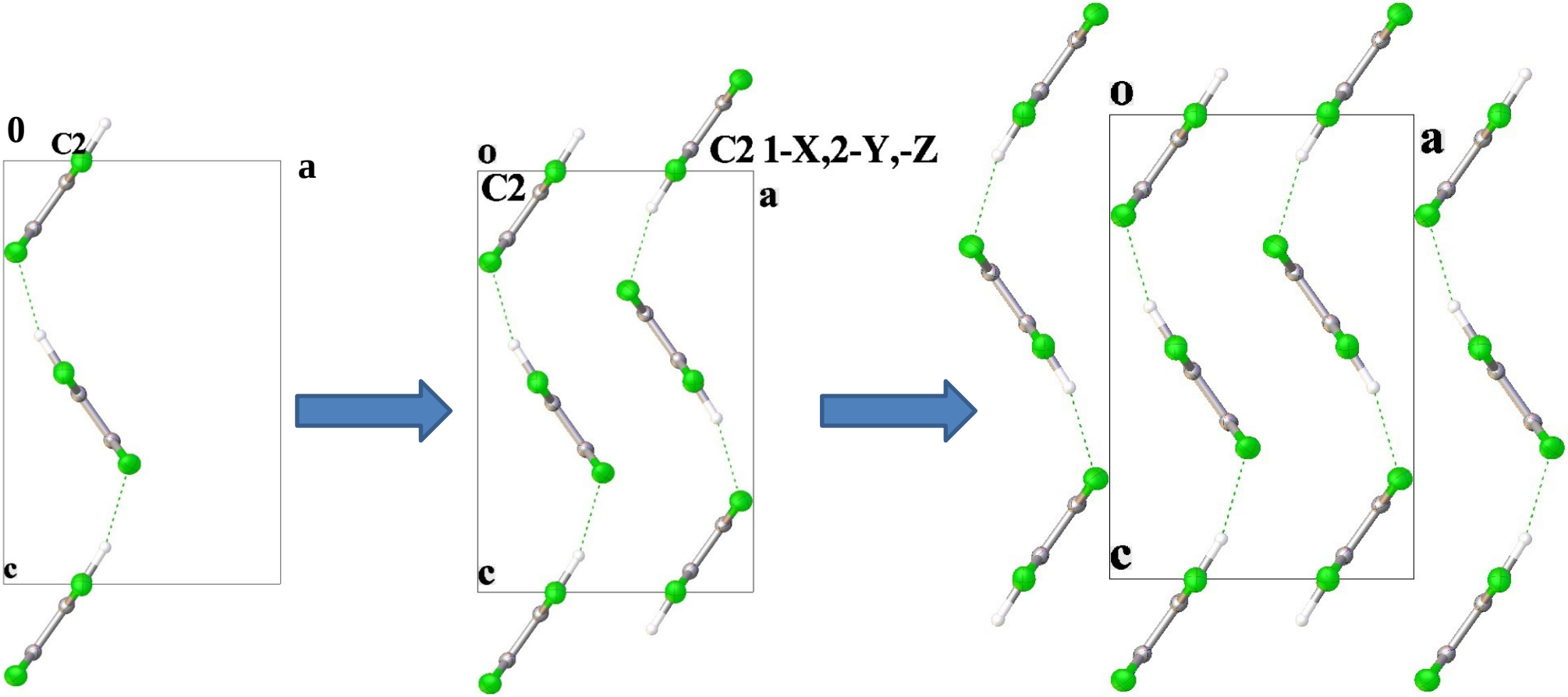
Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Vervollständigung



Ein Beispiel: 2,3,5,6-Tetrafluorpyridin

Andere Perspektive (Blick entlang b)



Durchführung eines Experimentes

Kristallzucht

↓

Kristall-Präparation (Auswahl, ggf. Schnitt, Montage)

↓

Indizierung und Bestimmung der Einheitszelle (+ ihre Orientierung)

↓

Bestimmung der Zell-Symmetrie

↓

Daten-Sammlung

↓

Daten–Reduktion, dabei Berücksichtigg. von Absorption und Extinktion

↓

Daten-Analyse: Struktur-Lösung

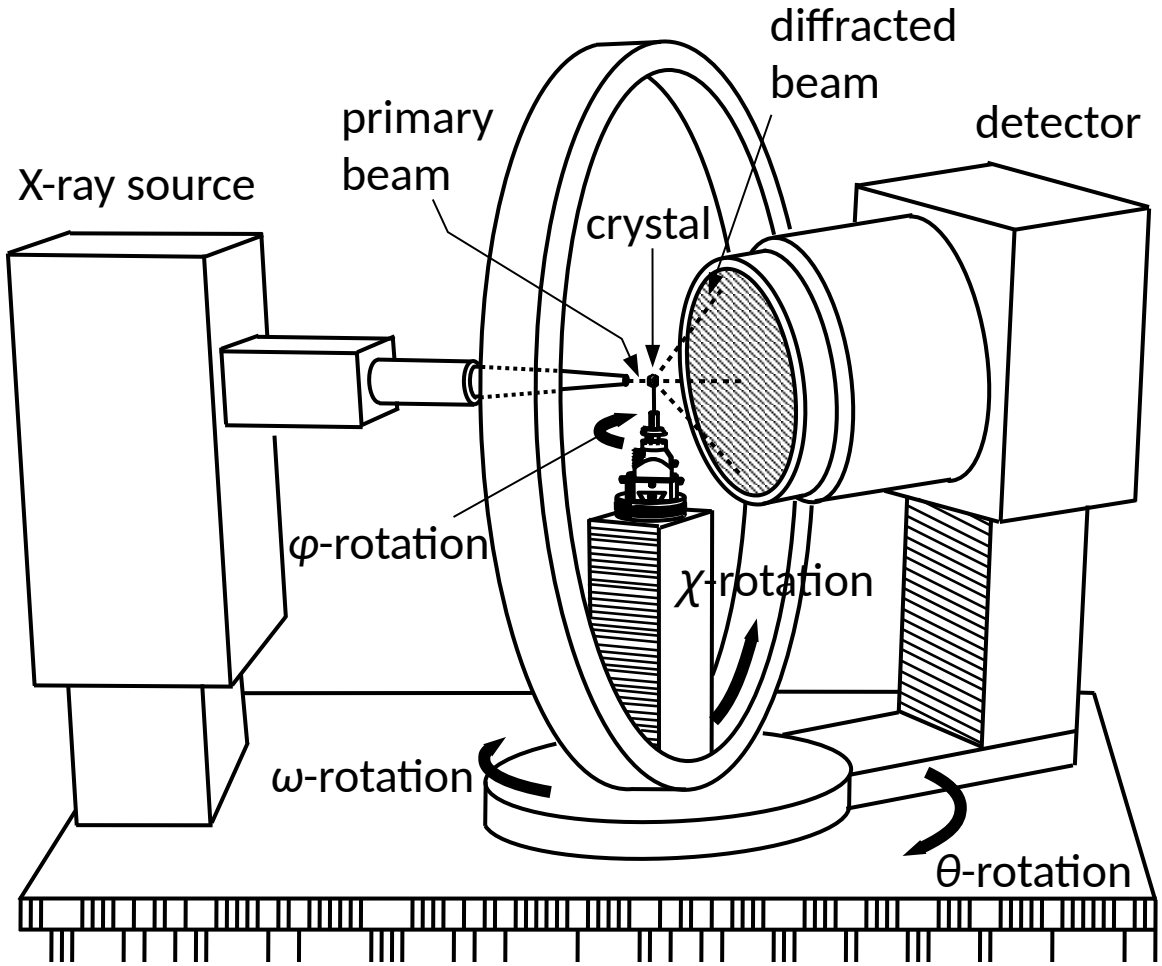
↓

Daten-Analyse: Struktur-Verfeinerung

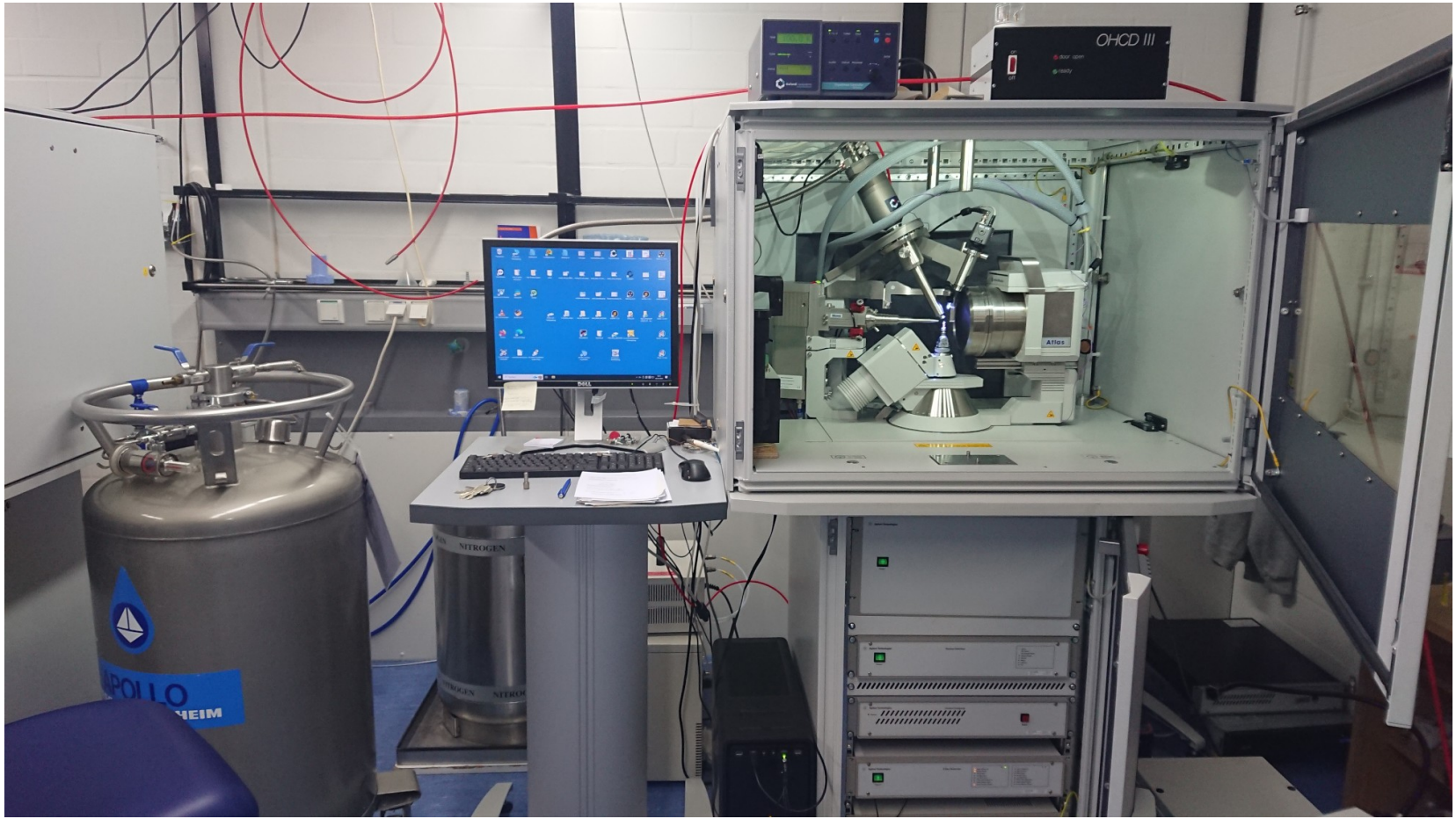
↓

Daten-Nachbehandlung und Dokumentation

Diffraktometer

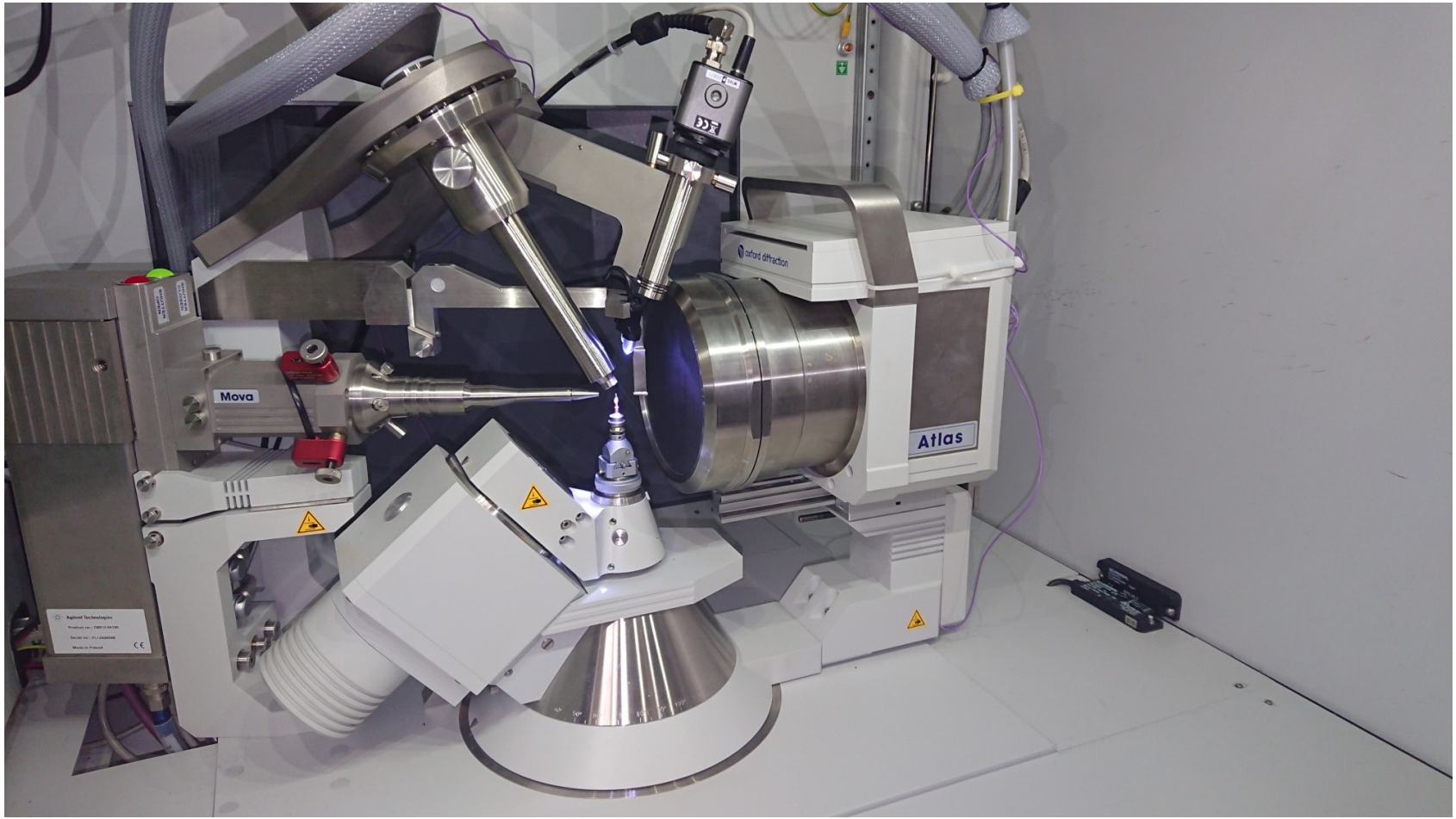


Diffraktometer



Rigaku Supernova Diffractometer @ Uni-Bielefeld (AK Mitzel)

Diffraktometer

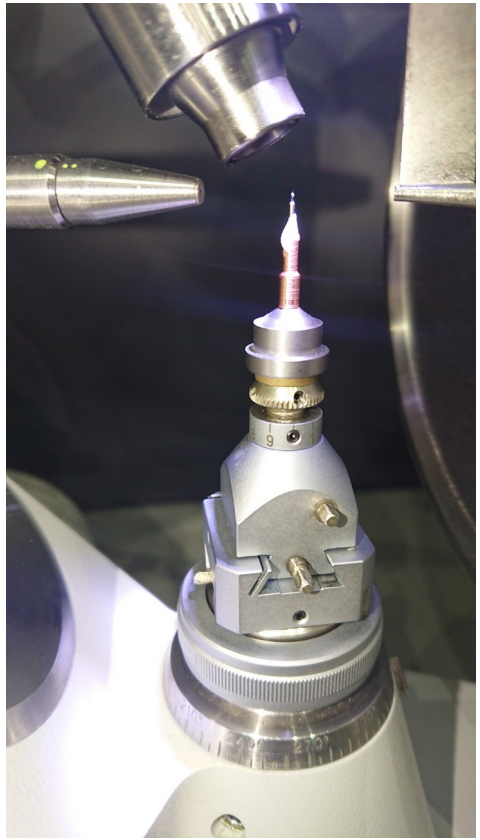


Rigaku Supernova Diffractometer @ Uni-Bielefeld (AK Mitzel)

