



Pyrit



Zinnober



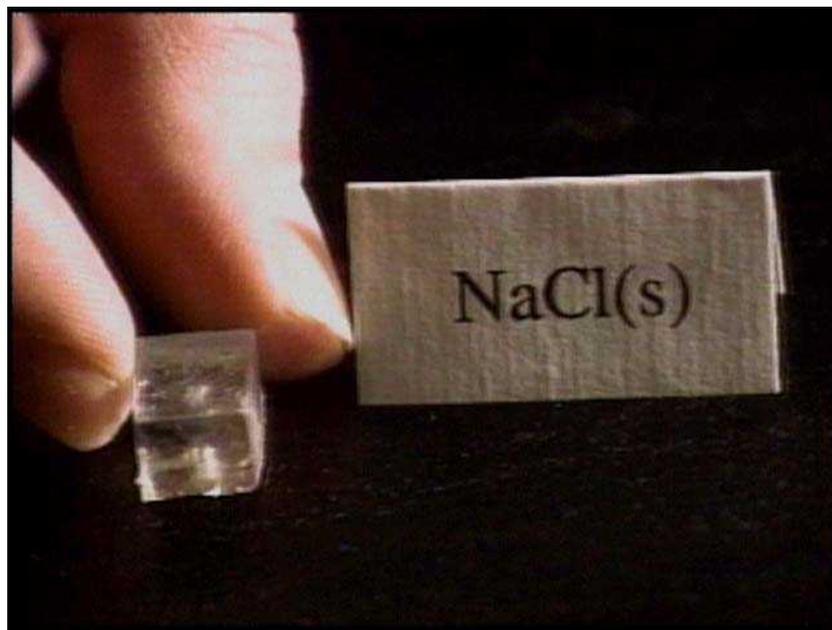
Quarz, durch Hämatit verfärbt

Small crystal of NaCl: transparent, 90° angles.

Tap knife blade parallel to one side: crystal cleaves into 2 pieces with very clean plane edges.

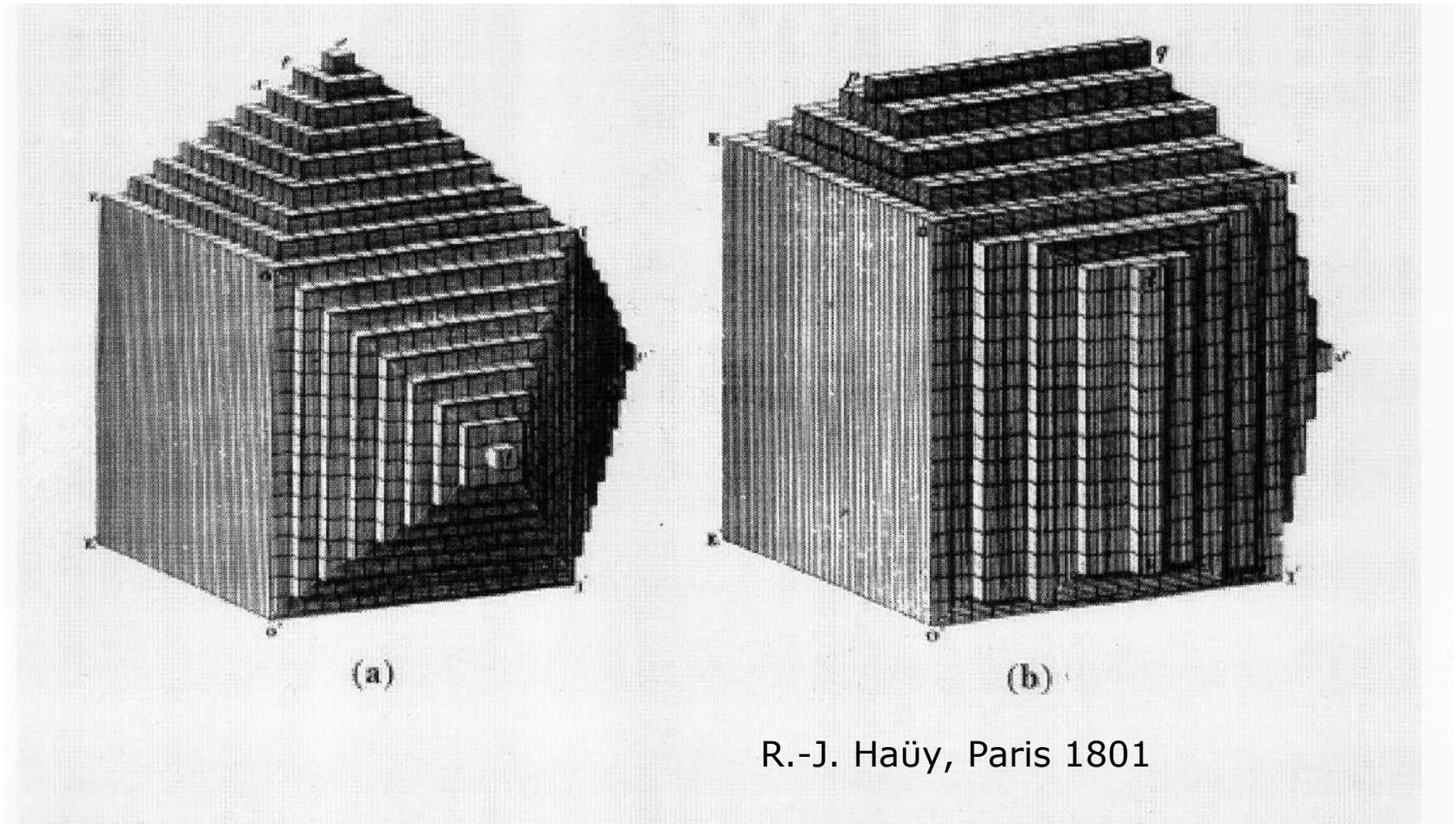
Next the blade is placed at a 45° angle to a side and tapped with a hammer.

The crystal shatters, but part of it cleaves parallel to a side.



Hypothese:

Kristall = symmetrische Anordnung identischer Strukturelemente

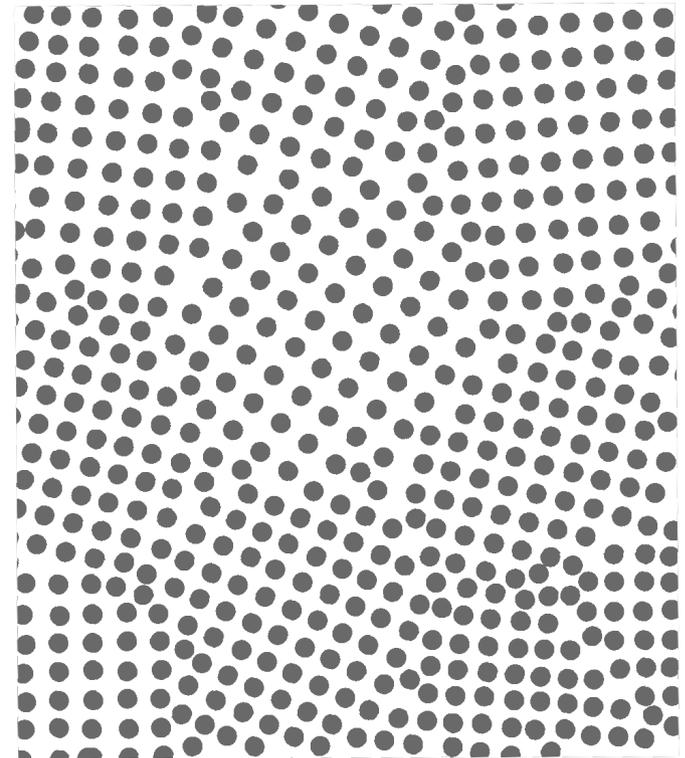
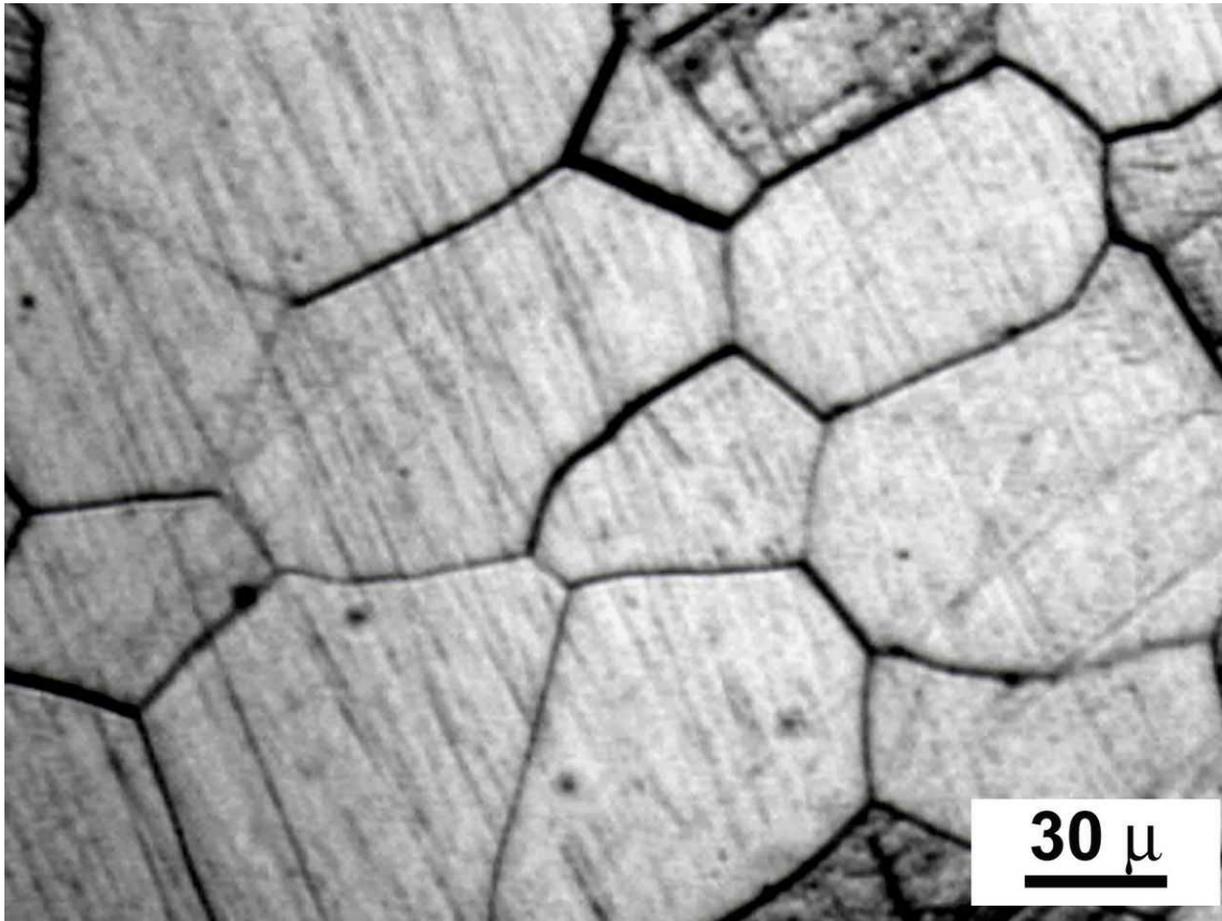


R.-J. Haüy, Paris 1801

Nachweis durch Röntgenbeugung
1913

Warum sehen wenige Festkörper aus wie "Kristalle"?

Mikrofotografie eines **polykristallinen** Metalls
Korngrenzen durch Ätzung sichtbar gemacht



Bravais lattice

(a) infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed

(b) set of points with position vectors \mathbf{R} of the form

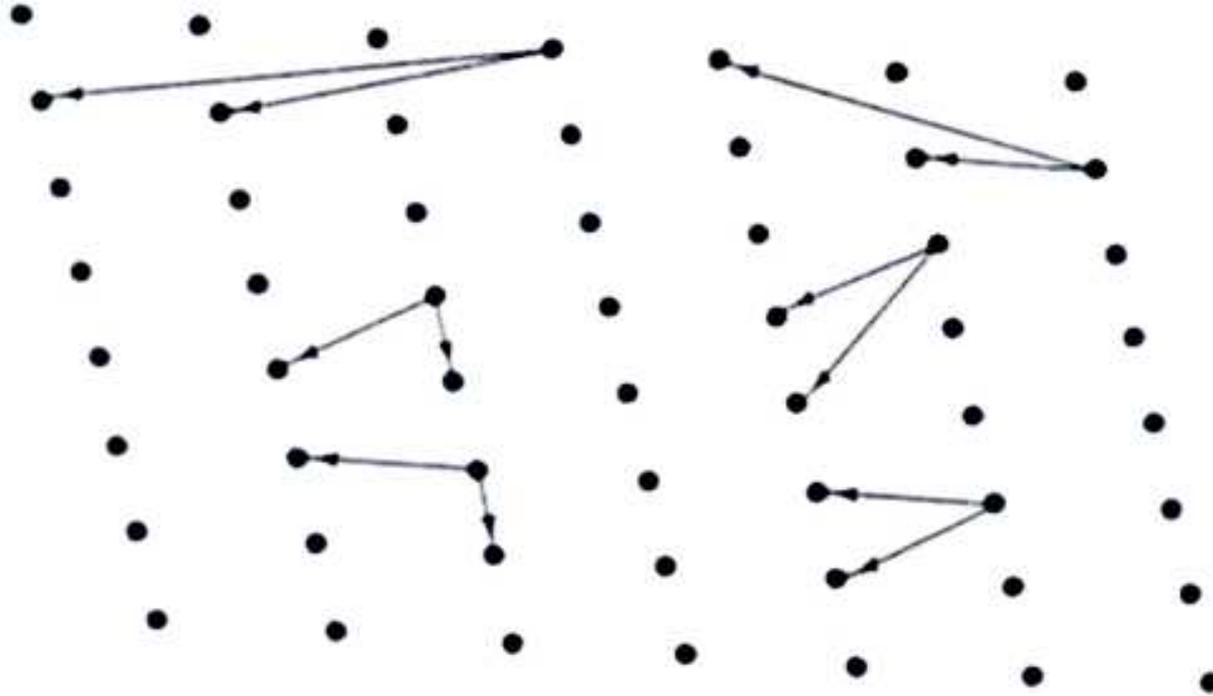
$$\mathbf{R} = \sum n_i \mathbf{a}_i$$

where \mathbf{a}_i is a set of 3 (2) vectors not all in the same plane (direction) and

$$n_i \in \mathbb{Z}$$

\mathbf{a}_i are called primitive vectors, which generate or span the lattice

Primitive vectors \mathbf{a}_i are not unique

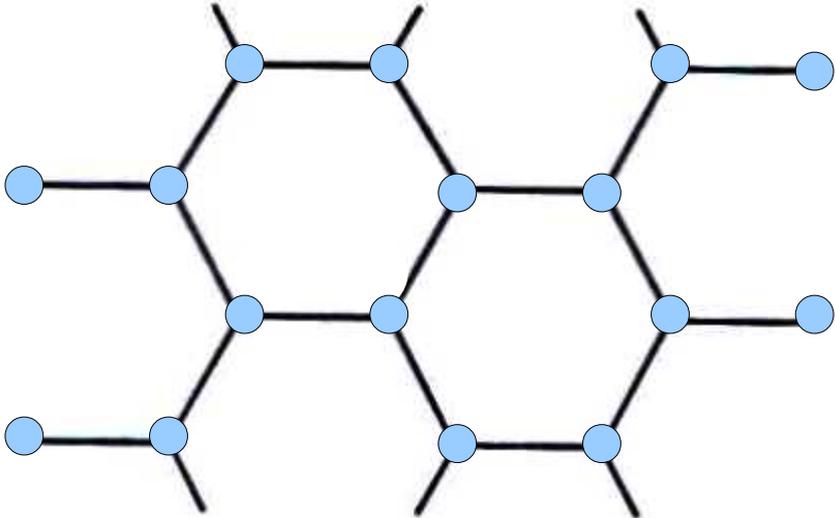
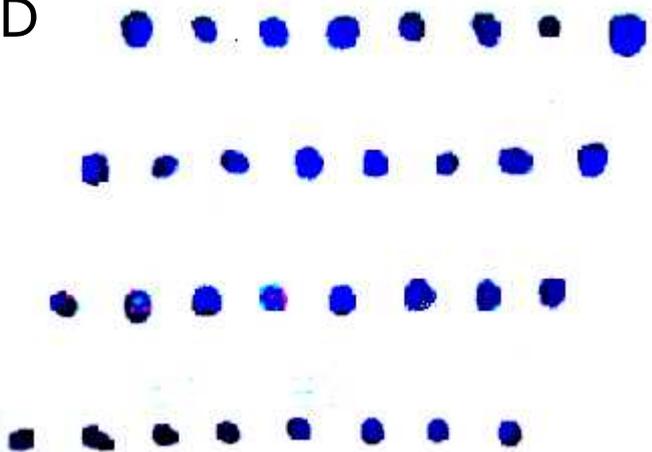