Diffraktometer

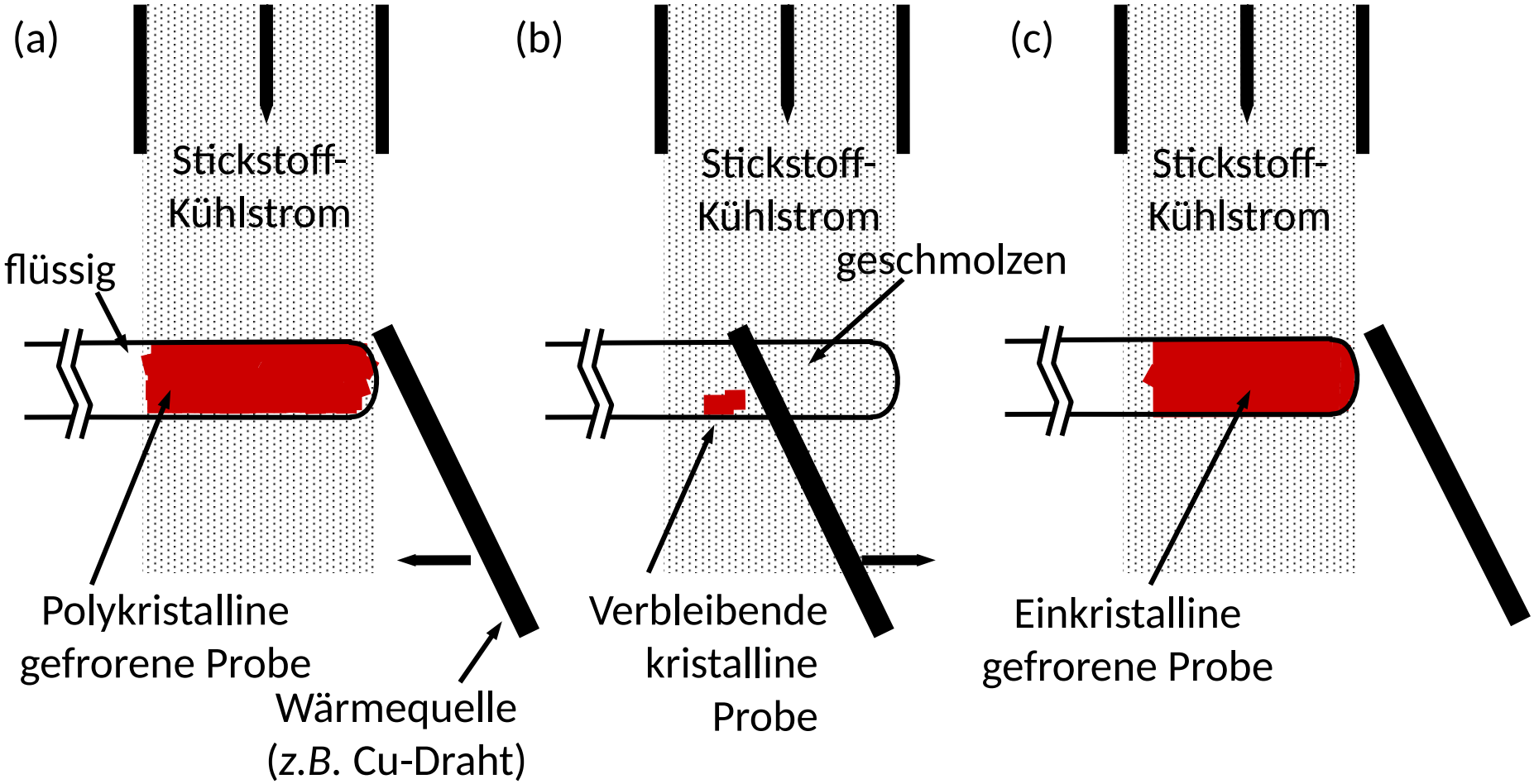
Micro-Fokus Röntgenstrahlung Quelle

Anode:	Cr	Fe	Co	**Cu**	**Mo**	Ag
Kα (Å):	2.29	1.94	1.79	**1.54**	**0.71**	0.56

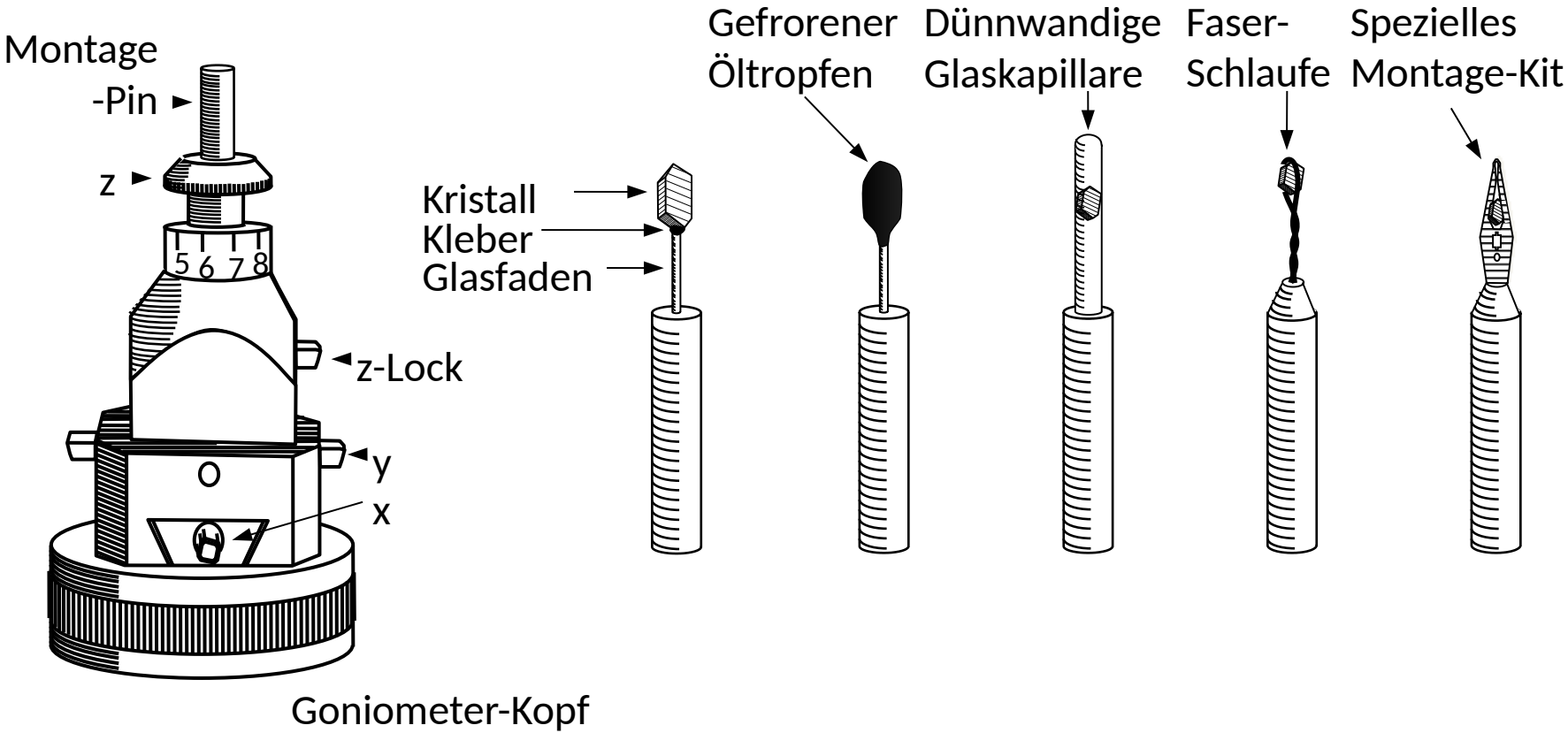


Goniometer Kopf

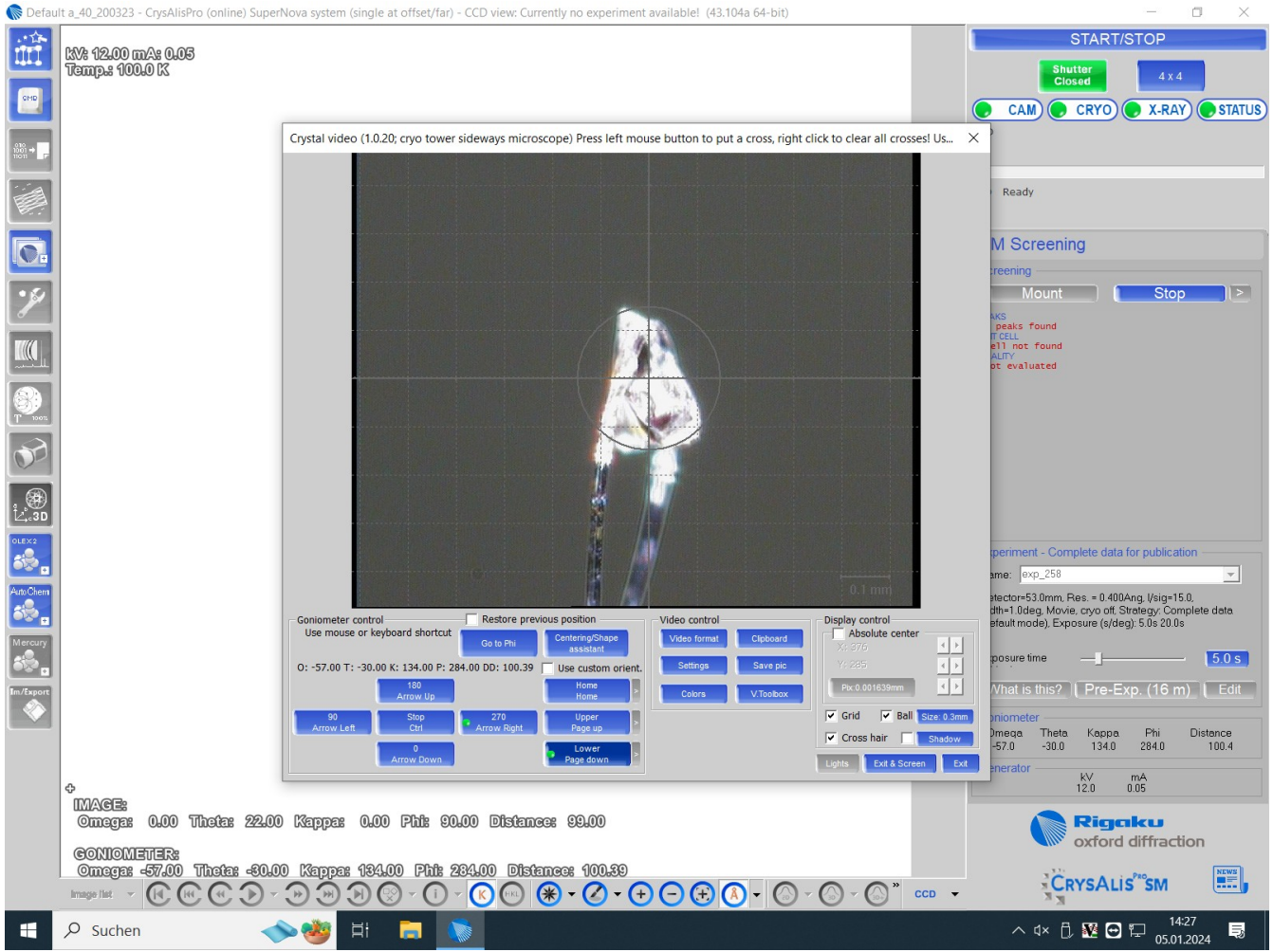
Kristallzucht



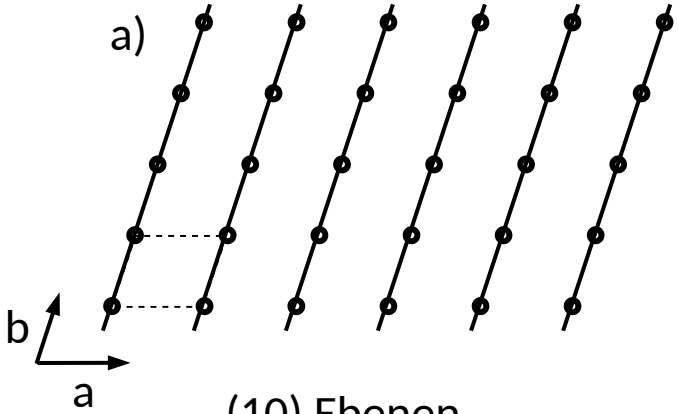
Kristall-Montage



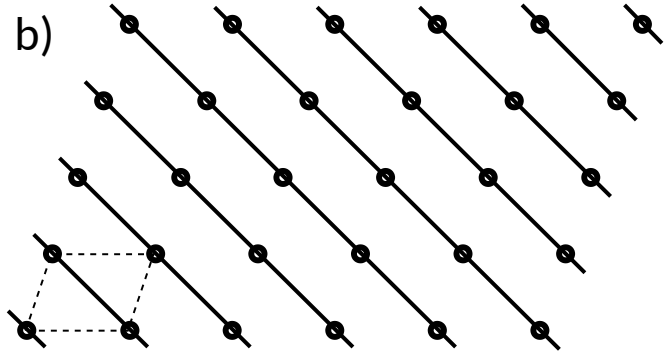
Kristall-Montage



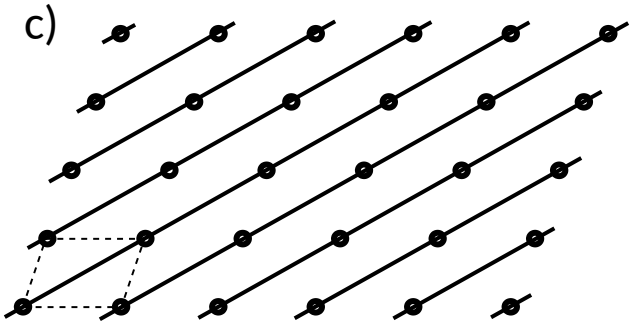
Indizierung, Netzebenen in 2D



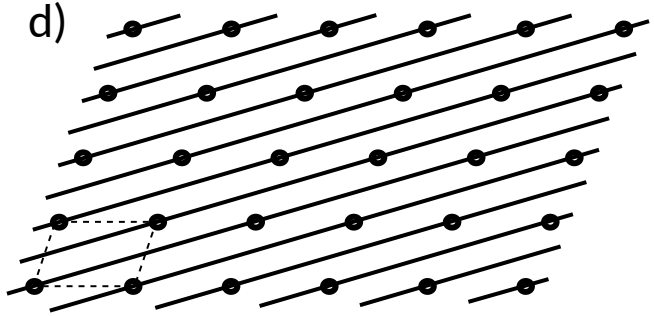
(10) Ebenen



(11) Ebenen



$(1\bar{1})$ Ebenen

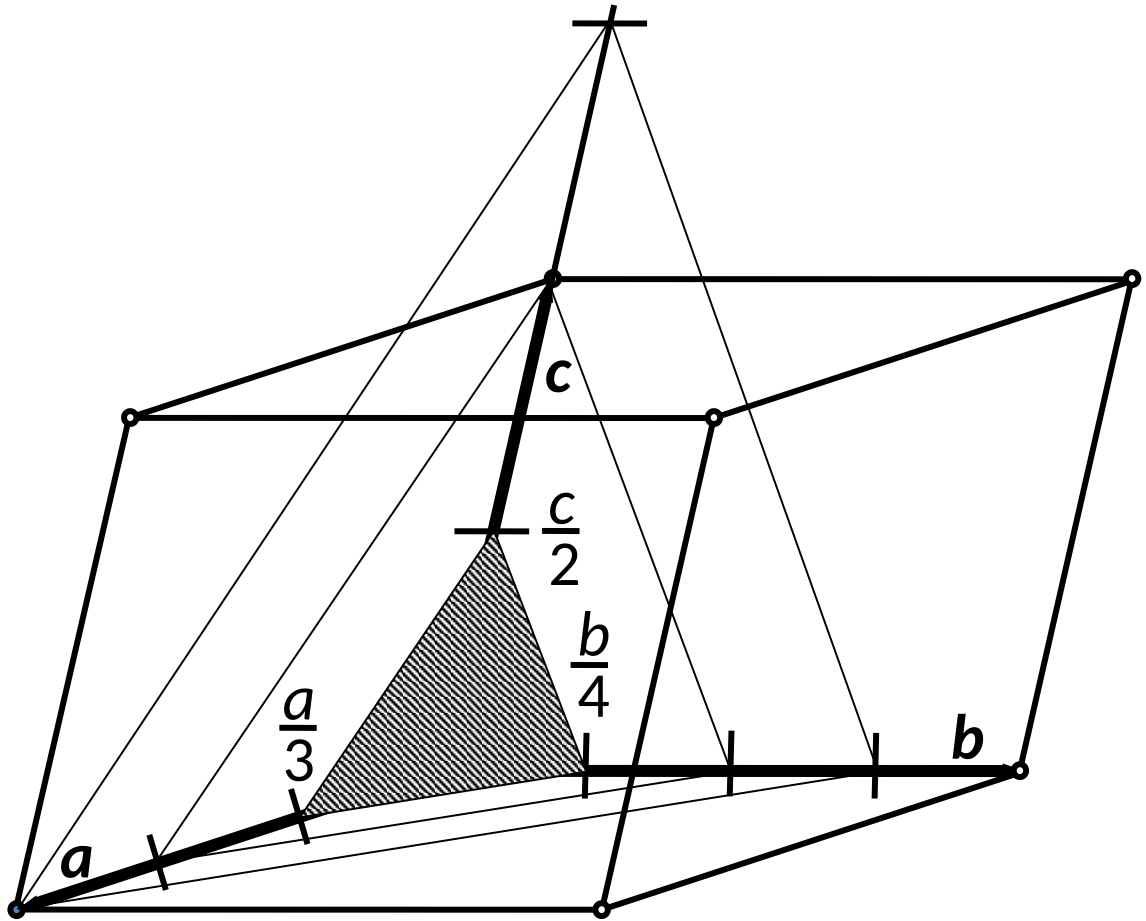


$(1\bar{2})$ Ebenen

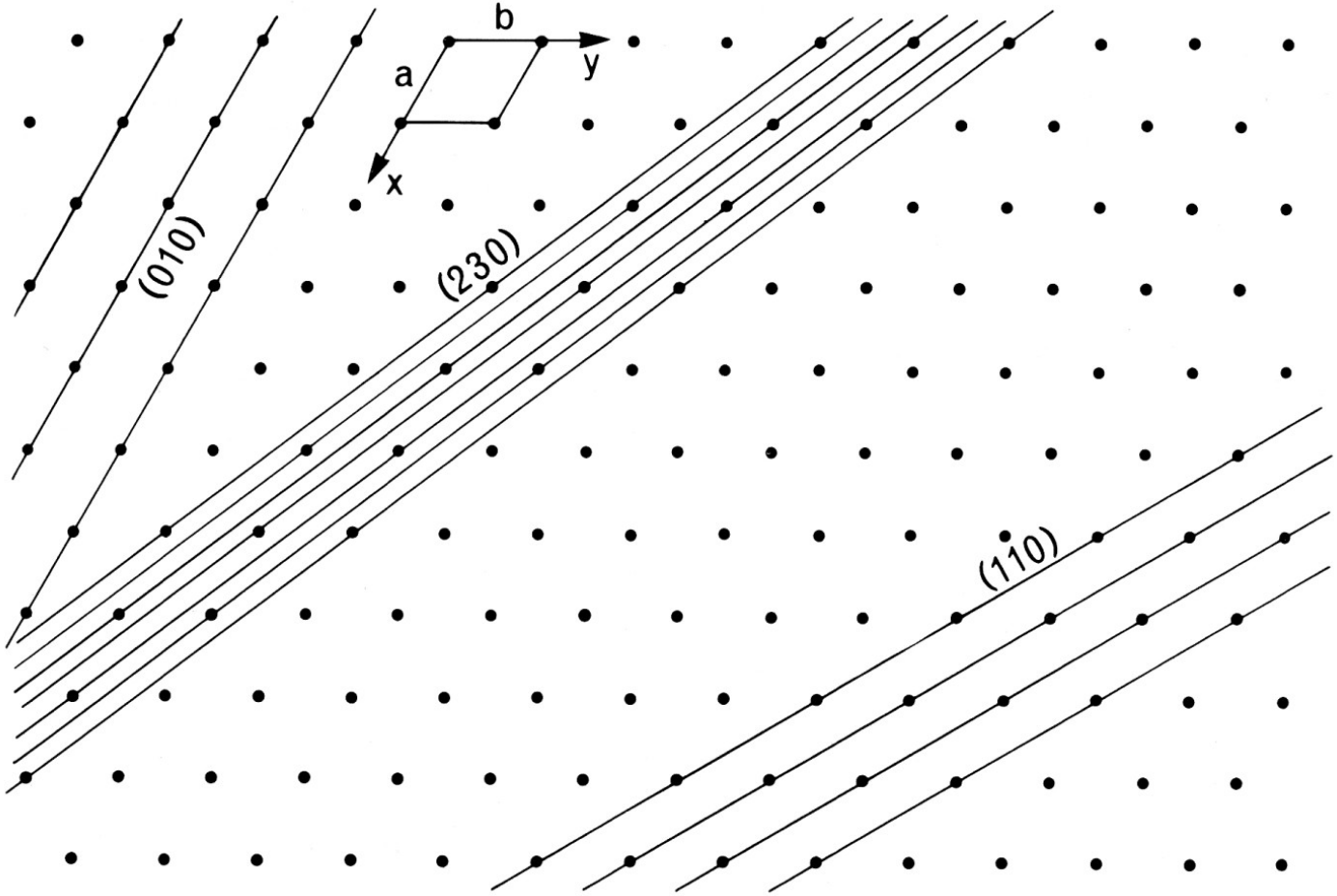
Miller‘sche Indizes für Netzebenen

Beispiel:

$h = 3$, $k = 4$, $l = 2$
Ebene (3 4 2)

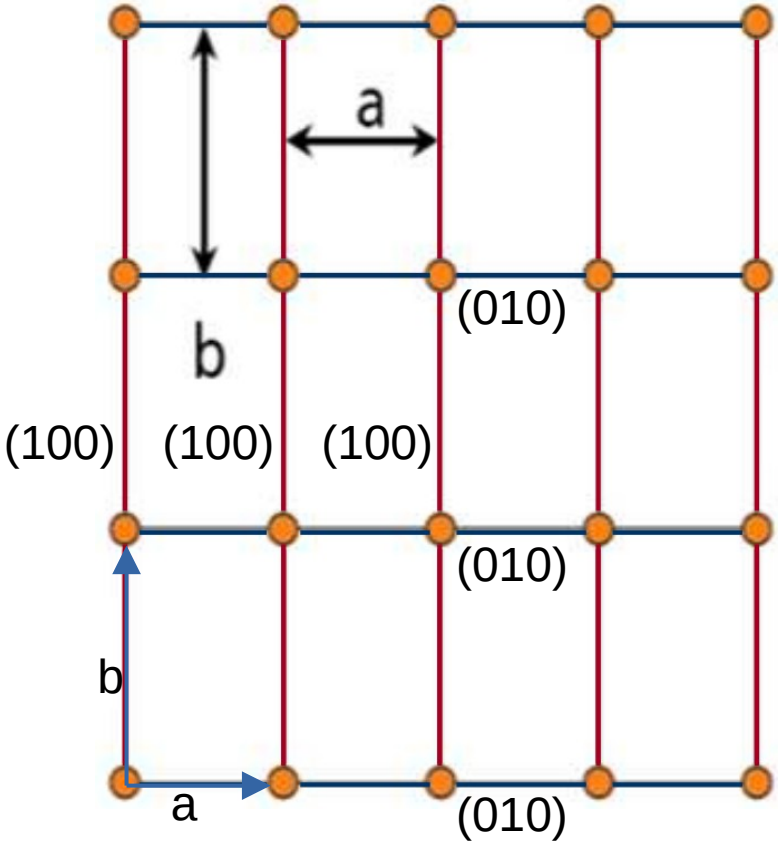


Miller‘sche Indizes für Netzebenen: Graphit



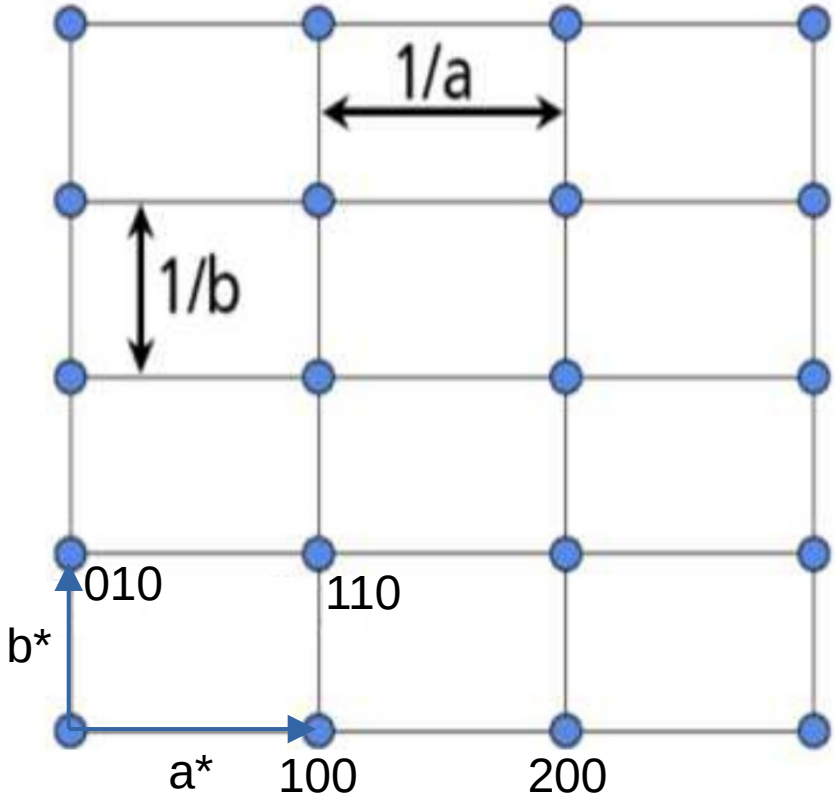
Indizierung

Kristallgitter (Netzebene)

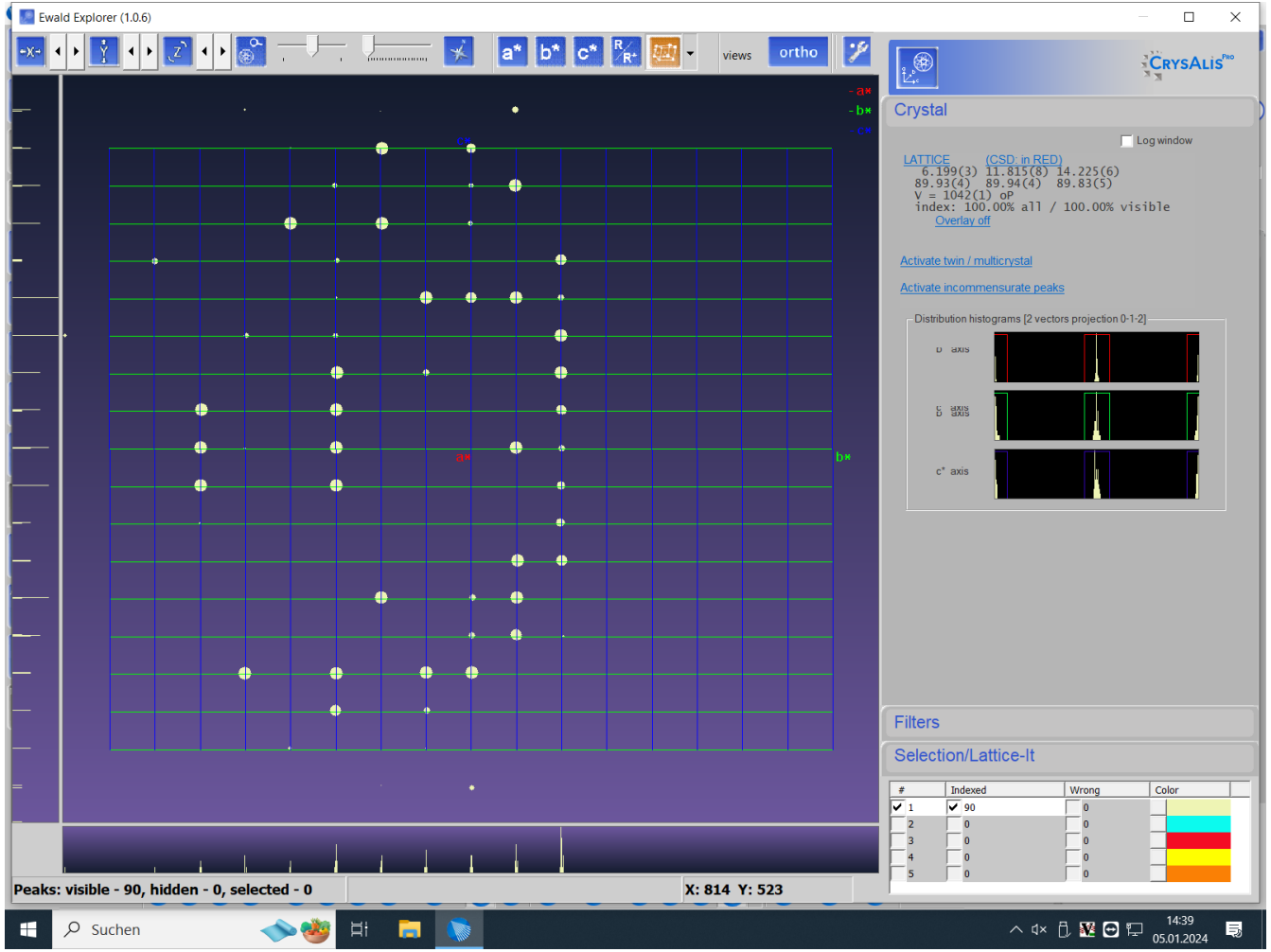


FT

Reziprokes Gitter (Reflexe)



Indizierung



Ein Beispiel – Daten-File $Ti(ONMe_2)_4$

h	k	l	INT	ESD	0
0	0	5	0.19	0.21	0
0	0	6	1482.37	7.42	0
0	0	7	-0.27	0.27	0
0	0	8	301.38	3.12	0
0	0	9	0.21	0.31	0
0	0	10	101.36	2.01	0
0	0	11	0.20	0.40	0
0	0	12	128.75	2.66	0
0	0	13	0.51	0.43	0
0	1	13	57.66	1.97	0
0	1	12	16.73	0.99	0
0	1	11	14.55	0.88	0
0	1	10	11.79	0.77	0
0	1	9	238.71	3.07	0
0	1	8	11.96	0.67	0
0	1	7	1077.47	6.45	0
0	1	6	0.73	0.26	0
0	1	5	134.87	1.61	0
0	1	4	1.97	0.26	0
0	1	3	3.41	0.42	0
0	1	2	221.00	1.53	0
…	…	…	…	…	...

Ein Beispiel – Input-File $Ti(ONMe_2)_4$

```
TITL TiONMe24
CELL 0.71073 9.4828 9.618 7.8488 90 90 90
ZERR 2 0.0013 0.001 0.0015 0 0 0
LATT -1
SYMM -X,-Y,+Z
SYMM 0.5+X,0.5-Y,-Z
SYMM 0.5-X,0.5+Y,-Z
SFAC C H N O Ti
UNIT 16 48 8 8 2

L.S. 4
PLAN  20
SIZE 0.93 0.52 0.36
TEMP -123
FMAP 2
WGHT 0.1
FVAR 0.9

HKLF 4 1 0 1 0 0 0 1 1 0 0

END
```

Streuamplituden im Komplexen

Strukturfaktor *F* ~ Intensität

$$\left|F_{hkl}\right| = \sqrt{A^2 + B^2}$$

Phase des Strukturfaktors *F*

$$\Phi_{hkl} = \tan^{-1}\left(B/A\right)$$

$$A_{hkl} = \sum_i f_i \cos[2\pi(hx_i + ky_i + lz_i)] \cdot e^{-\frac{8\pi^2 U_i \sin 2\theta}{\lambda^2}}$$

$$B_{hkl} = \sum_i f_i \sin[2\pi(hx_i + ky_i + lz_i)] \cdot e^{-\frac{8\pi^2 U_i \sin 2\theta}{\lambda^2}}$$

Strukturfaktor – Zusammenhang mit Elektronendichte ρ(r)

$$F_{\mathbf{h}} = \int \rho(\mathbf{r})\, e^{2\pi i \mathbf{hr}} \mathrm{d}V$$

h: Vektor aus *h*, *k*, *l*

Ein Beispiel – Struktur $Ti(ONMe_2)_4$

X-Ray crystallography

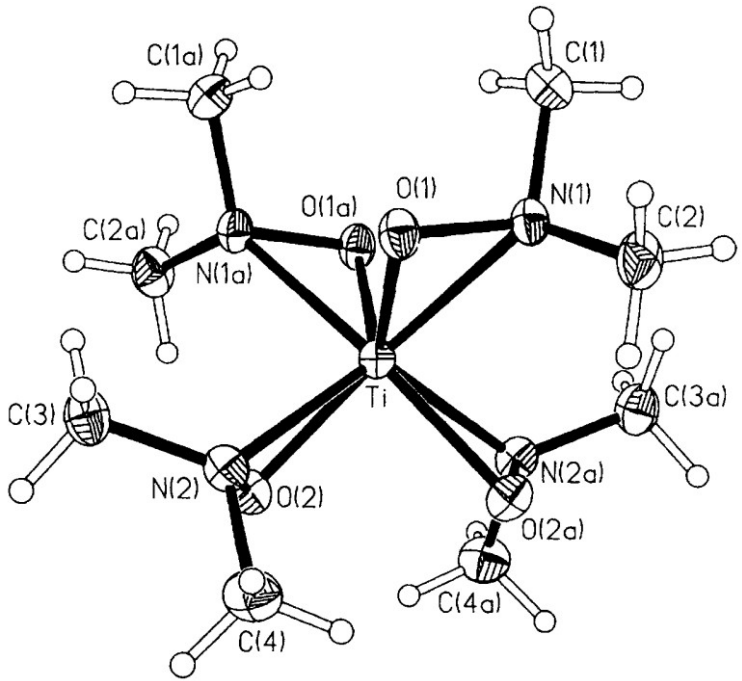
Crystals were transferred and examined under inert perfluoro-polyether oil (RS3000) and mounted on glass fibres. Data were collected on a Stoe Stadi-4 four-circle diffractometer fitted with an Oxford Cryosystems low-temperature device[11] and graphite-monochromated Mo-KαX-radiation (λ = 0.710 73 Å). The structures were solved for all non-H atoms by direct methods,[12,13] and refined against F^2 with full-matrix least-squares analysis.[14] The non-H atoms were refined with anisotropic thermal displacement parameters. The hydrogen atoms on the methyl groups were located in a difference synthesis and freely refined with isotropic thermal displacement parameters.

$Ti(ONMe_2)_4$ 1. $C_8H_{24}N_4O_4Ti$, M = 288.21, orthorhombic, space group $P2_12_12$, a = 9.4828(13), b = 9.618(1), c = 7.849(2) Å, U = 715.9(2) Å^3, Z = 2, D_c = 1.337 g cm^{-3}, $F(000)$ = 308. Colourless cuboid, 0.93 × 0.52 × 0.36 mm. T = 150(2) K, 2076 reflections collected (ω–2θ scans, $-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 13$, $-6 \leqslant l \leqslant 11$), 1225 independent ($R_{int}$ = 0.0362). Semiempirical absorption correction by ψ scans (maximum, minimum transmission factors = 0.730, 0.612). The refinement converged with a conventional R value of 0.0184 [based on F and 1188 data with $I \geqslant 2\sigma(I)$] and a $wR2$ value of 0.0532 (based on F^2 and all 1225 data for 127 refined parameters). In the final difference synthesis the maximum and minimum residual electron densities were 0.22 and −0.24 e Å^{-3}, respectively. Weighting scheme employed: $w = [\sigma^2(F_o^2) + 0.0234P^2 + 0.0802P]^{-1}$, where $P = 0.333\,33(F_o^2 + 2F_c^2)$.