Primitive Vektoren spannen Elementarzelle auf

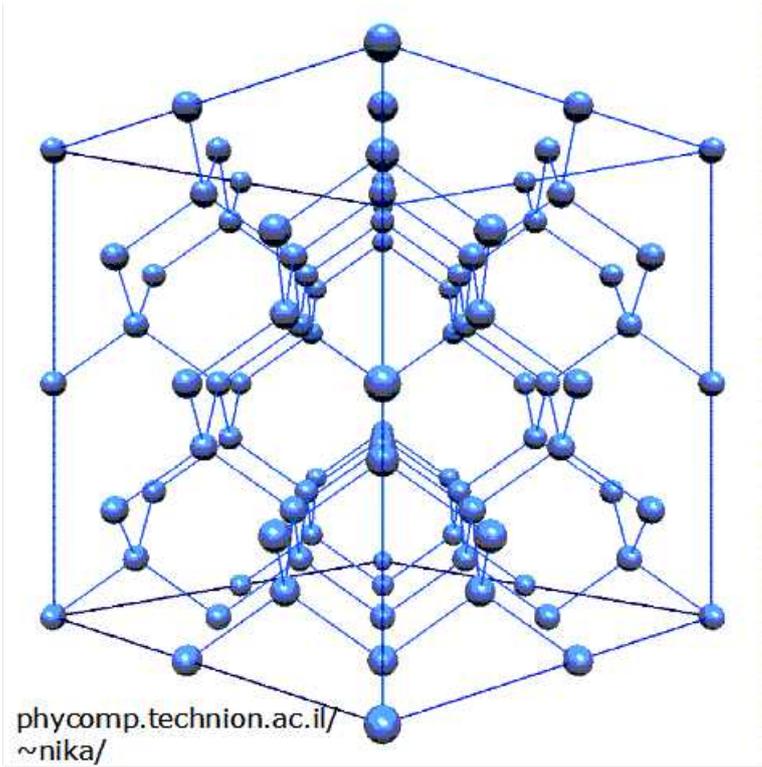
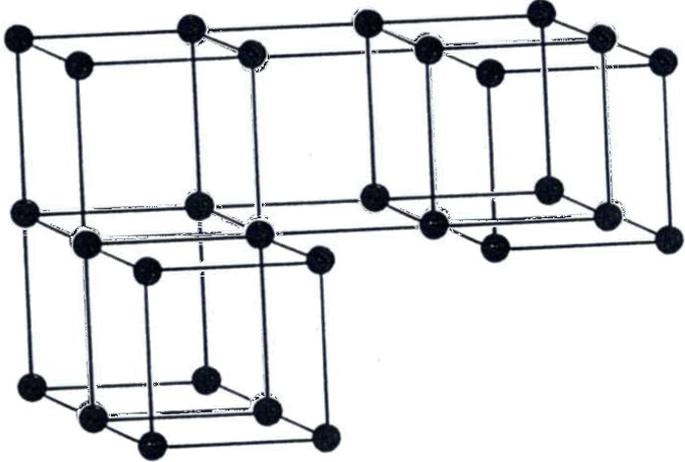
Primitive Zelle: Elementarzelle mit minimalem Volumen

BRAVAIS-Gitter ?

2D



3D



Gitter mit Basis

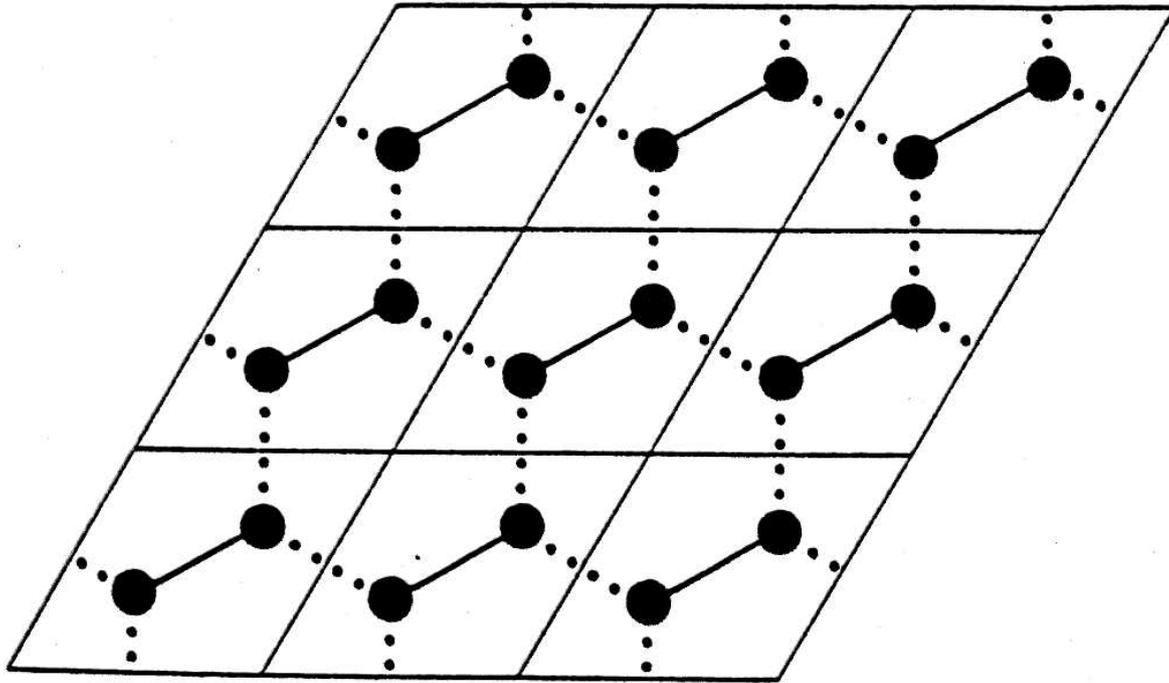
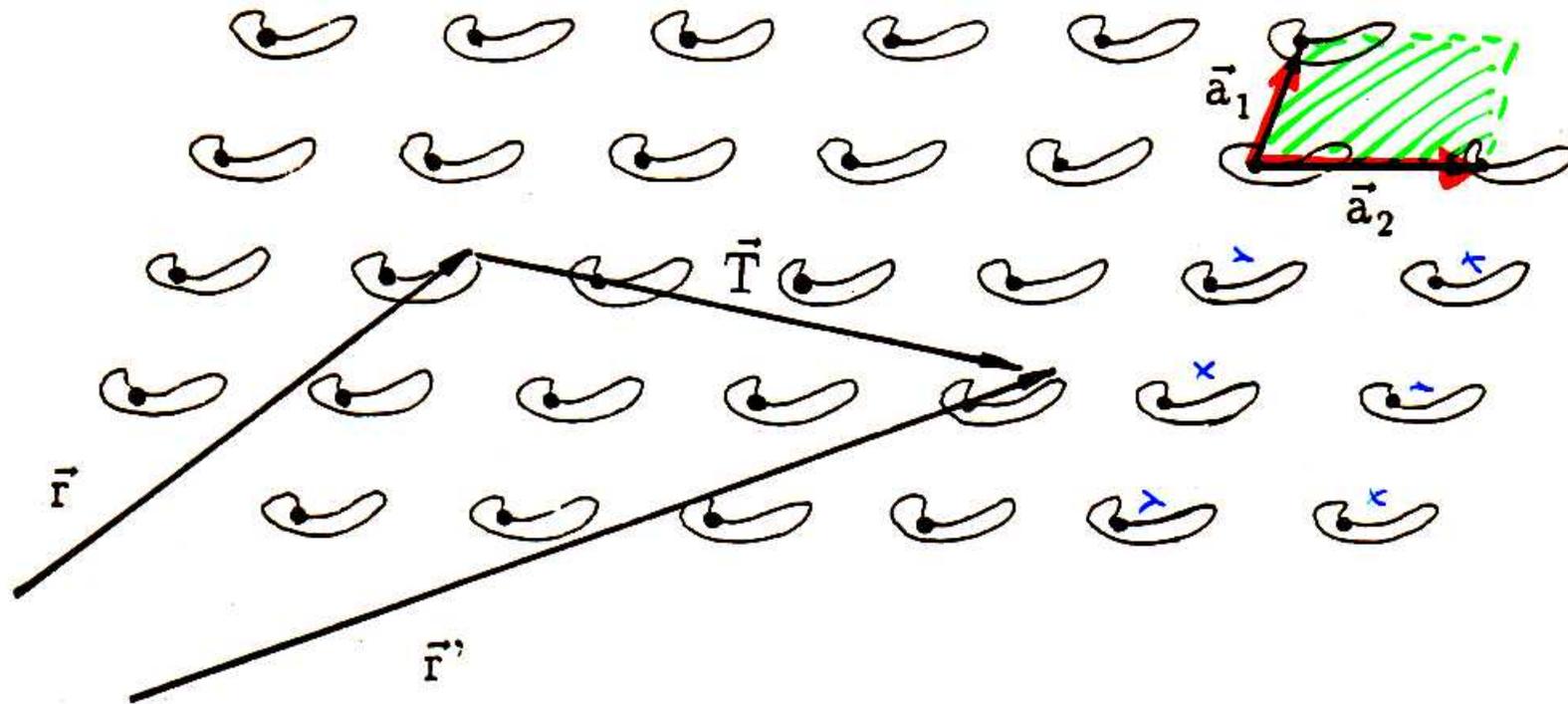


Figure 4.17

The honeycomb net, drawn so as to emphasize that it is a Bravais lattice with a two-point basis. The pairs of points joined by heavy solid lines are identically placed in the primitive cells (parallelograms) of the underlying Bravais lattice.