	$Ti(ONMe_2)_4$
M–O(1)	1.918(1)
M–O(2)	1.976(1)
M–N(1)	2.230(1)
M–N(2)	2.095(1)
O(1)–N(1)	1.432(1)
N(1)–C(1)	1.465(2)
N(1)–C(2)	1.468(2)
O(2)–N(2)	1.424(1)
N(2)–C(4)	1.461(2)
N(2)–C(3)	1.469(2)

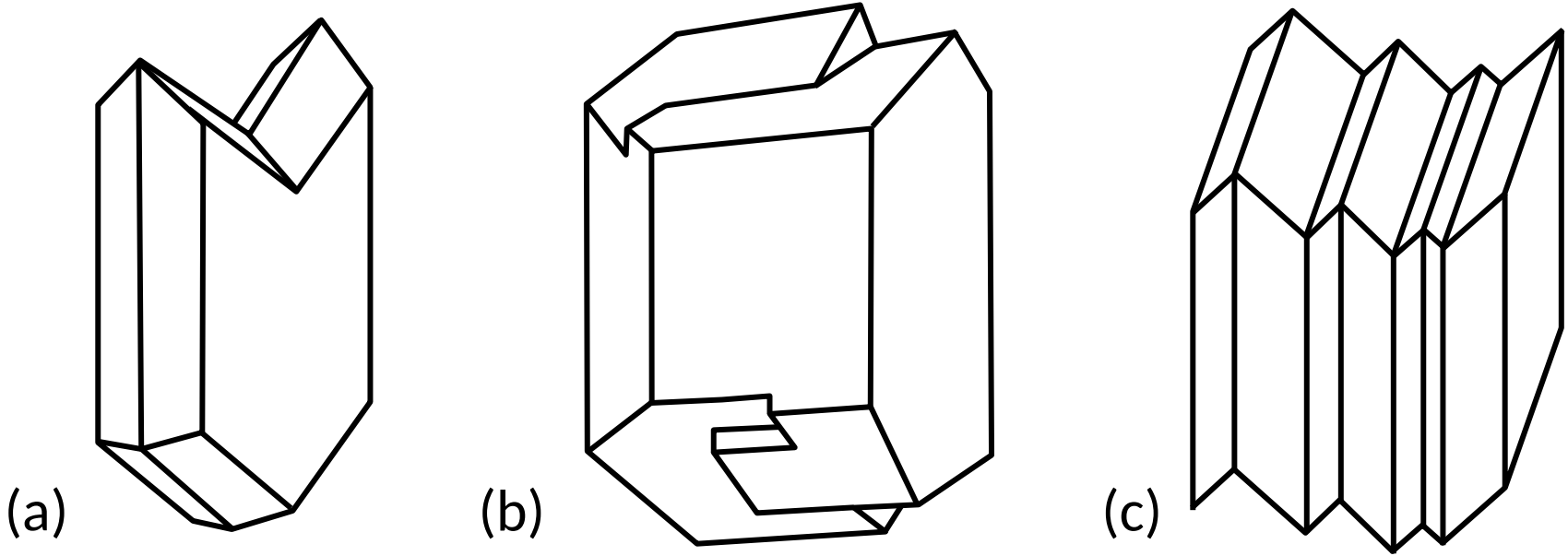
$$wR2 = \sqrt{\frac{\sum_{hkl}\left[w\left(\left|\vec{F}_{hkl}^{\mathrm{beob}}\right|^2 - \left|\vec{F}_{hkl}^{calc}\right|^2\right)^2\right]}{\sum_{hkl}\left[w\left(\left|\vec{F}_{hkl}^{beob}\right|^2\right)^2\right]}}$$

$$R1 = \frac{\sum_{hkl}\left|\left|\vec{F}_{hkl}^{\mathrm{beob}}\right| - \left|\vec{F}_{hkl}^{\mathrm{calc}}\right|\right|}{\sum_{hkl}\left|\vec{F}_{hkl}^{\mathrm{beob}}\right|}$$

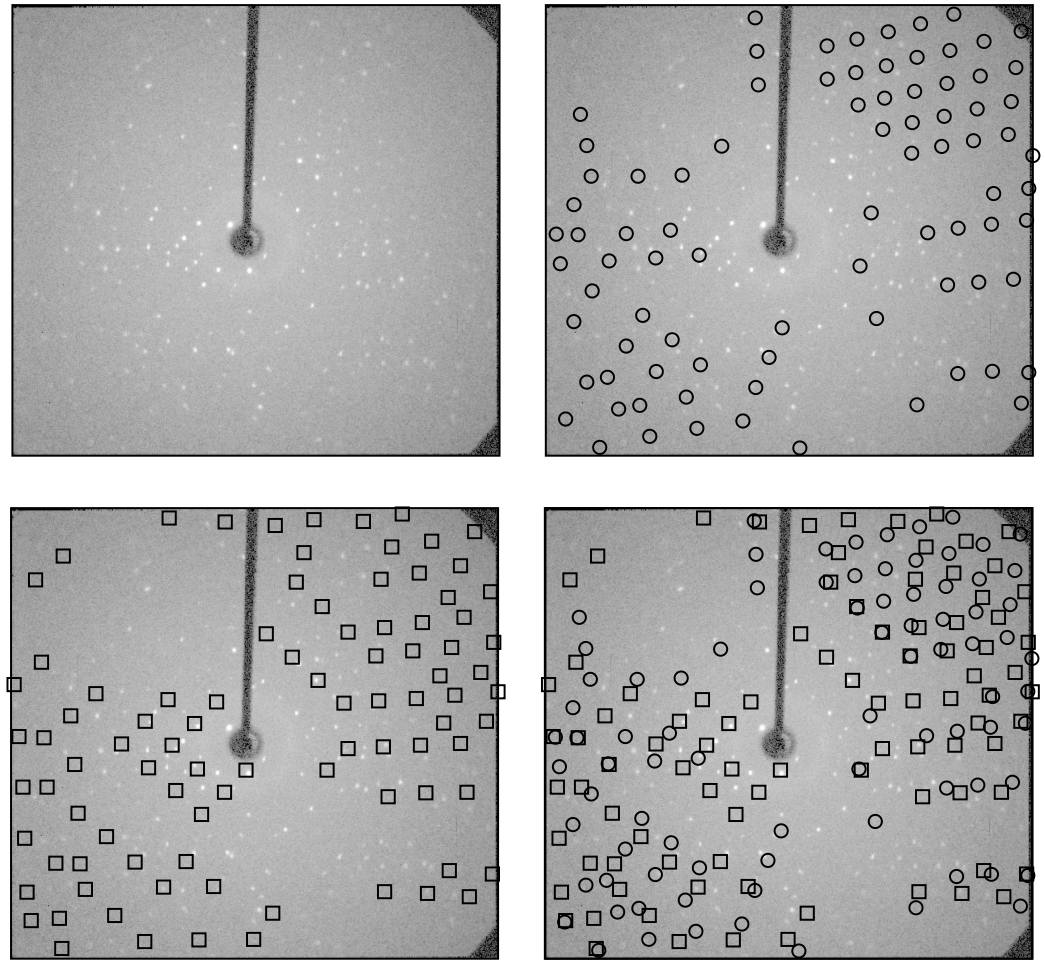


N. W. Mitzel, S. Parsons, A. J. Blake, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.* 1996, 2089–2093.

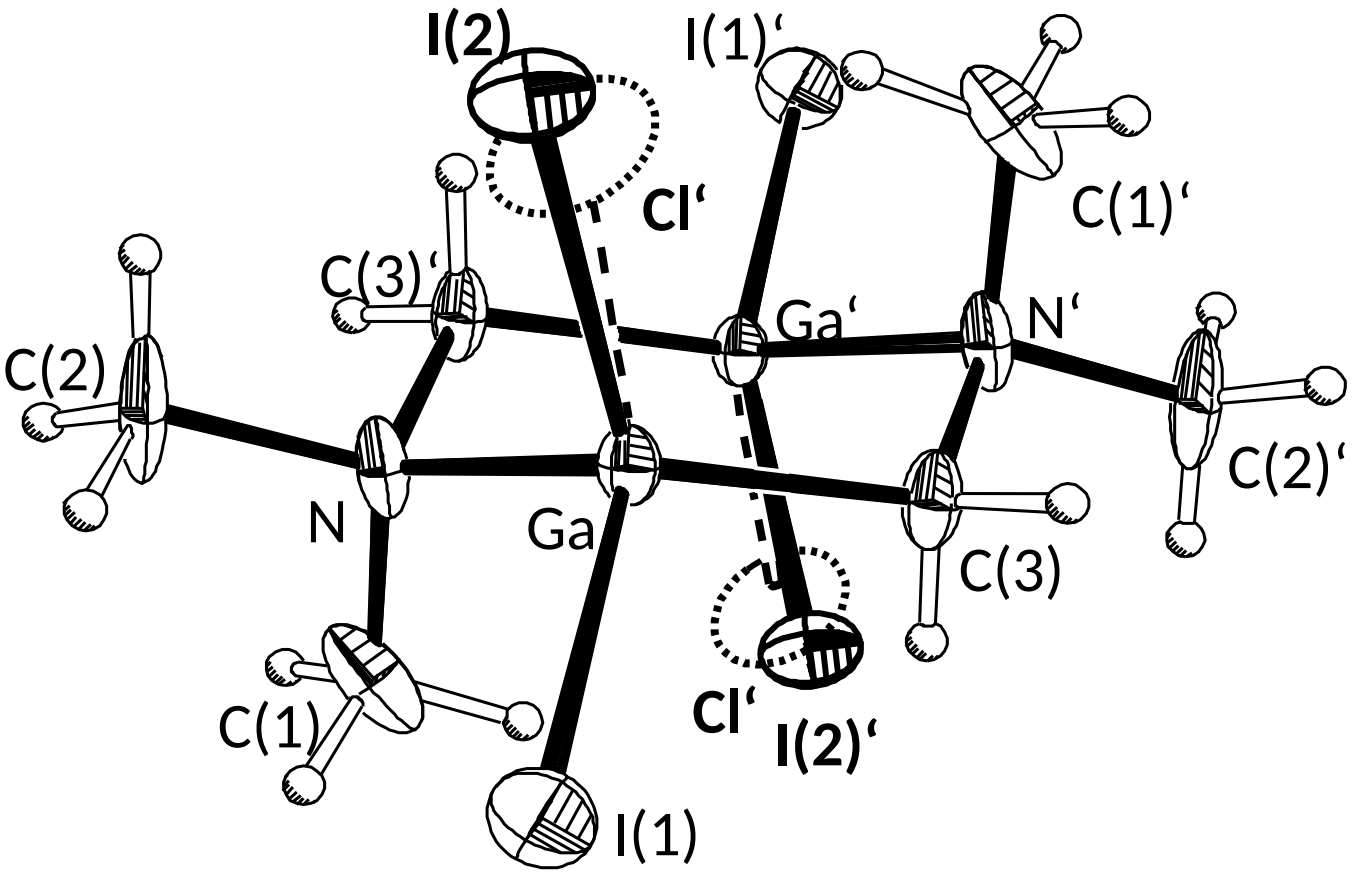
Verzwillingung



Verzwillingung – Beugungspattern

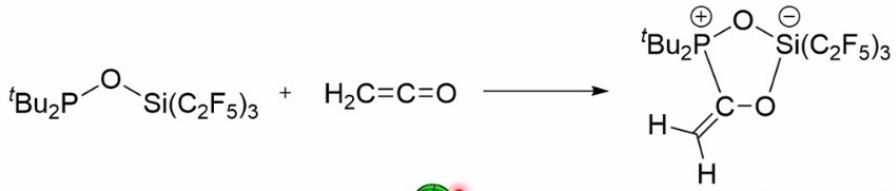


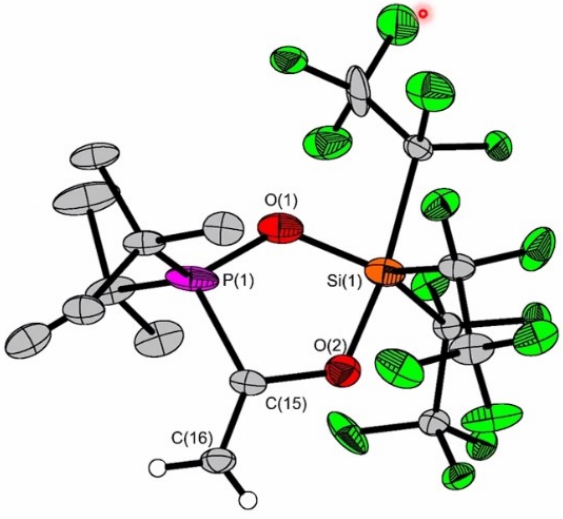
Fehlordnung



aminomethylgallium halide $[Me_2NCH_2GaX_2]_2$ (X = Cl, I)

Hilfe aus Rechnungen



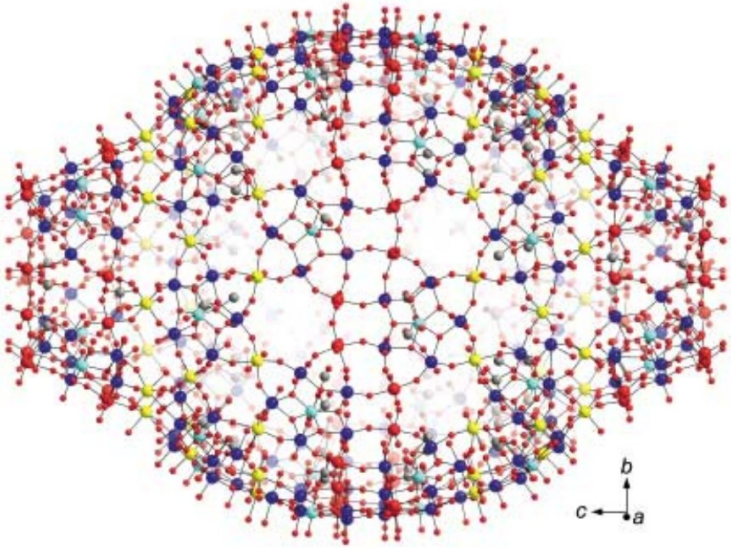


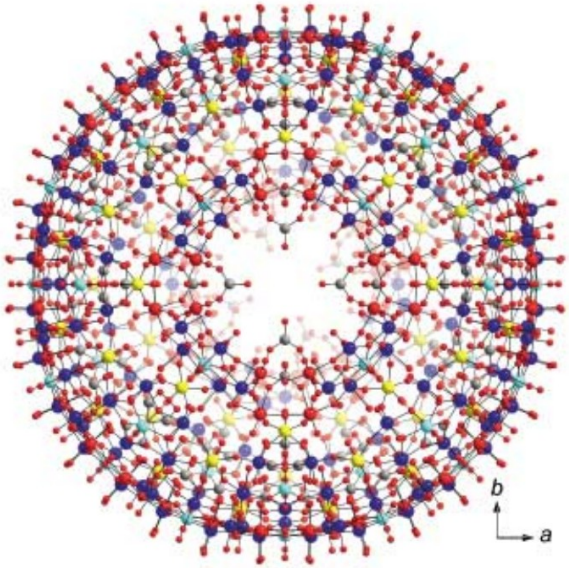
	Variante 1	Variante 2	Rechnungen, freie Moleküle	Rechnung, Kristall
Ausgewählte Bindungslängen				
Si(1)-O(1): 1.730(9) Å		1.743(13)	1.767	1.762
Si(1)-O(2): 1.757(20) Å		1.715(30)	1.768	1.772
P(1)-O(1): 1.556(5) Å			1.561	1.597
Si(1)-O(1)-P(1): 118.0(2)°			122.6	122.0
Vergleich mit freiem FLP				
Si(1)-O(1): 1.583(1) Å			1.596	
P(1)-O(1): 1.708(1) Å			1.693	
Si(1)-O(1)-P(1): 142.0(1)°			144.0	

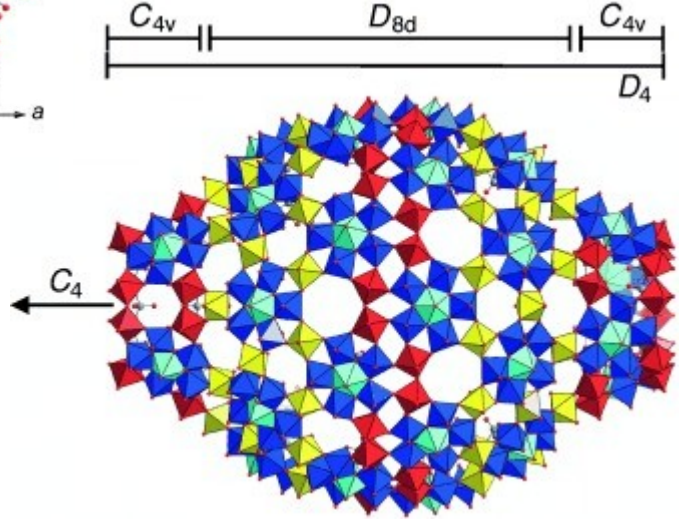
„Twinned crystal: component 2 rotated by 6.9842 around [0.34 -0.93 -0.16] (reciprocal) or [0.18 -0.98 -0.01] (direct). Disorder of P1, Si1, O1, O2, F1 to F5, F11 to F15, C1, C2, C5, and C6 over two sites (45:55).“

PBE0-D3BJ/def2-TZVPP
PBE-D3BJ/DZVP-MOLOPT-SR-GTH (PW+Gauss)

Nano-Igel $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$





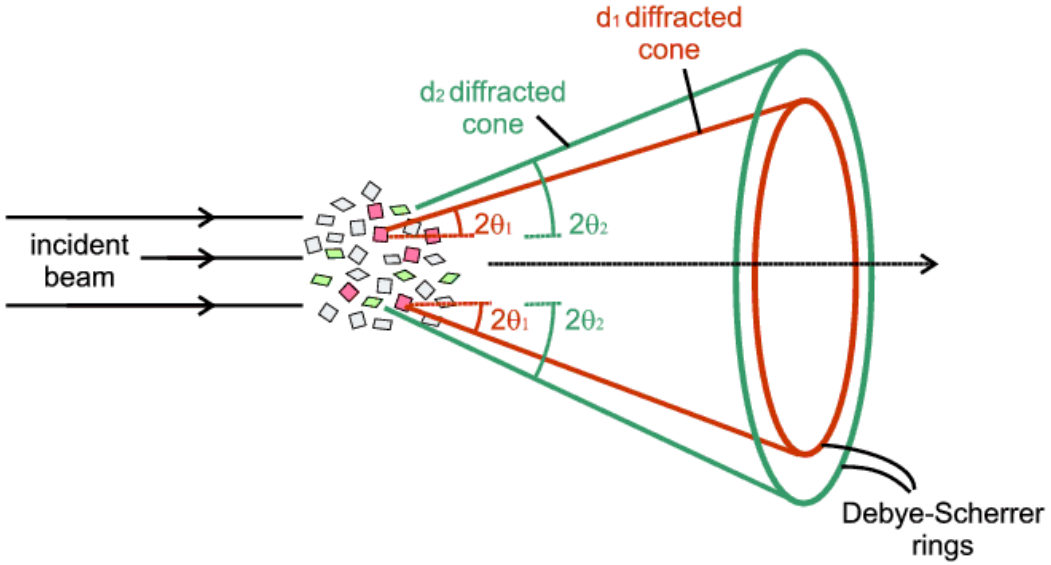


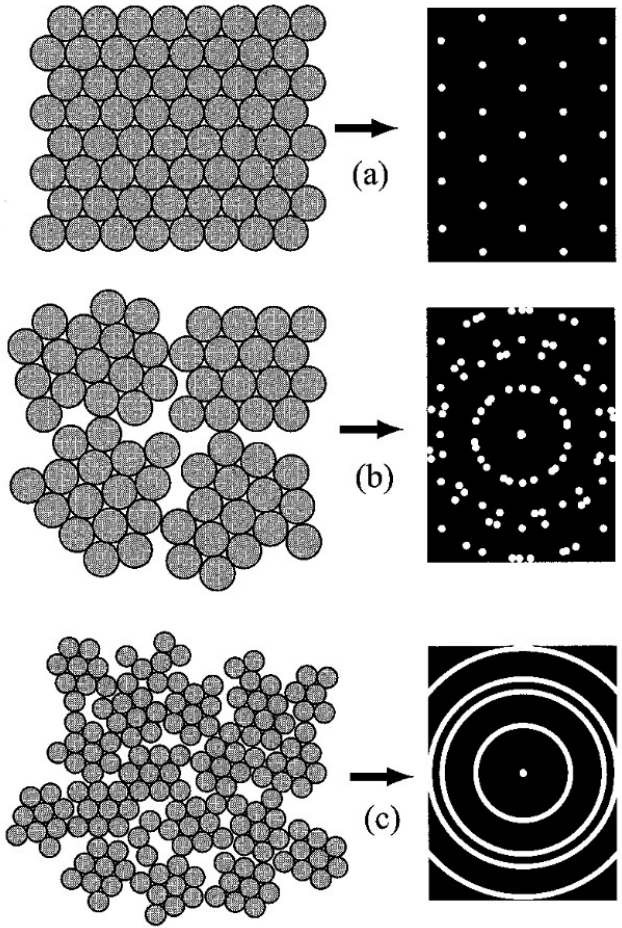
„Building units $\{Mo_1\}$ yellow, $\{Mo_2\}$ red, $\{Mo(Mo_5)\}$ blue with blue-turquoise pentagonal bipyramids; O atoms small red spheres, S atoms gray spheres.“

A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, A. Dress, *Angew. Chem. Int. Ed.* 2002, 41, 1162.

Pulverdiffraktion

$$n\lambda = 2d_{hkl} \sin \theta$$

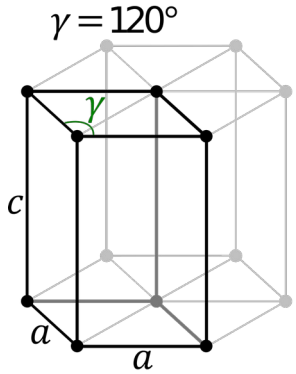




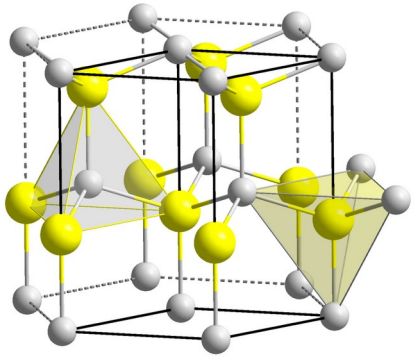
Pulverdiffraktion

Beispiel:

ZnO
Elektronen-Beugung
λ = 0.04055 Å
L = 598 mm

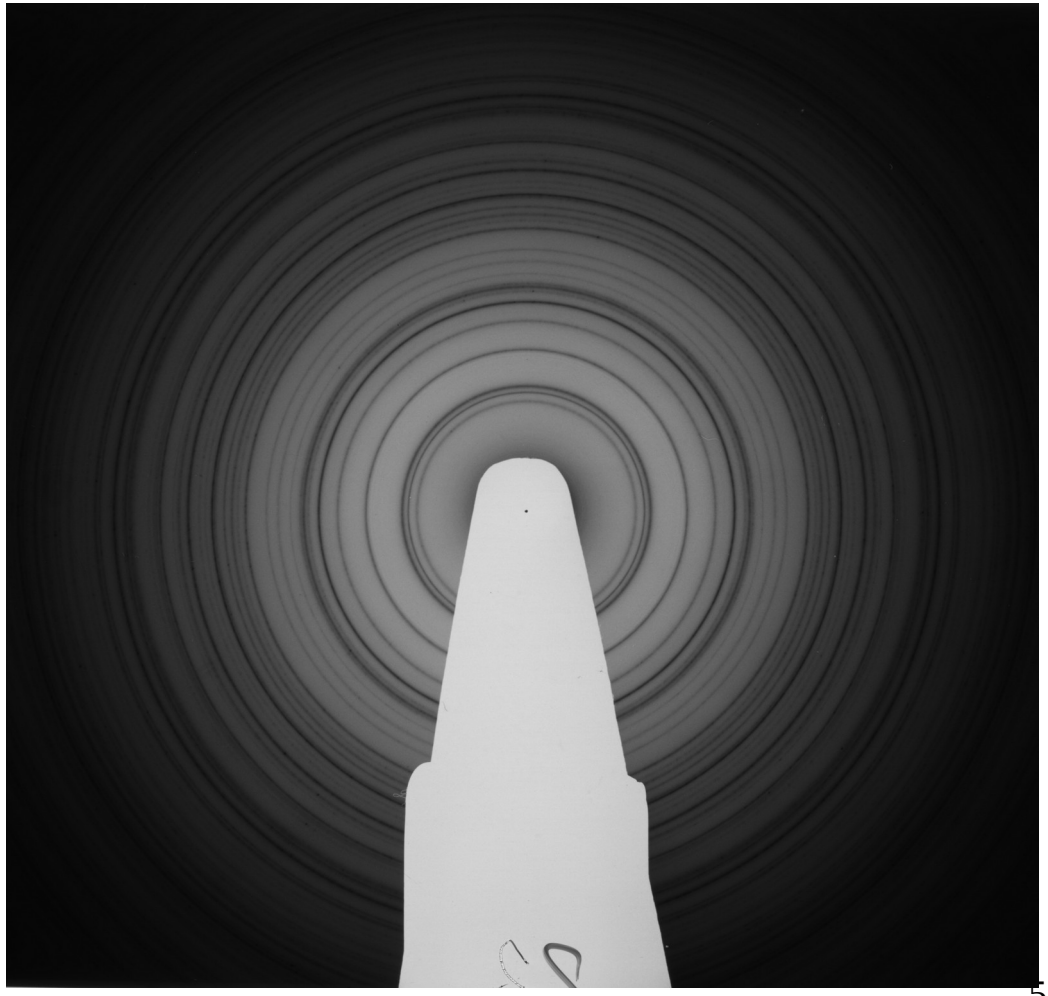


P6₃mc

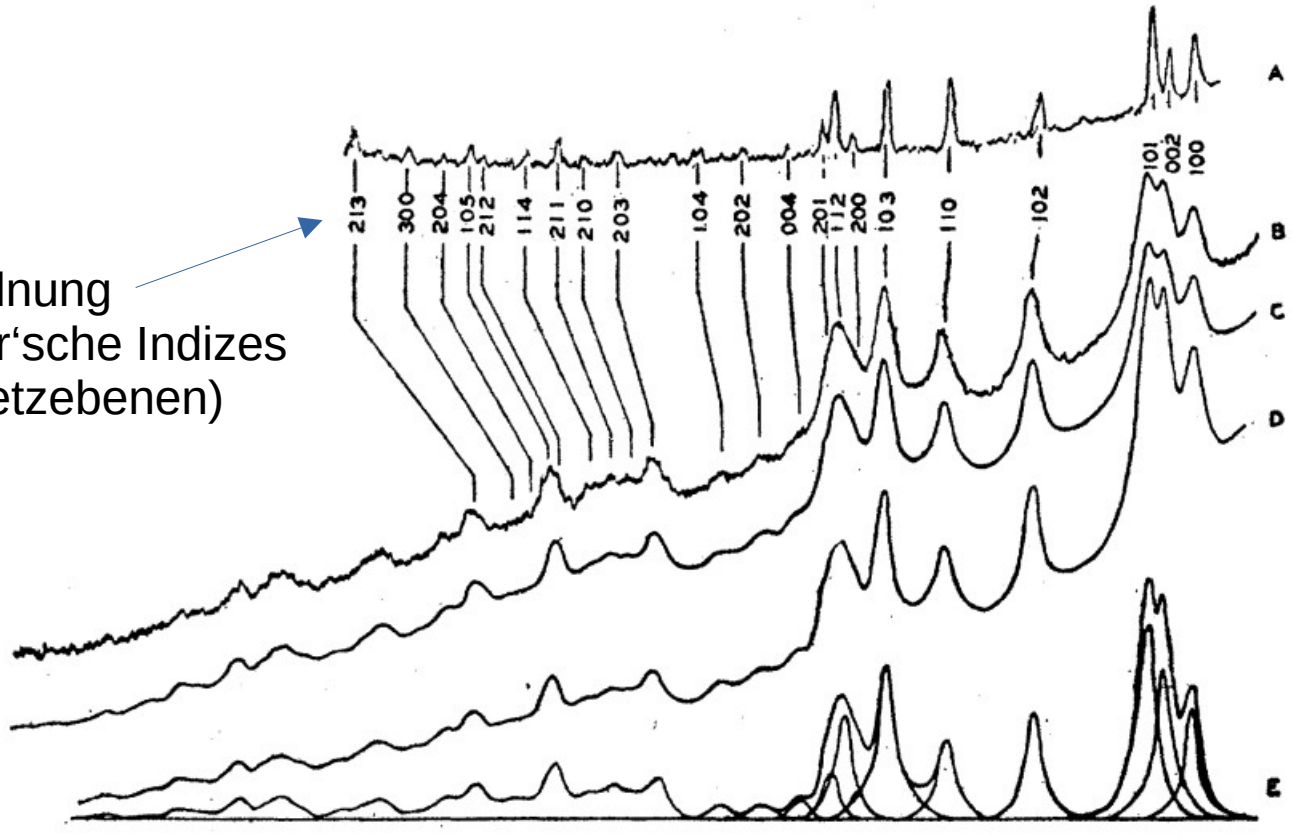


a = 3.2495 Å

c = 5.2069 Å



Pulverdiffraktion: Zinkoxid

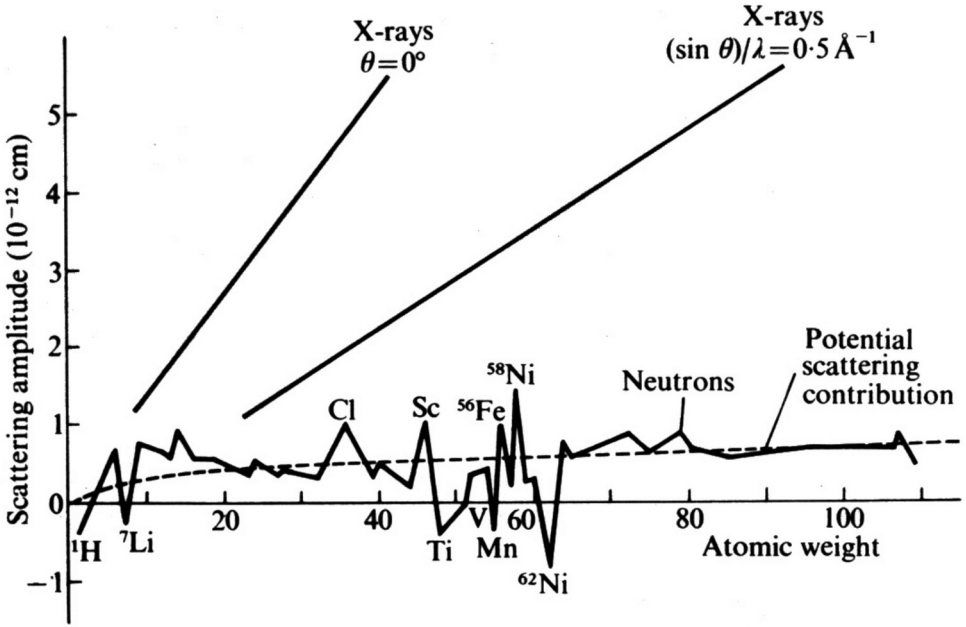


Röntgenbeugung

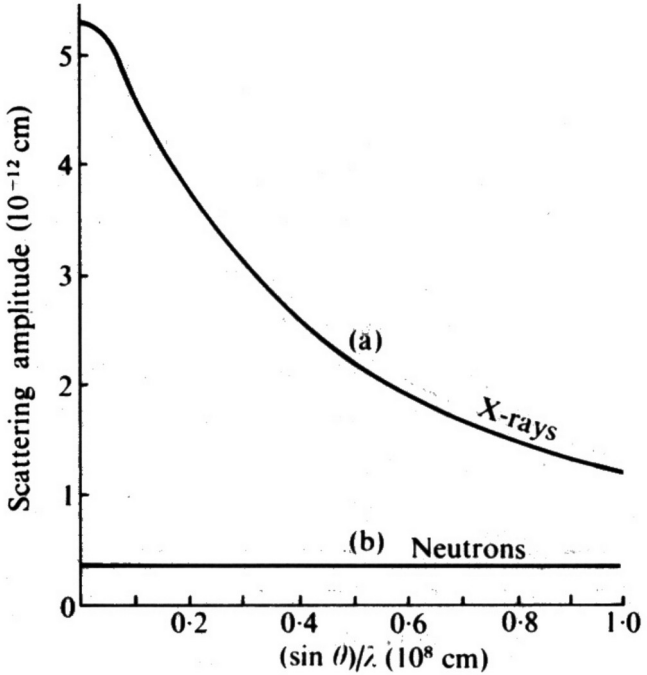
Zuordnung
(Miller'sche Indizes
für Netzebenen)

Elektronenbeugung

Neutronendiffraktion

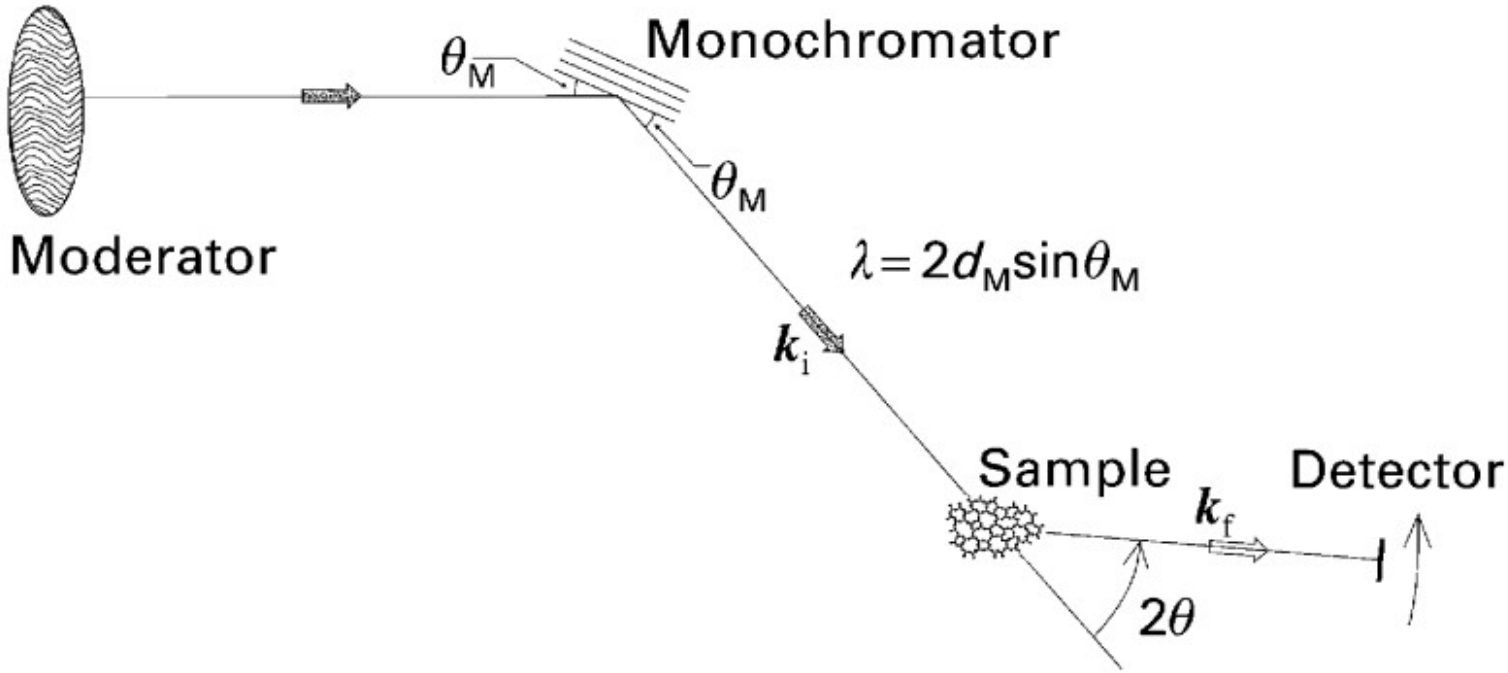


Irregular variation of neutron scattering amplitude with atomic weight due to superposition of 'resonance scattering' on the slowly increasing 'potential scattering'; for comparison the regular increase for X-rays is shown. (From *Research (London)* **7**, 257 (1954).)