Kristallstruktur – mehr als ein Punktgitter



Idealer Kristall:

unendlich ausgedehnte Wiederholung identischer Struktureinheiten

fundamentale Translationsvektoren $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$

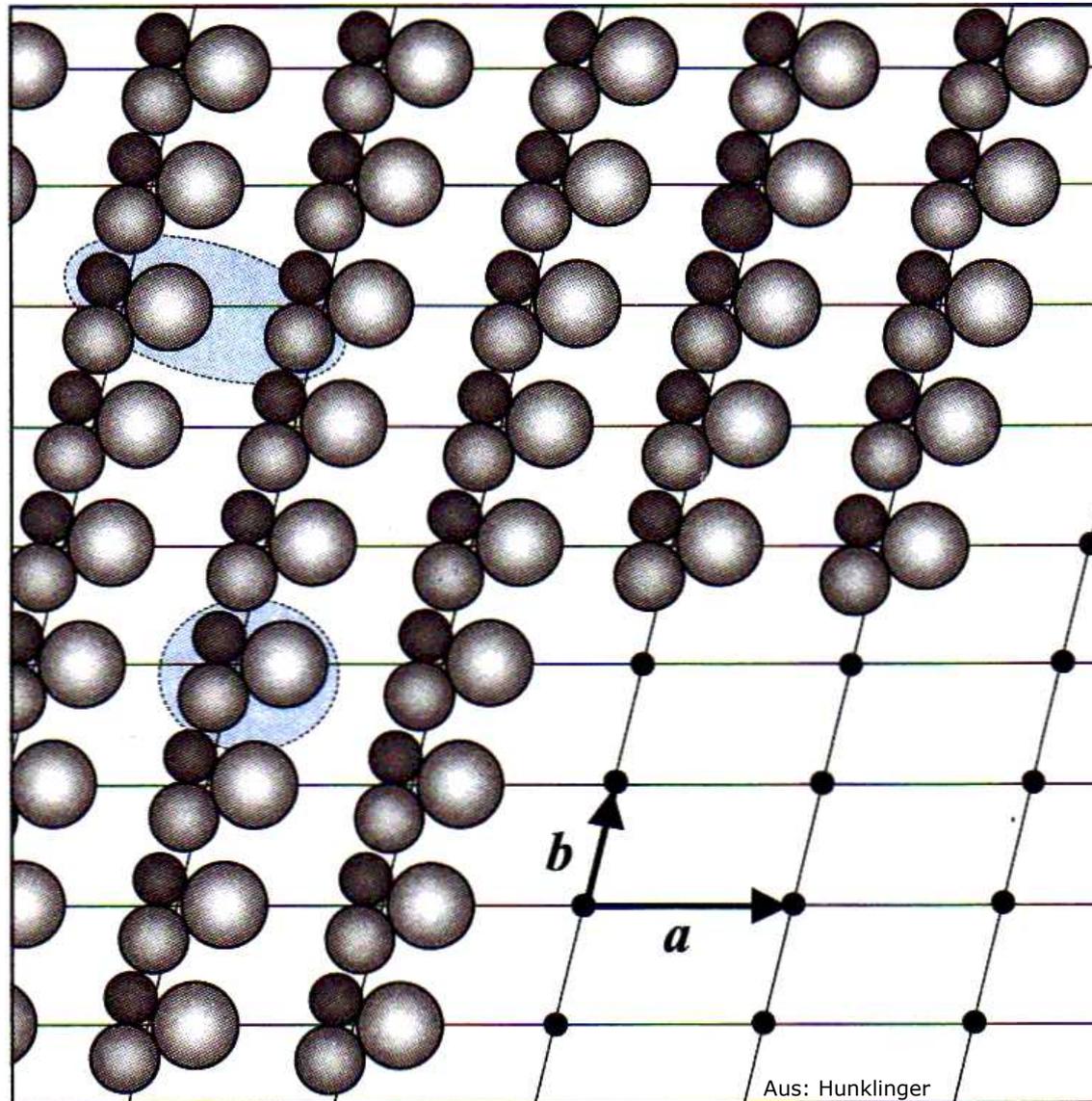
Einheitszelle

Gitter: $\mathbf{r} = \mathbf{r}' + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ mit n_i aus \mathbb{Z}

Basis: $\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3$ mit x, y, z aus $[0,1]$

"Kristall = Gitter + Basis"

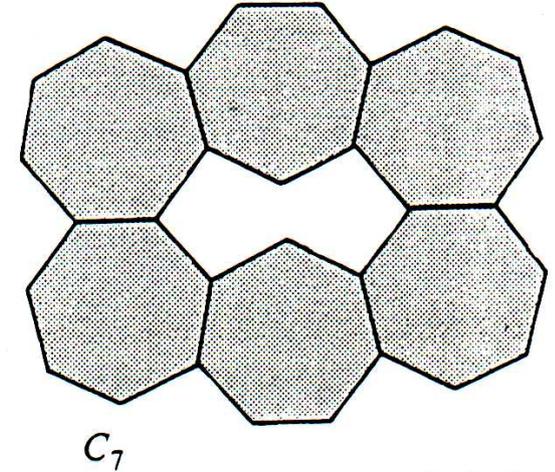
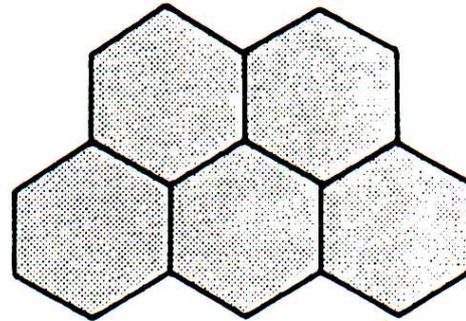
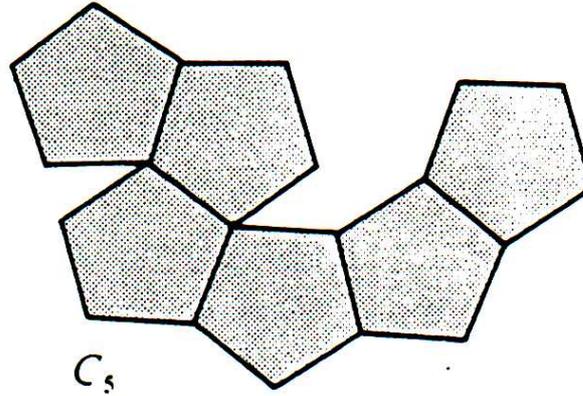
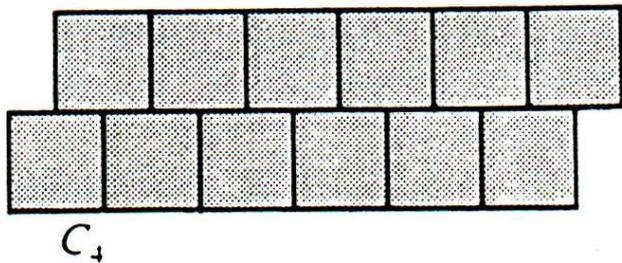
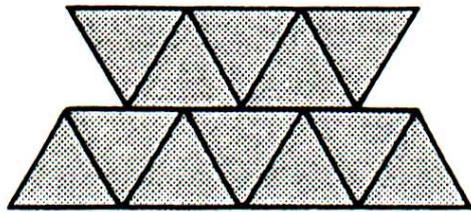
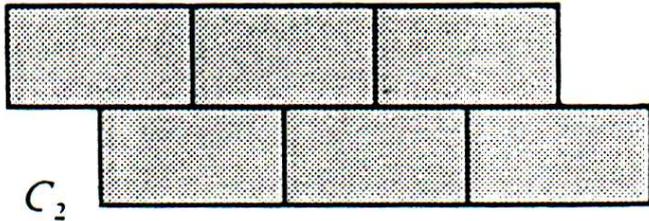
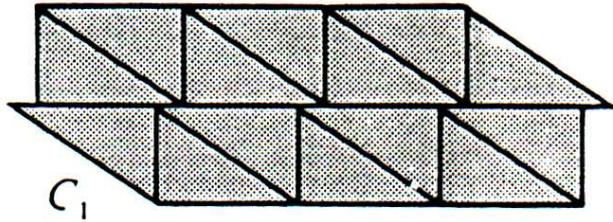
Kristallstruktur und Punktgitter



Primitive Vektoren a , b legen schiefwinkliges Koordinatensystem fest

Basis: Anordnung der Atome und Wahl des Ursprungs im Punktgitter sind ohne Bedeutung.

Klassifikation: Drehsymmetrien



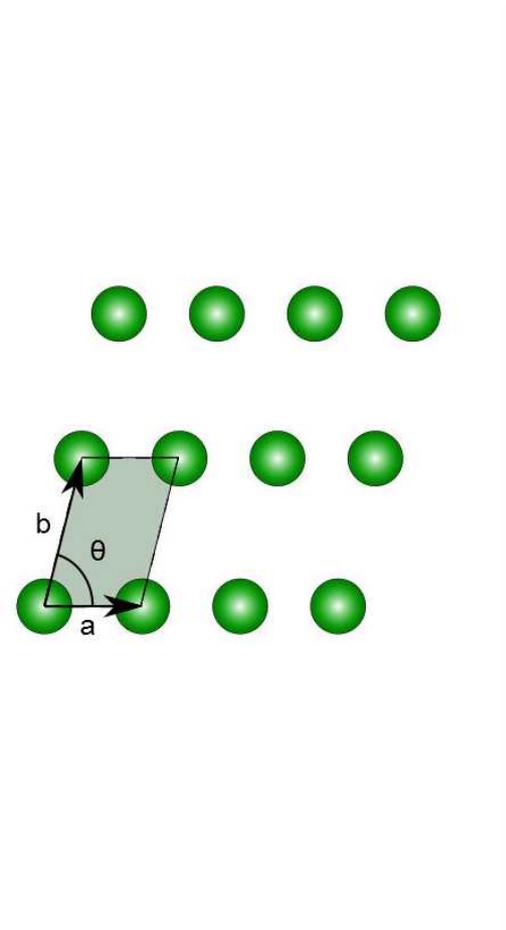
Vollständige Füllung einer Fläche ist nur mit Figuren möglich, die 1, 2, 3, 4 oder 6-zählige Achsen enthalten.

Klassifikation der Bravaisgitter:

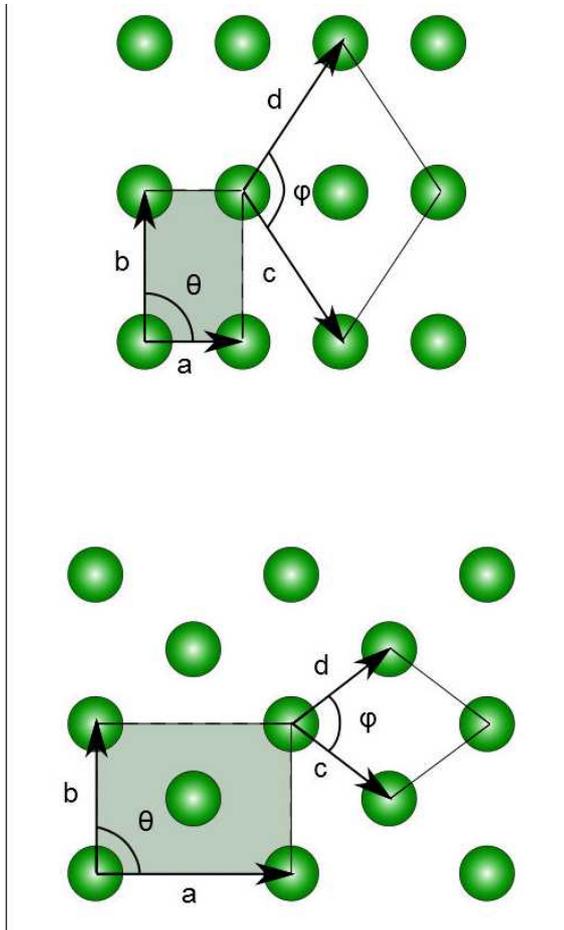
in 2d ist das übersichtlich ...

Invarianz bzgl. Drehungen

Wikipedia

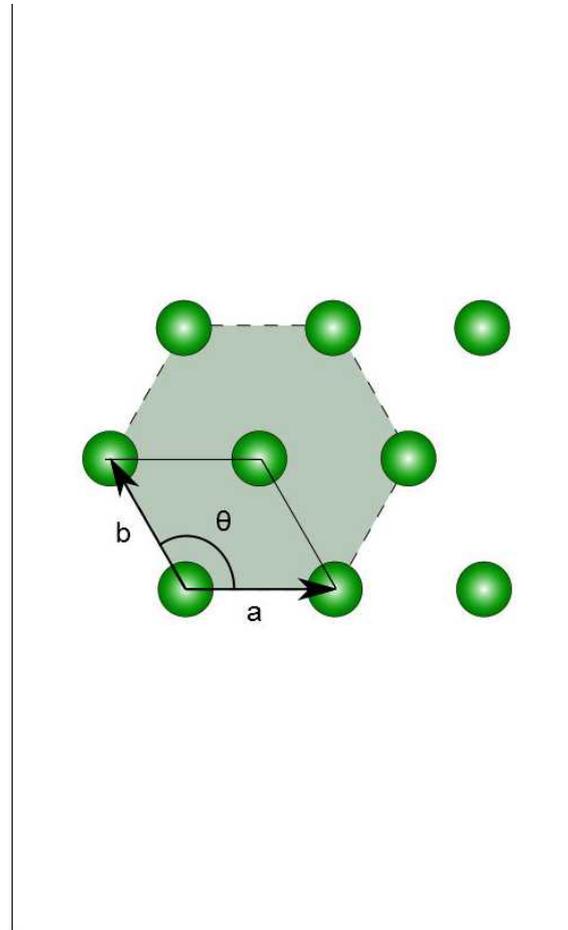


$$|a| \neq |b|, \theta \neq 90^\circ$$

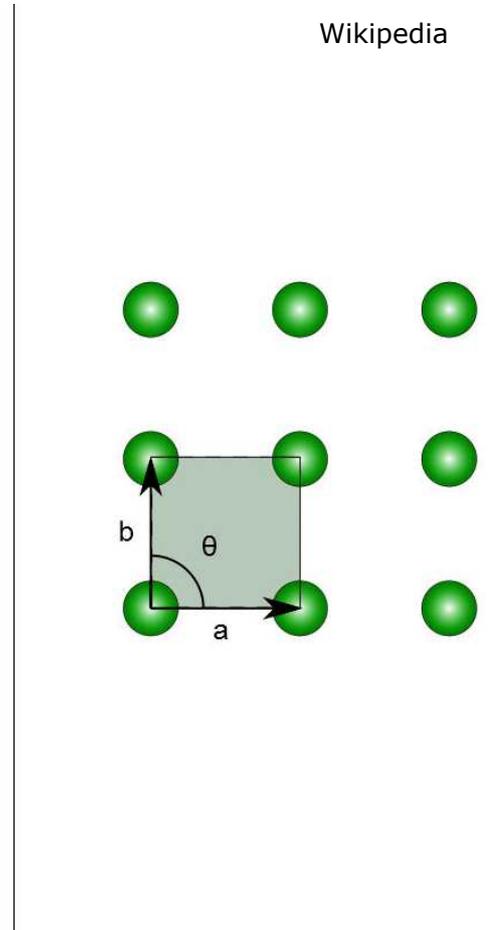


$$|a| \neq |b|, \theta = 90^\circ$$

$$|c| = |d|, \phi \neq 90^\circ$$



$$|a| = |b|, \theta = 120^\circ$$



$$|a| = |b|, \theta = 90^\circ$$

Klassifikation der 3d Bravaisgitter:

"etwas" aufwendiger ...

ersteinmal Beispiele

Kubisch-raumzentriertes Gitter (krz)

Body-centered cubic lattice (bcc)

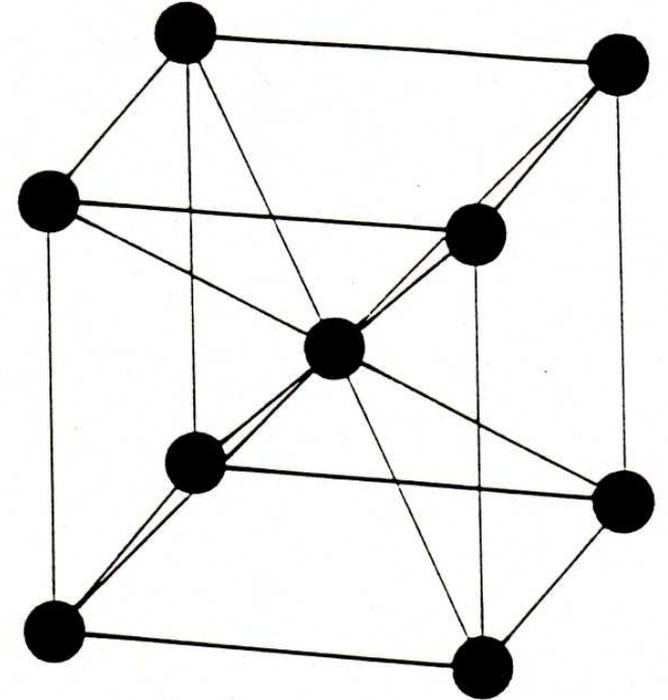
Koordinationszahl 8, aber 6 NNN mit wenig mehr Abstand)