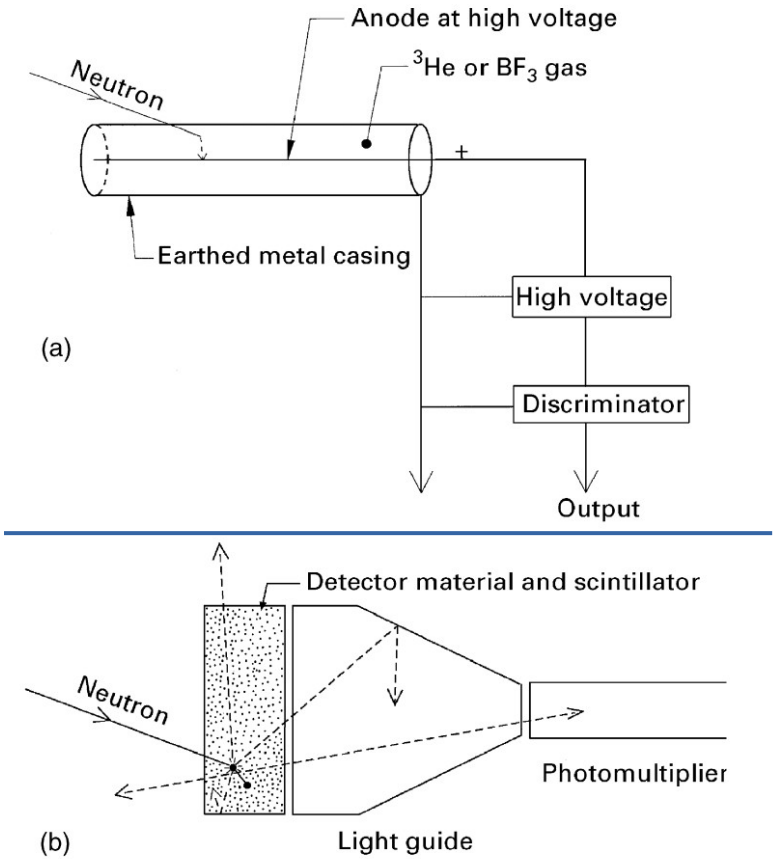


X-ray and neutron scattering amplitudes for a potassium atom.

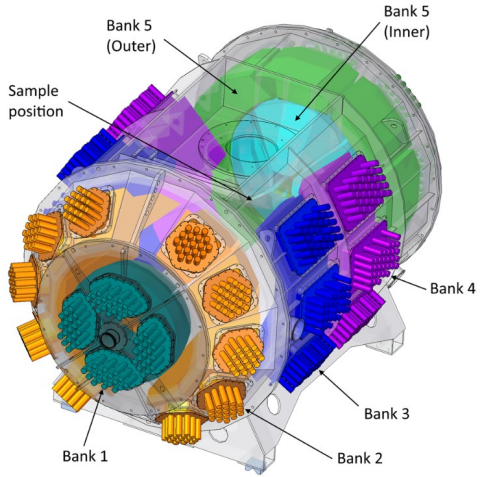
Neutronendiffraktion



Neutronendiffraktion: Detektor



Gas Detektor



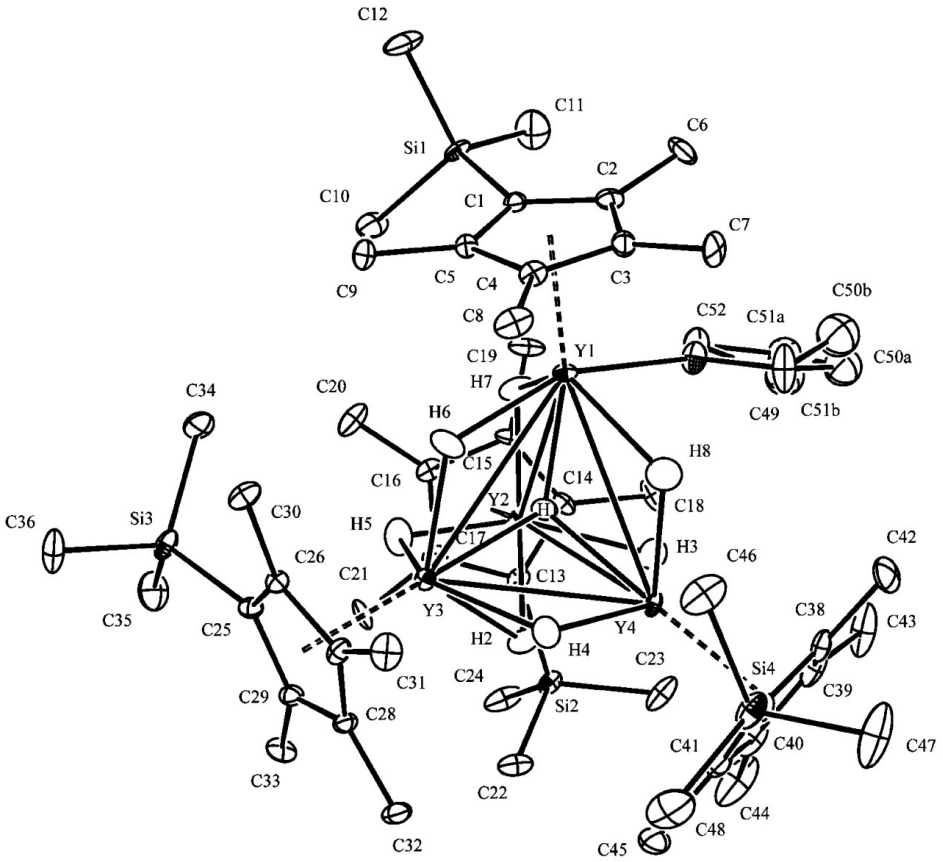
Scintillator Detektor

z.B. ZnS scintillator-based [Rutherford Appleton Laboratory (UK) $6° \leq 2\theta \leq 168°$]

ND, ein Beispiel: $Y_4H_8(Cp')_4(THF)$

Neutron Crystallographic Data for $[(C_5Me_4SiMe_3)YH_2]_4(THF)$

empirical formula	$C_{52}H_{100}OSi_4Y_4$	
fw	1209.36	
cryst syst	triclinic $P\bar{1}$	
Z	2	
	VIVALDI (ILL)	*SXD (ISIS)*
unit cell parameters[a]	$a = 13.009(2)$ Å	$a = 12.988(2)$ Å
	$b = 13.146(2)$ Å	$b = 13.134(2)$ Å
	$c = 19.688(4)$ Å	$c = 19.626(3)$ Å
	$\alpha = 80.526(3)°$	$\alpha = 80.443(11)°$
	$\beta = 86.782(3)°$	$\beta = 86.673(10)°$
	$\gamma = 74.290(2)°$	$\gamma = 74.379(10)°$
V	3196.7(9) Å^3	3179.2(9) Å^3
T	150(2) K	100(2) K
cryst size	$2.0 \times 2.0 \times 1.0$ mm^3	$2.0 \times 2.0 \times 2.0$ mm^3
wavelength range	0.9−2.7 Å	0.37−8.8 Å
min d spacing observed	0.72 Å	0.38 Å
no. of patterns	13	10
data-collection time	13 h	125 h
no. of reflns collected	18 589	11 132
no. of unique reflns	4900	4171
no. of params refined	1434	1434
no. of reflns ($I > 2\sigma$)	3566	4171
final R[$I > 2\sigma(1)$ data]	R1 = 0.1094 wR2 = 0.2347	R1 = 0.0885 wR2 = 0.2240

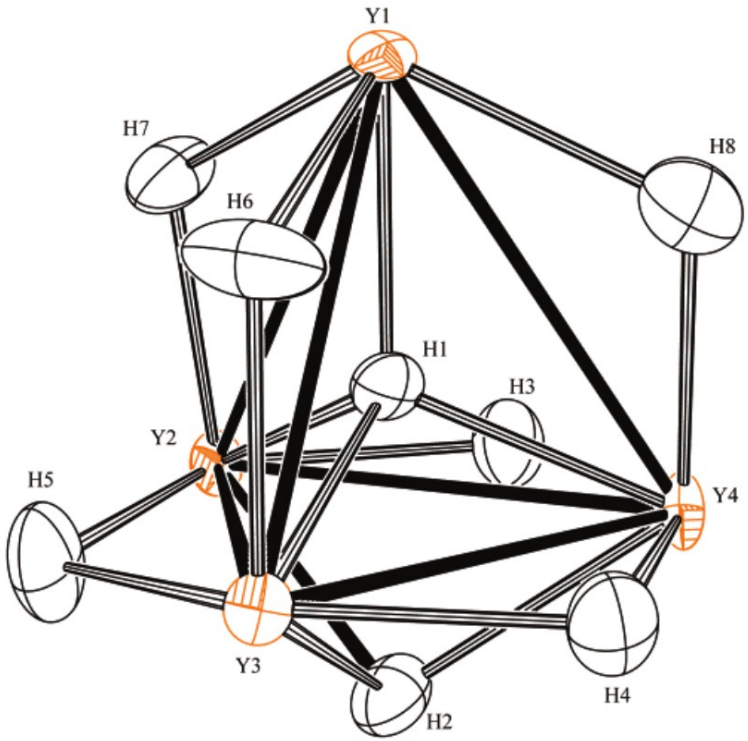


M. Yousufuddin, M. J. Gutmann, J. Baldamus, O. Tardif, Z. Hou, S. A. Mason, G. J. McIntyre, R. Bau, *J. Am. Chem. Soc.* 2008, 130, 3888–3891.

ND, ein Beispiel: $Y_4H_8(Cp')_4(THF)$

Key Distances and Angles in the Y_4H_8 Cores (the ILL Data Represent Results from the VIVALDI Instrument, whereas the ISIS Data Represent Results from the SXD Instrument)

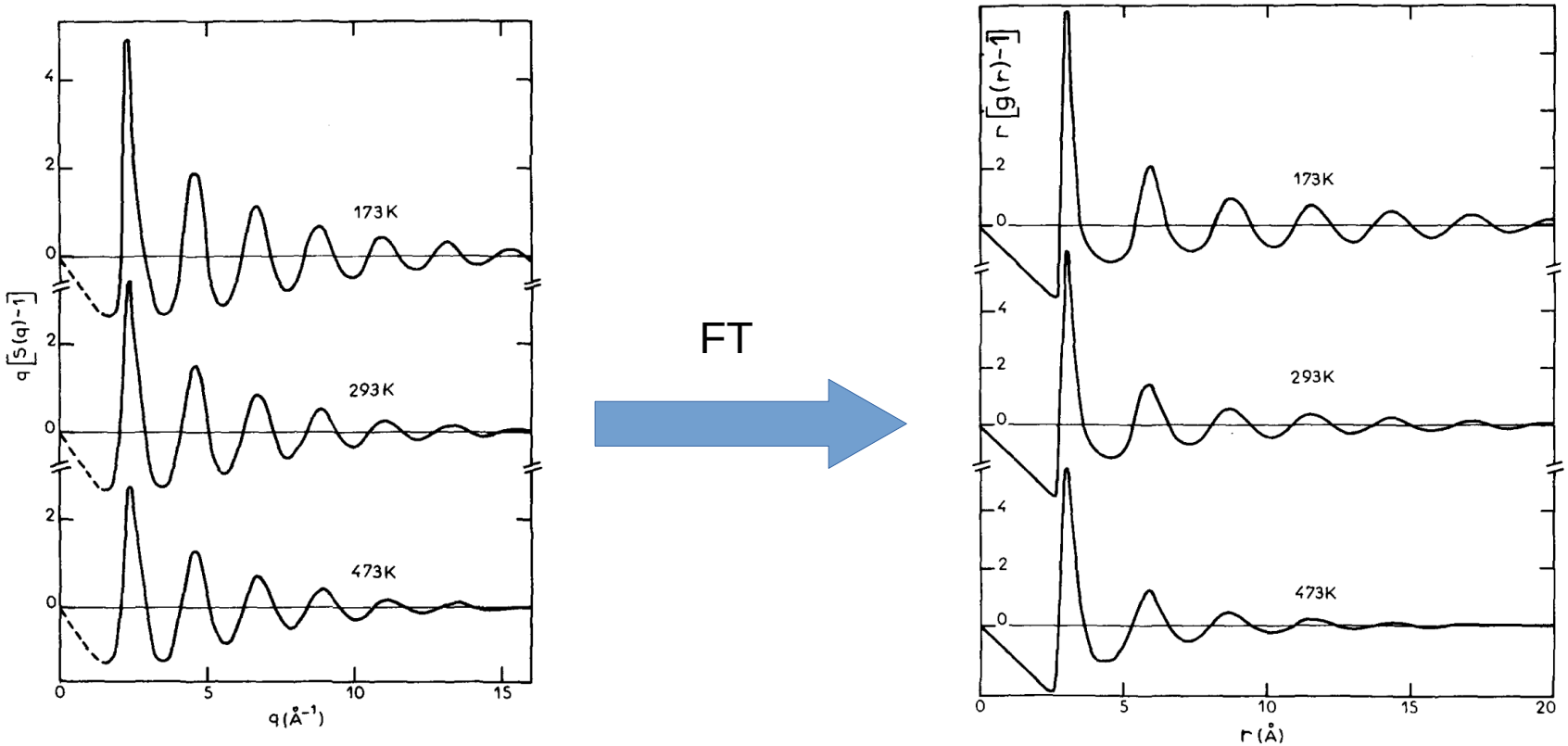
	ILL results	ISIS results
	Y−Y Distances	
Y(1)−Y(2)	3.670(6)	3.685(4)
Y(1)−Y(3)	3.702(5)	3.699(4)
Y(1)−Y(4)	3.683(5)	3.695(3)
avg	3.685	3.693
Y(2)−Y(3)	3.430(4)	3.429(4)
Y(2)−Y(4)	3.492(4)	3.510(4)
Y(3)−Y(4)	3.432(4)	3.438(4)
avg	3.451	3.459
	Y−(central H) Distances	
Y(1)−H(1)	2.163(10)	2.179(6)
Y(2)−H(1)	2.189(9)	2.187(7)
Y(3)−H(1)	2.229(8)	2.222(6)
Y(4)−H(1)	2.195(7)	2.198(6)
avg	2.193	2.197
	Y−(face-bridging H) Distances	
Y(2)−H(2)	2.342(8)	2.344(6)
Y(3)−H(2)	2.368(9)	2.348(7)
Y(4)−H(2)	2.329(9)	2.339(8)
avg	2.346	2.344
	Y−(edge-bridging H) Distances	
Y(2)−H(3)	2.216(8)	2.203(7)
Y(4)−H(3)	2.196(8)	2.202(7)
Y(3)−H(4)	2.133(8)	2.142(7)
Y(4)−H(4)	2.139(8)	2.123(7)
Y(2)−H(5)	2.127(8)	2.135(8)
Y(3)−H(5)	2.149(8)	2.127(8)
Y(1)−H(6)	2.203(8)	2.189(7)
Y(3)−H(6)	2.138(10)	2.132(7)
Y(1)−H(7)	2.182(9)	2.184(8)
Y(2)−H(7)	2.165(11)	2.184(7)
Y(1)−H(8)	2.197(8)	2.203(8)
Y(4)−H(8)	2.191(11)	2.171(9)
avg	2.170	2.166
H(1)···H(2)	2.175(14)	2.153(9)



M. Yousufuddin, M. J. Gutmann, J. Baldamus, O. Tardif, Z. Hou, S. A. Mason, G. J. McIntyre, R. Bau, *J. Am. Chem. Soc.* 2008, 130, 3888–3891.