Bravais Gitter * 2 Atome / Einheitszelle

* Basis $(0,0,0)$, $\frac{1}{2}(1,1,1)$

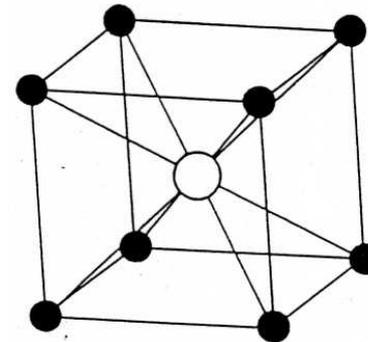
Packungsdichte 68 %

Alkalis, V, Nb, Fe, Cr



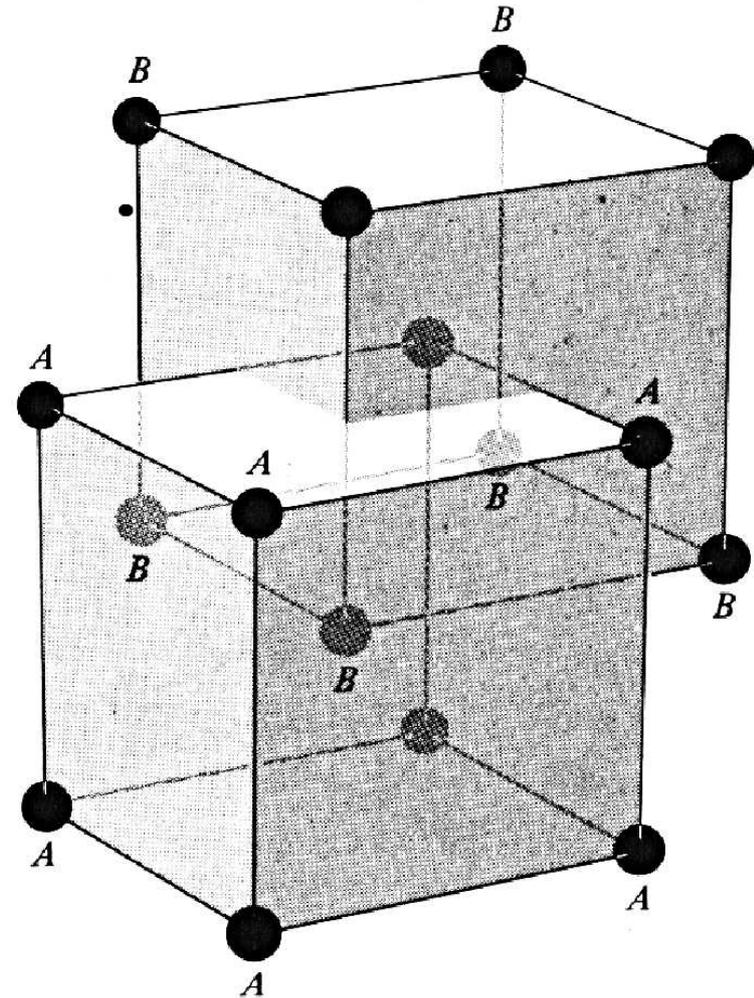
mit 2 Atomsorten in Basis: CsCl-Struktur

BeCu, NiAl, CuZn, NH_4Cl



The body-centered cubic lattice is a Bravais lattice:

A few sites from a body-centered cubic Bravais lattice. Note that it can be regarded either as a simple cubic lattice formed from the points *A* with the points *B* at the cube centers, or as a simple cubic lattice formed from the points *B* with the points *A* at the cube centers. This observation establishes that it is indeed a Bravais lattice.



ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

SOME COMPOUNDS WITH THE CESIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

Kubisch-flächenzentriertes Gitter (kfz)

Face-centered cubic lattice (fcc)

Koordinationszahl 12

Bravais Gitter * 4 Atome / Einheitszelle

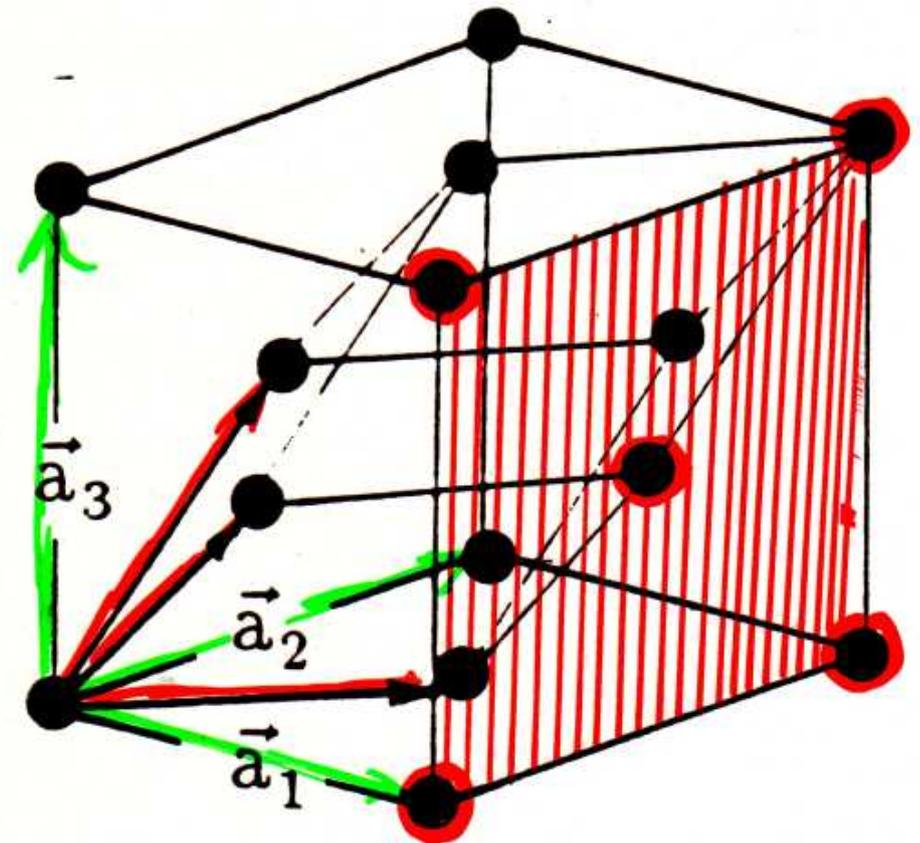
* Basis $(0,0,0)$, $\frac{1}{2}(1,1,0)$, $\frac{1}{2}(1,0,1)$, $\frac{1}{2}(0,1,1)$

primitive Einheitszelle rhomboedrisch

* $V = \mathbf{a}_1 (\mathbf{a}_2 \times \mathbf{a}_3)$

* $|\mathbf{a}_1| = |\mathbf{a}_2| = |\mathbf{a}_3|$

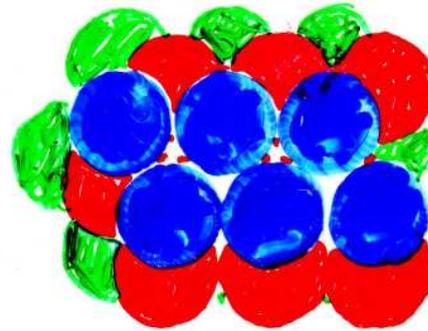
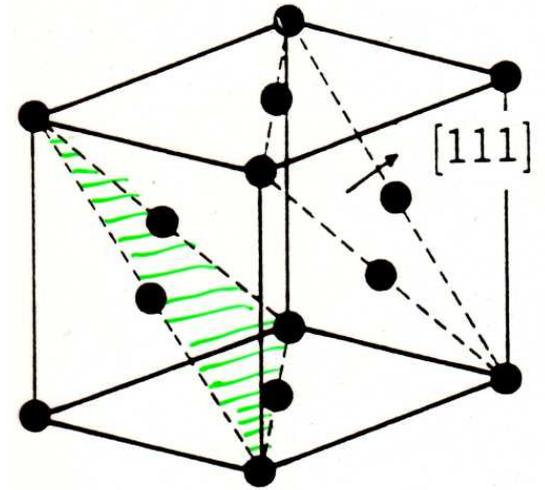
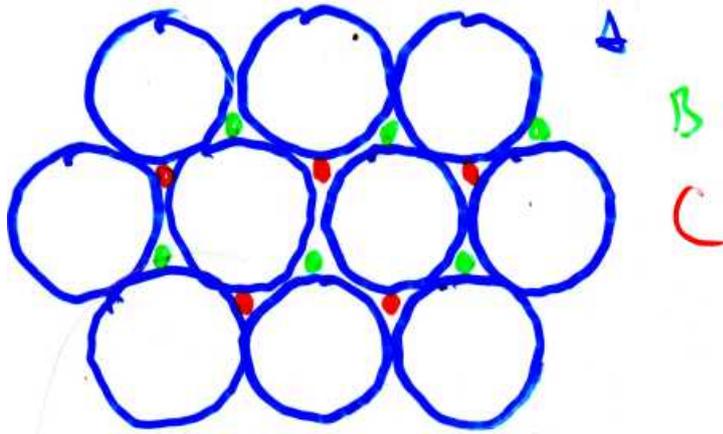
* $\alpha = \beta = \gamma < 120^\circ$



Aufbauprinzip:

Ebenen mit dichtester Kugelpackung (111)

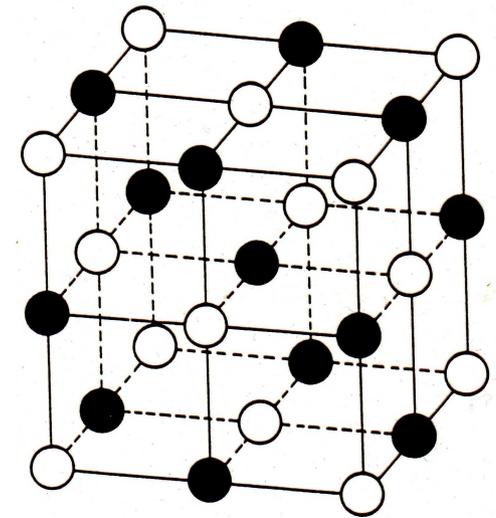
Stapelfolge ABCABCA...



Packungsdichte 74 %

NaCl Gitter

Cl: (0,0,0) Na: $\frac{1}{2}$ (1,1,1) $a = 5,63 \text{ \AA}$



**ELEMENTS WITH THE MONATOMIC FACE-CENTERED
CUBIC CRYSTAL STRUCTURE**

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ -Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β -Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

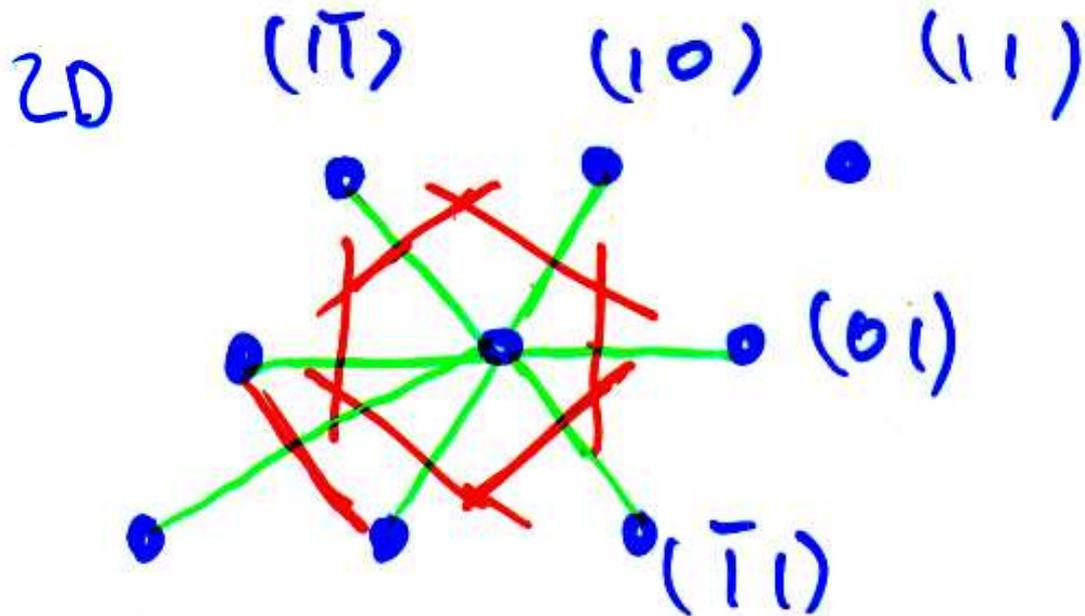
Wigner - Seitz - Zelle

(eine) Zelle kleinsten Volumens

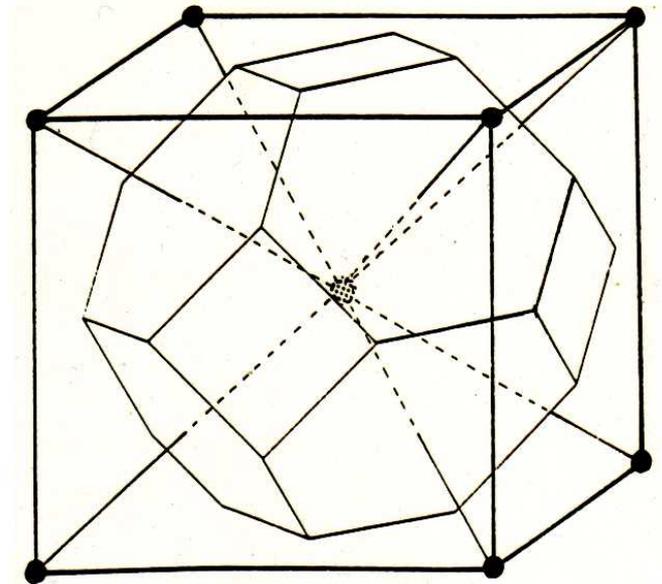
mit voller Symmetrie des Gitters!

Konstruktionsvorschrift:

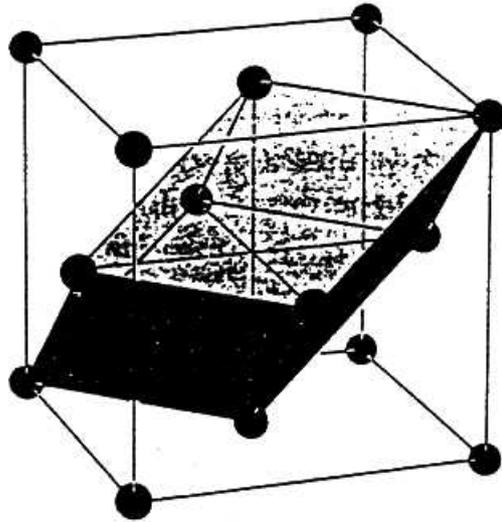
- Verbindungslinien zu Nachbarn
- Dazu Mittelsenkrechten Ebenen
- Dadurch begrenztes Volumen



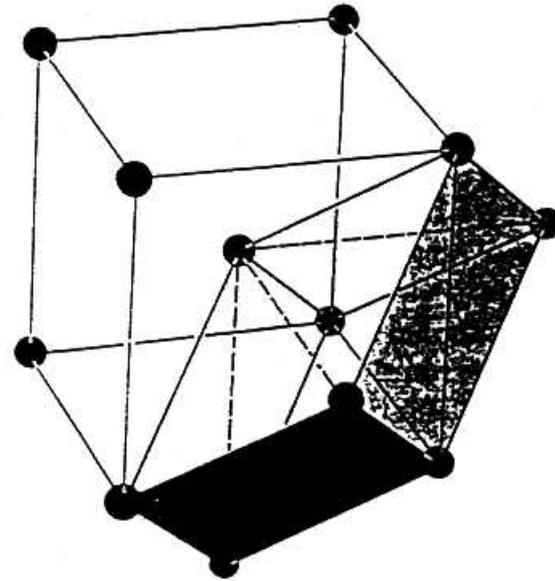
3D bcc



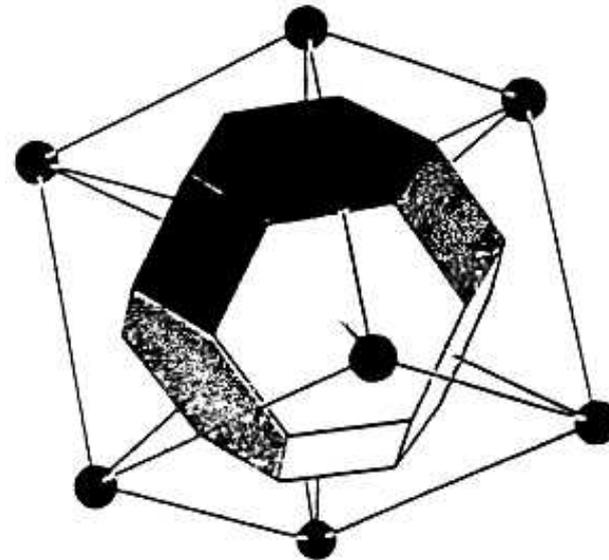
Primitive (Wigner Seitz) & Conventional Unit Cells