Beugung an Flüssigkeiten

Z.B. Röntgenbeugung am flüssigen Quecksilber bei T = 173 – 473 K

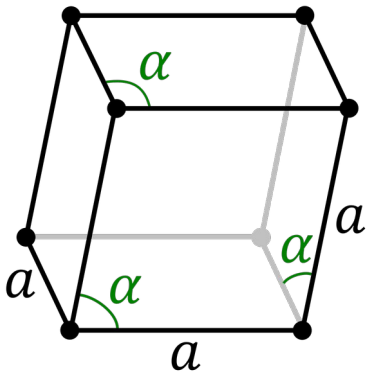


L. Bosio, R. Cortes, C. Segaud, *J. Chem. Phys.* 1979, 71, 3595.

Beugung am flüssigen Quecksilber

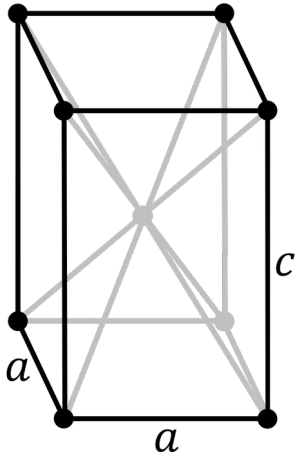
α-Hg

Rhomboedrisch



β-Hg

Tetragonal innenzentriert



r(Hg—Hg):

Krystall:	6 x **3.00** Å	2 x **2.83** Å
	6 x **3.47** Å	8 x **3.16** Å
Flüssigkeit:	**3.00** Å	

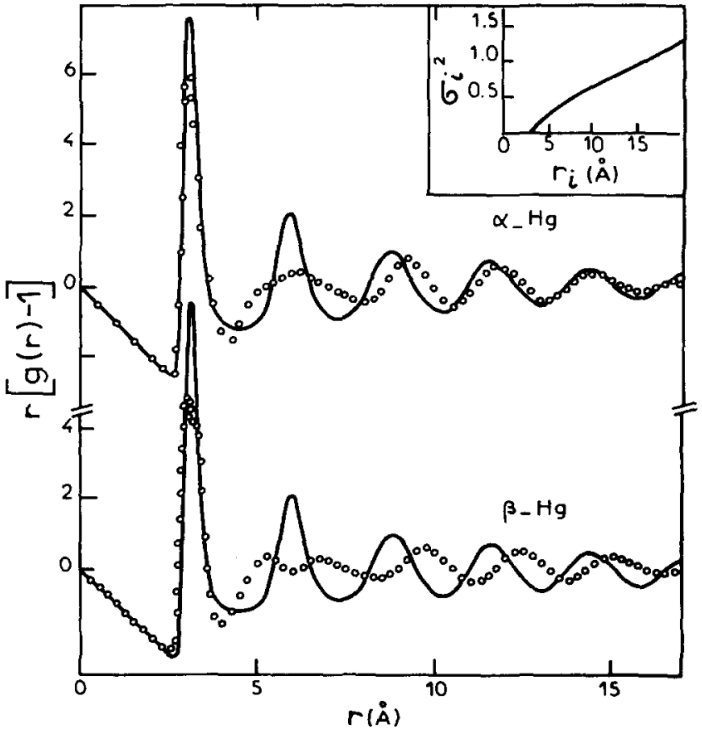
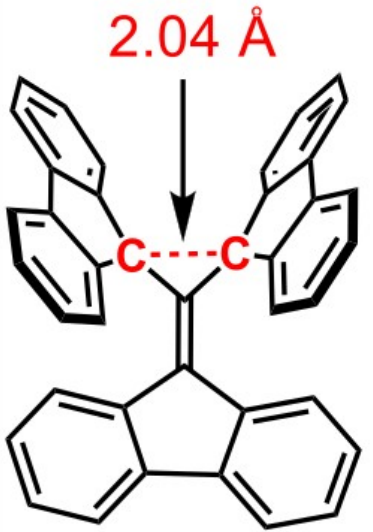


FIG. 6. Comparison between the radial distribution functions $r[g(r)-1]$ observed at 173 K (full line) and those computed from the relaxed structures of α-Hg and β-Hg phases (open circles). In the inset, we have drawn the function relating the variance σ_i^2 to the distance r_i.

Ergebniss: fl. Hg ist näher zu α-Hg

L. Bosio, R. Cortes, C. Segaud, *J. Chem. Phys.* 1979, 71, 3595.

Molekül(e) des Tages



$\Delta\rho$ = 0.03 e/Å^3

λ = 518 nm

δ (^{13}C) = 82.9 ppm

WBI = 0.485

ΔE(S-T) = 138 kJ/mol

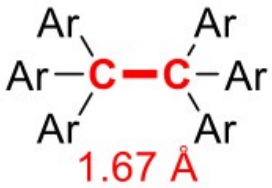
Diradical Index = 12.8%

Long Carbon−Carbon Bonding beyond 2 Å in Tris(9-fluorenylidene)methane

Takashi Kubo,* Yuki Suga, Daisuke Hashizume,* Hiroki Suzuki, Tatsuya Miyamoto, Hiroshi Okamoto, Ryohei Kishi, and Masayoshi Nakano

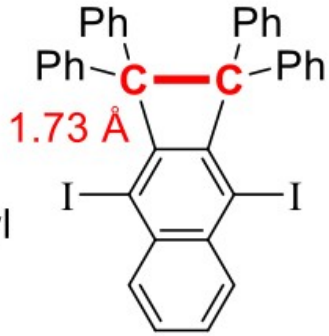
J. Am. Chem. Soc. 2021, 143, 14360−14366

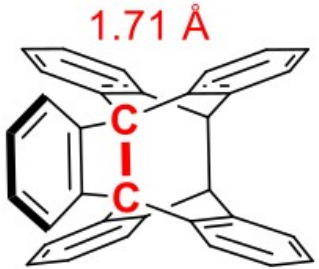
Lange C–C Bindungen

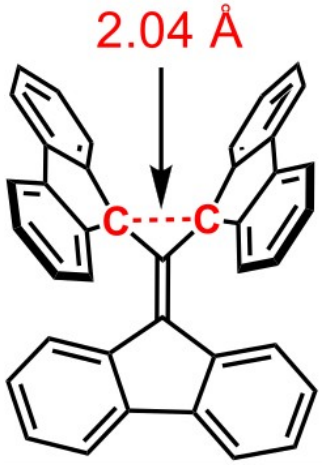


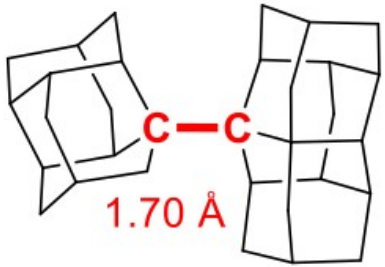
Ar = 3,5-di-*t*-butylphenyl

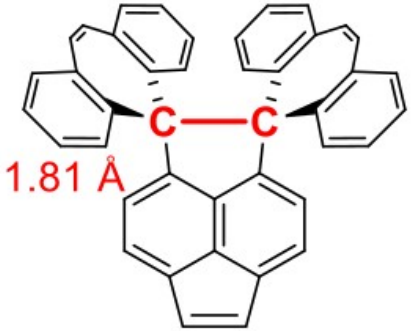
or 4-*t*-butyl

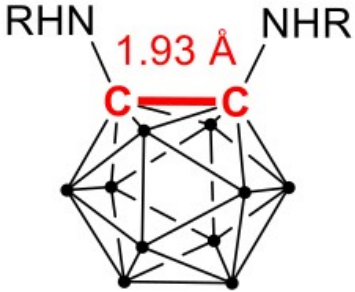






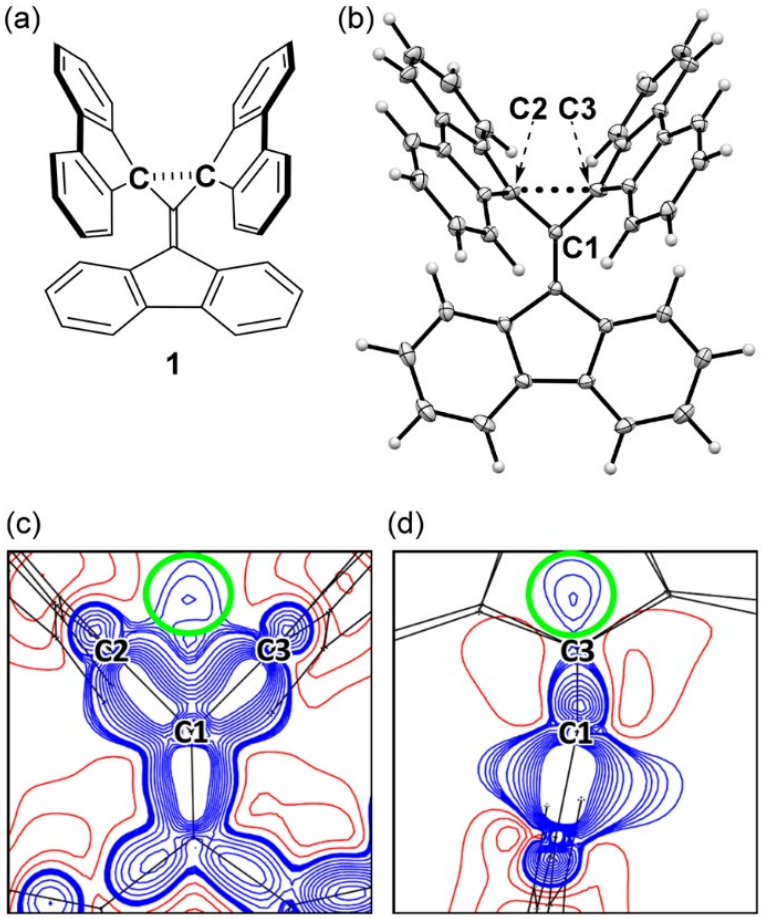






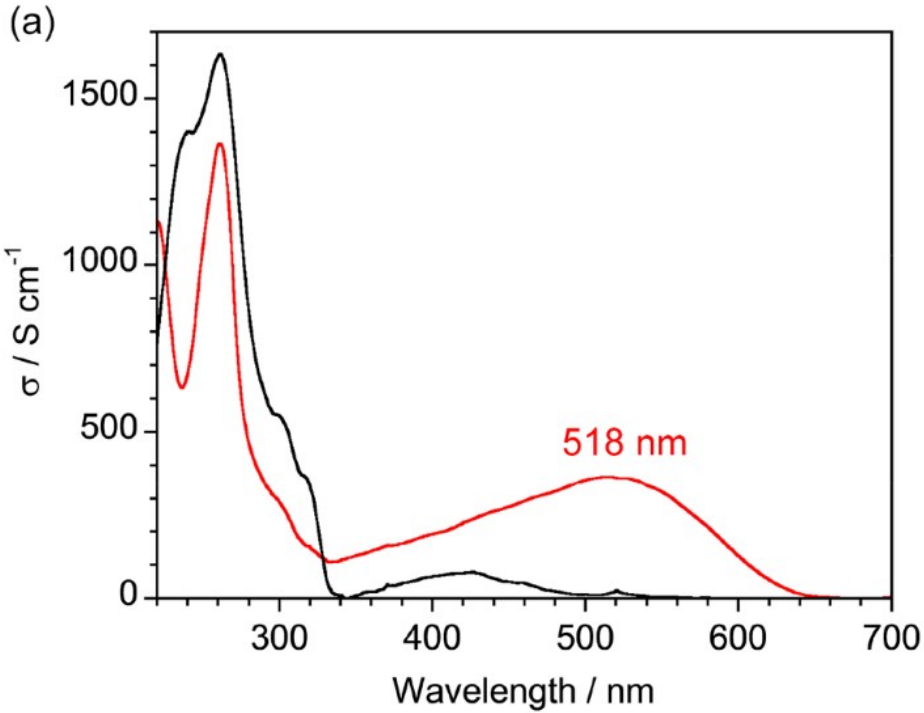
R = CH_2Mes

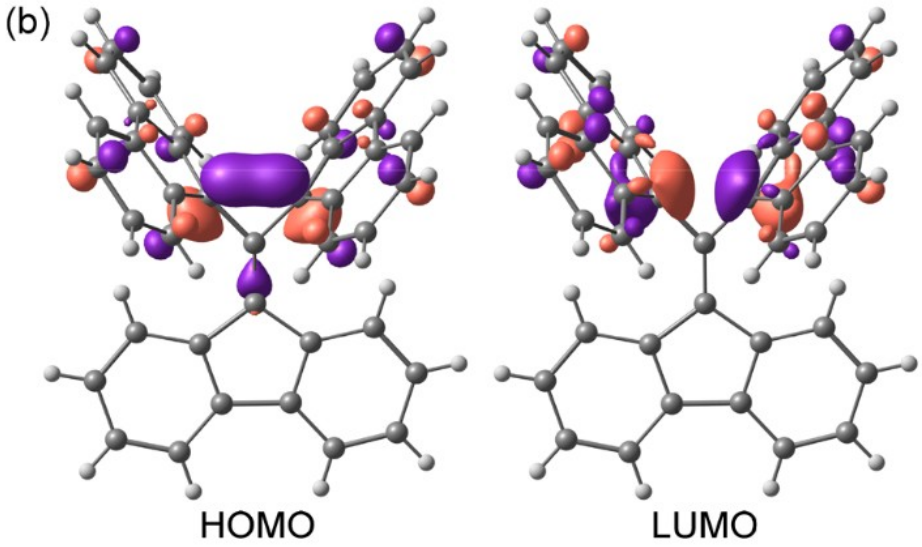
Elektronen-Dichte-Analyse



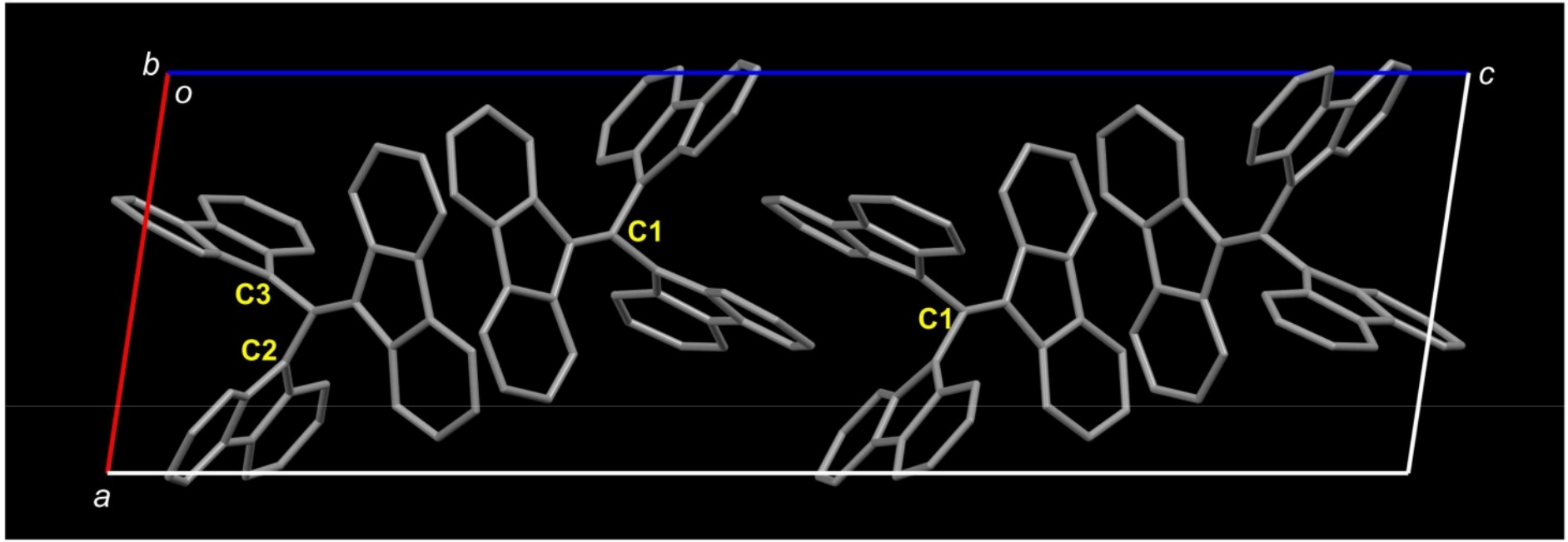
(a) Chemical structure of **1**. (b) An ORTEP drawing of **1** at 90 K. Thermal ellipsoids are drawn at the 50% probability level. (c) Static model deformation density maps on the C1–C2–C3 plane, and (d) cross-sectional view of the C1–C2–C3 plane along the line connecting C1 and the midpoint between the C2 and C3 atoms. The concentration of electron density between C2 and C3 is marked by a green circle. The blue lines represent positive contours from 0.01 to 0.05 e $Å^{-3}$ in steps of 0.01 e $Å^{-3}$ and from 0.10 to 0.50 e $Å^{-3}$ in steps of 0.05 e $Å^{-3}$. The red lines represent negative contours from −0.05 to −0.50 in steps of −0.05 e $Å^{-3}$.

UV/Vis-Spektroskopie





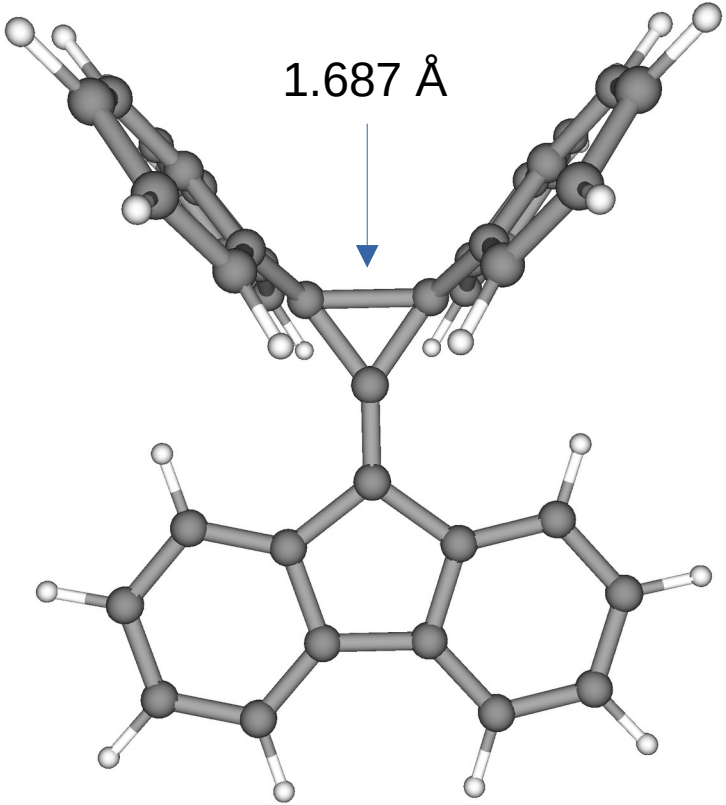
Packung im Kristall



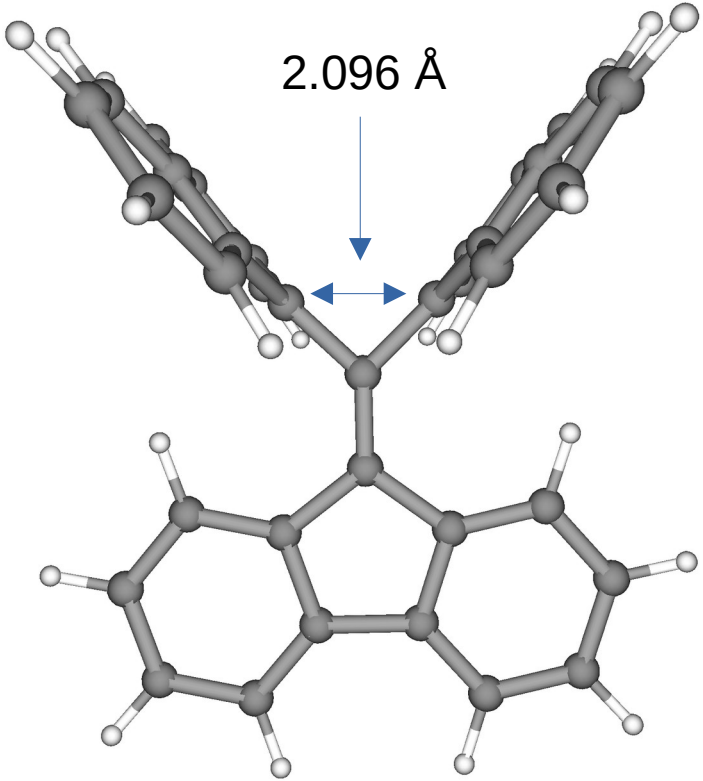
Rechnungen für freies Molekül

DFT method	Basis set	Interatomic distance [b] ($d_{C2–C3}$) / Å	Bond angle [b] ($\theta_{C2-C1-C3}$) / °
B3LYP	6-31G*	1.791	75.89
B3LYP	6-31G**	1.794	76.01
B3LYP	6-311G**	1.810	76.90
B3LYP-D3	6-31G*	1.801	76.69
B3LYP-D3	6-31G**	1.804	76.86
B3LYP-D3	6-31+G**	1.802	76.70
B3LYP-D3	6-311G*	2.047	89.25
B3LYP-D3	6-311G**	2.048	89.33
B3LYP-D3	6-311+G**	2.048	89.32
B3LYP-D3	cc-pVDZ	2.071	90.20
B3LYP-D3	cc-pVTZ	2.043	89.27
B3LYP-D3(BJ)	6-31G*	2.108	92.42
B3LYP-D3(BJ)	cc-pVTZ	2.100	92.26
B3PW91-D3	6-311G*	1.726	73.17
B3PW91-D3(BJ)	6-311G*	1.718	72.91
B3PW91-D3	cc-pVTZ	1.725	73.30
M06-2X	6-311G*	1.656	69.41
M06-2X	cc-pVTZ	1.653	69.44
wB97XD	6-31G*	1.667	69.96
wB97XD	6-311G*	1.668	70.08
wB97XD	cc-pVTZ	1.666	70.18
PBE0-D3	6-311G*	1.696	71.67
PBE0-D3(BJ)	6-311G*	1.692	71.53

Rechnungen für freies Molekül

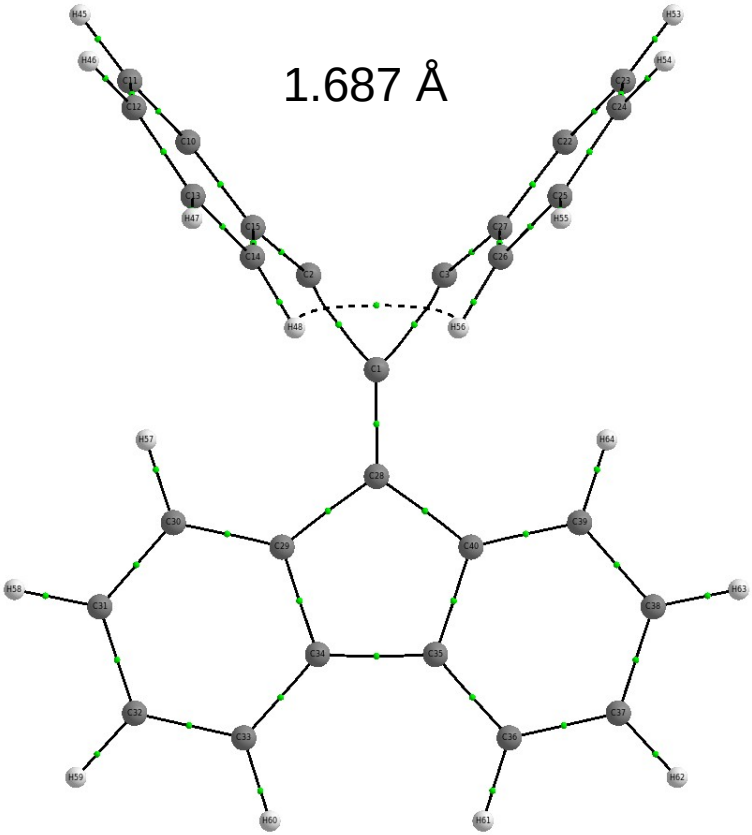


PBE0-D3BJ/def2-TZVPP
PBE0-D3BJ/def2-QZVPP

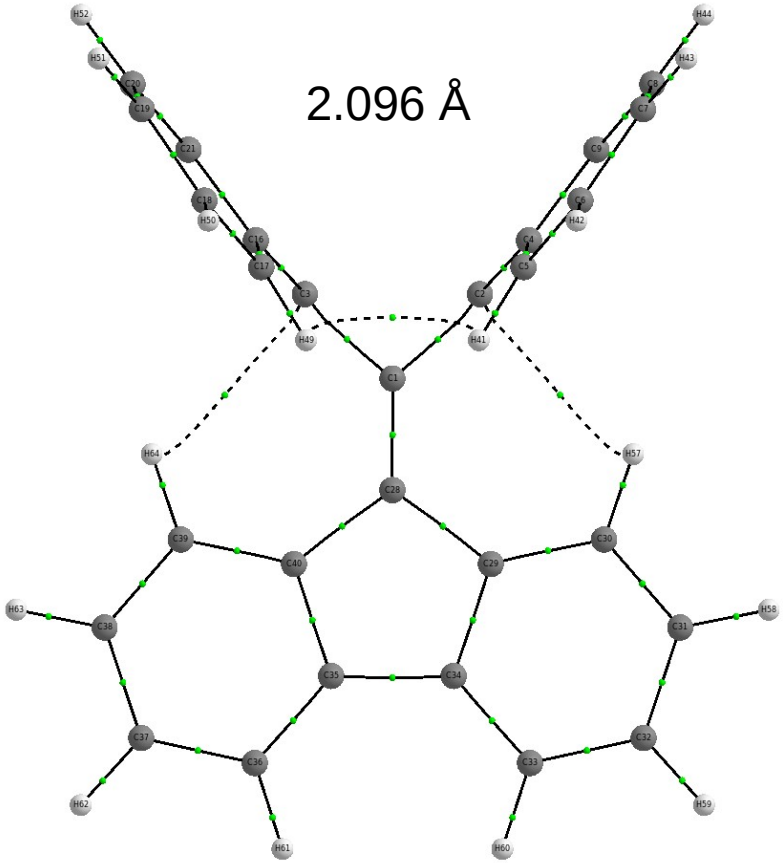


B3LYP-D3BJ/def2-TZVPP

QTAIM Analyse: kritische Punkte

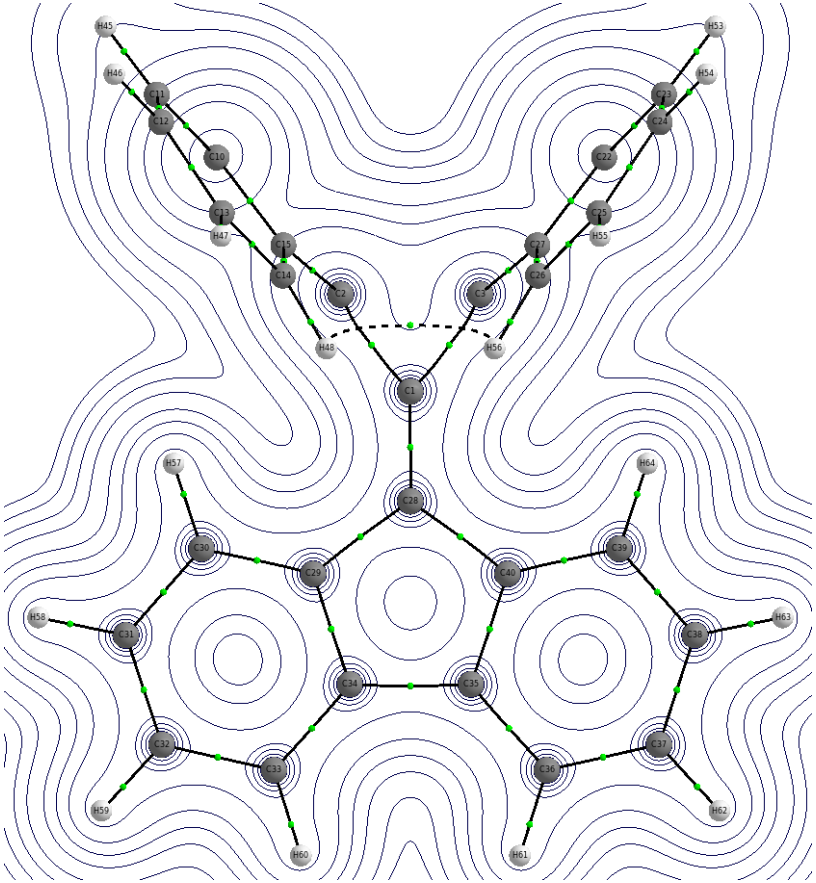


PBE0-D3BJ/def2-TZVPP

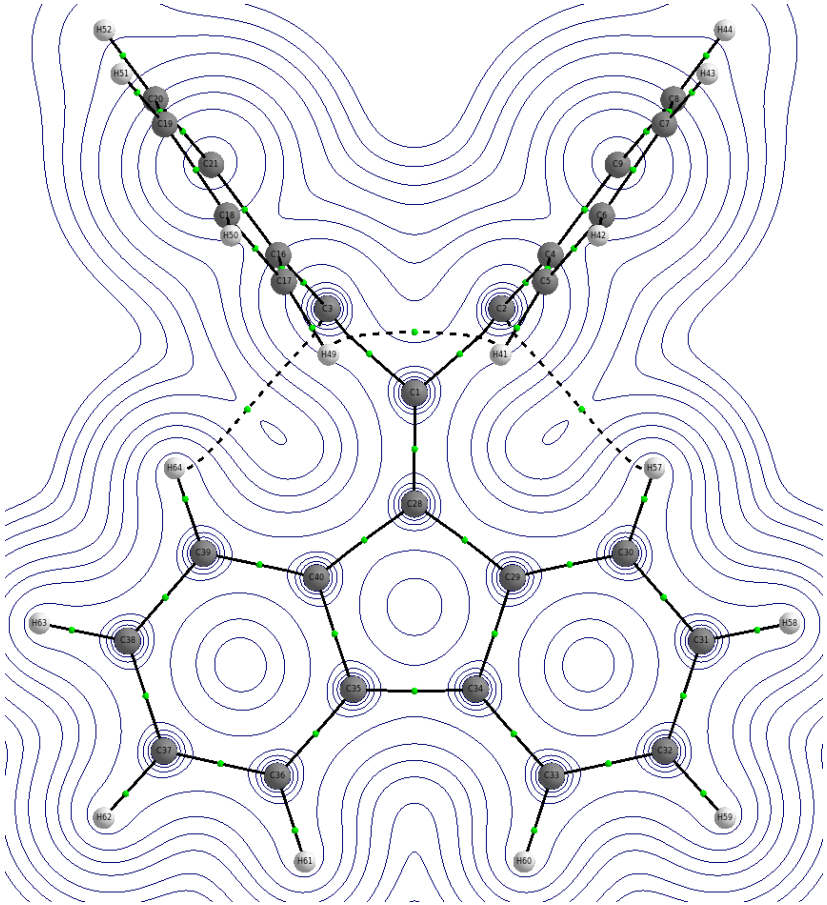


B3LYP-D3BJ/def2-TZVPP

QTAIM Analyse: Elektronendichte

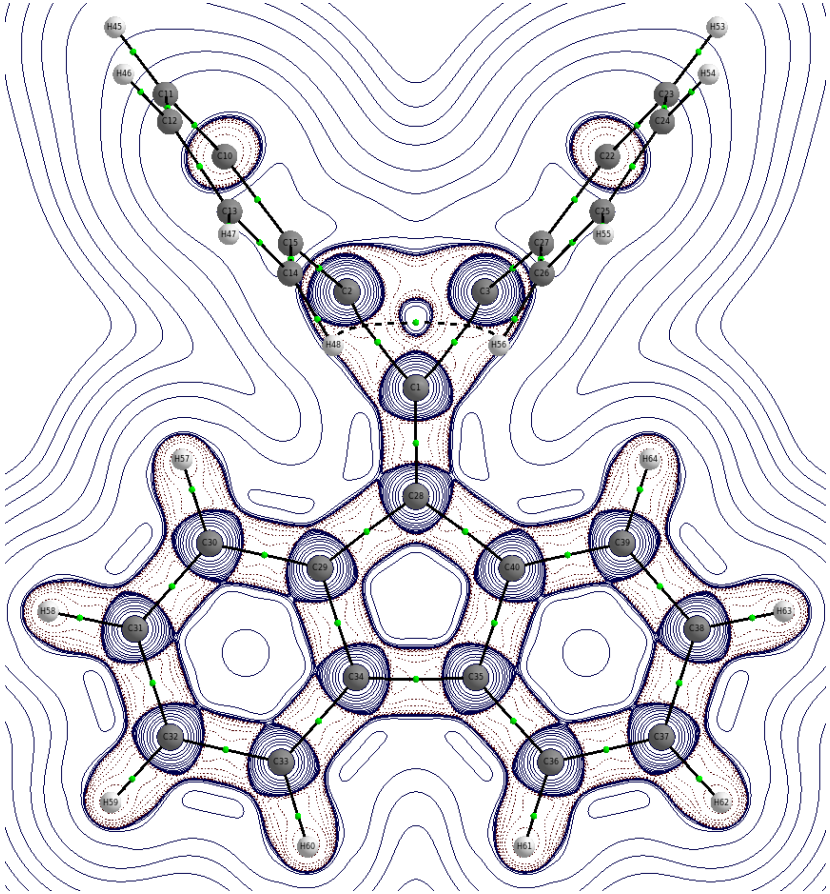


PBE0-D3BJ/def2-TZVPP

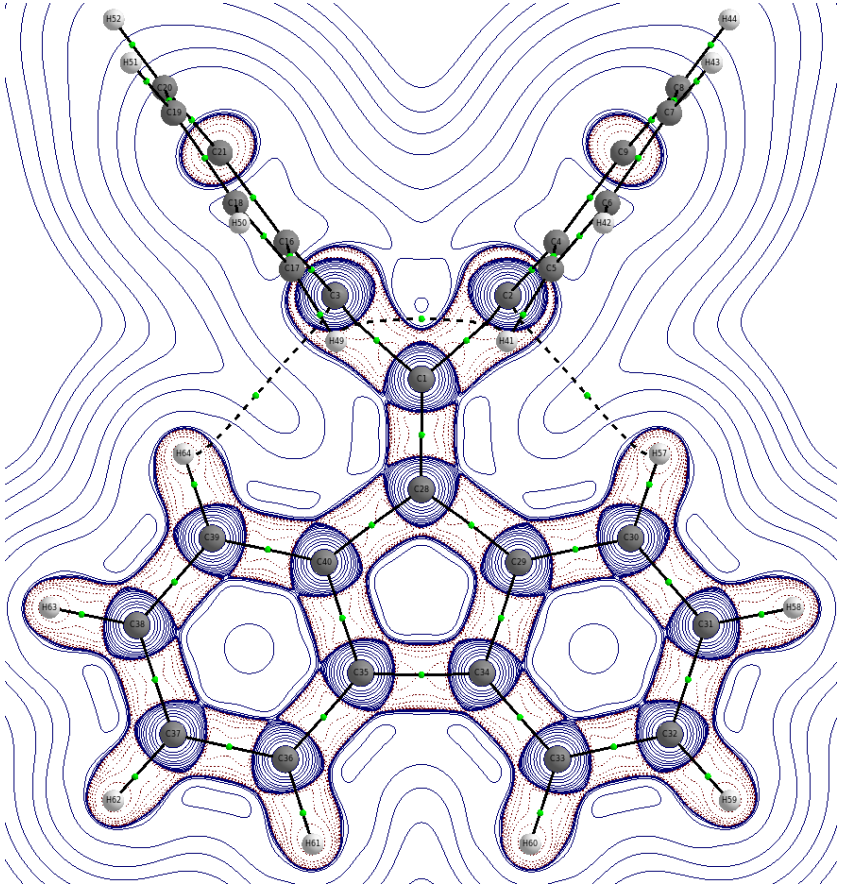


B3LYP-D3BJ/def2-TZVPP

QTAIM Analyse: Laplacian von El.-Dichte



PBE0-D3BJ/def2-TZVPP



B3LYP-D3BJ/def2-TZVPP

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