fcc



bcc



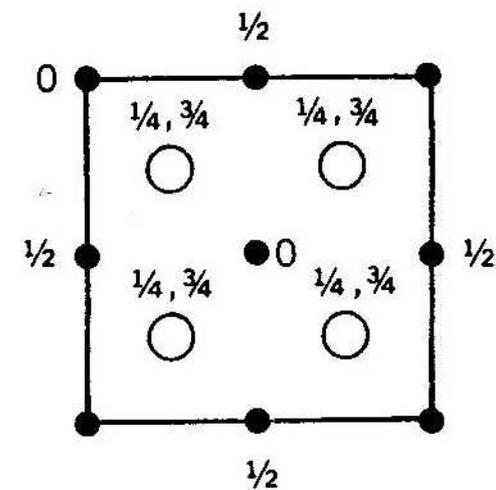
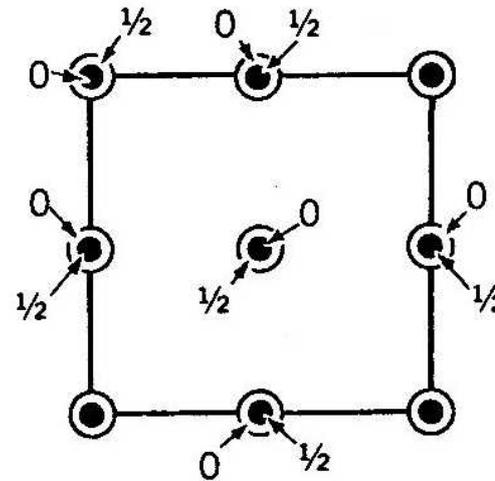
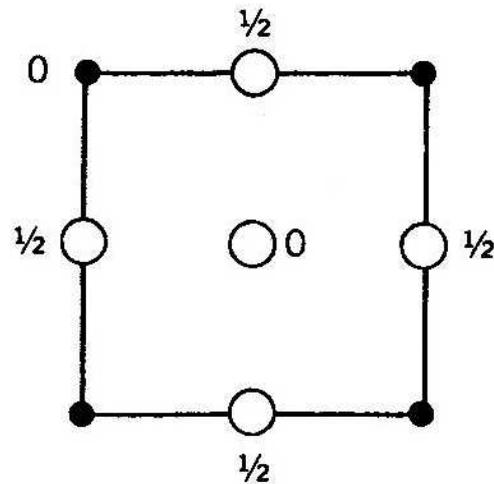
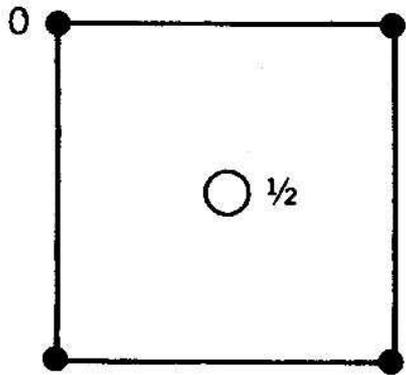
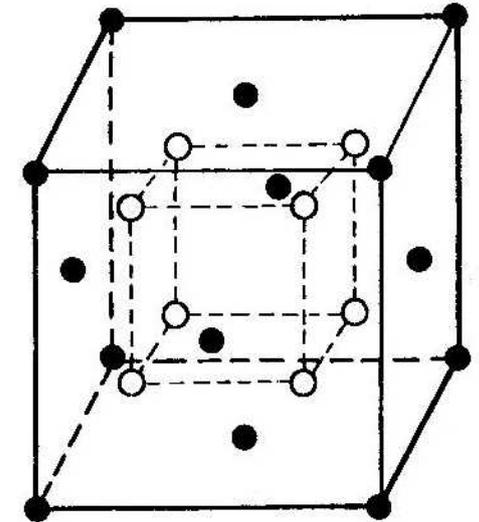
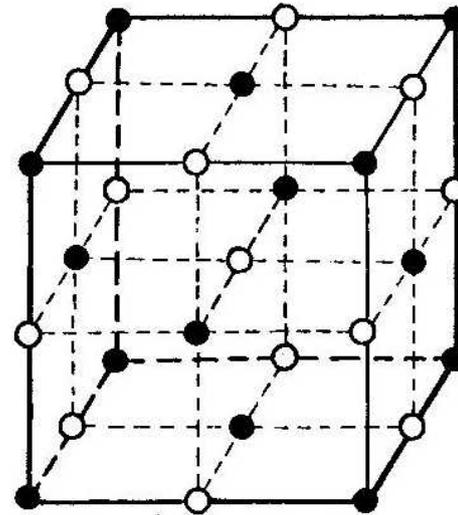
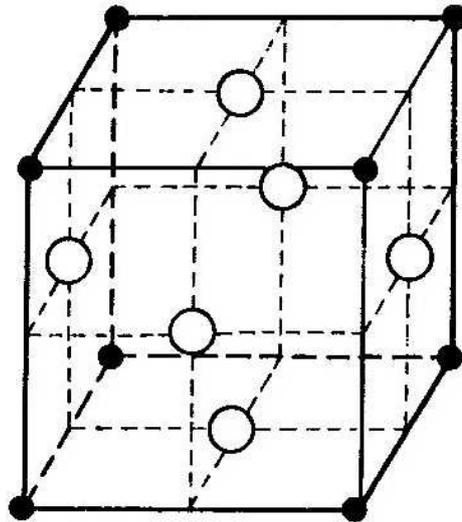
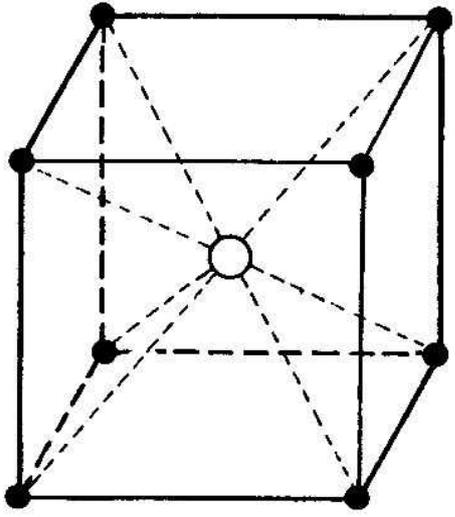
Kristallstrukturen mit kubischen Gittern

sc: CsCl

sc: Cu₃Au

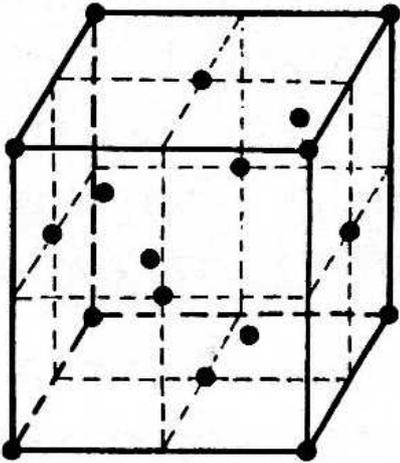
fcc: NaCl

fcc: CaF₂

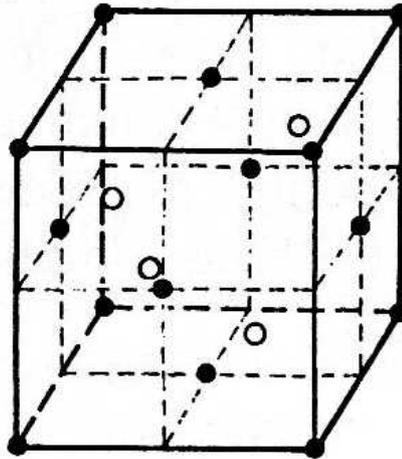


h/a bezogen auf Grundfläche

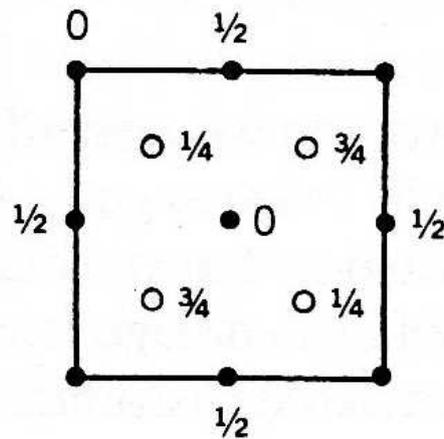
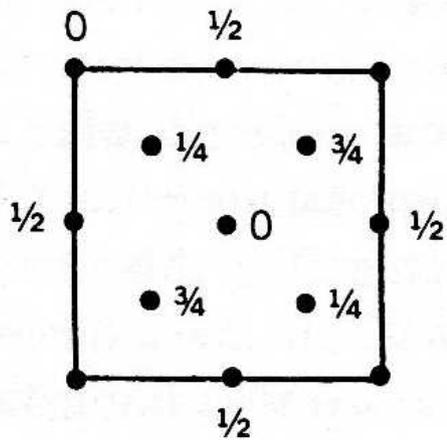
Diamant



Zinkblende



Sphalerit
oder
Zinkblende



h/a bezogen auf Grundfläche

SOME COMPOUNDS WITH THE SODIUM CHLORIDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
LiF	4.02	RbF	5.64	CaS	5.69
LiCl	5.13	RbCl	6.58	CaSe	5.91
LiBr	5.50	RbBr	6.85	CaTe	6.34
LiI	6.00	RbI	7.34	SrO	5.16
NaF	4.62	CsF	6.01	SrS	6.02
NaCl	5.64	AgF	4.92	SrSe	6.23
NaBr	5.97	AgCl	5.55	SrTe	6.47
NaI	6.47	AgBr	5.77	BaO	5.52
KF	5.35	MgO	4.21	BaS	6.39
KCl	6.29	MgS	5.20	BaSe	6.60
KBr	6.60	MgSe	5.45	BaTe	6.99
KI	7.07	CaO	4.81		

Diamantgitter

fcc Gitter mit Basis (000) , $\frac{1}{4}(1,1,1)$,

also 2 gegeneinander verschobene fcc Gitter

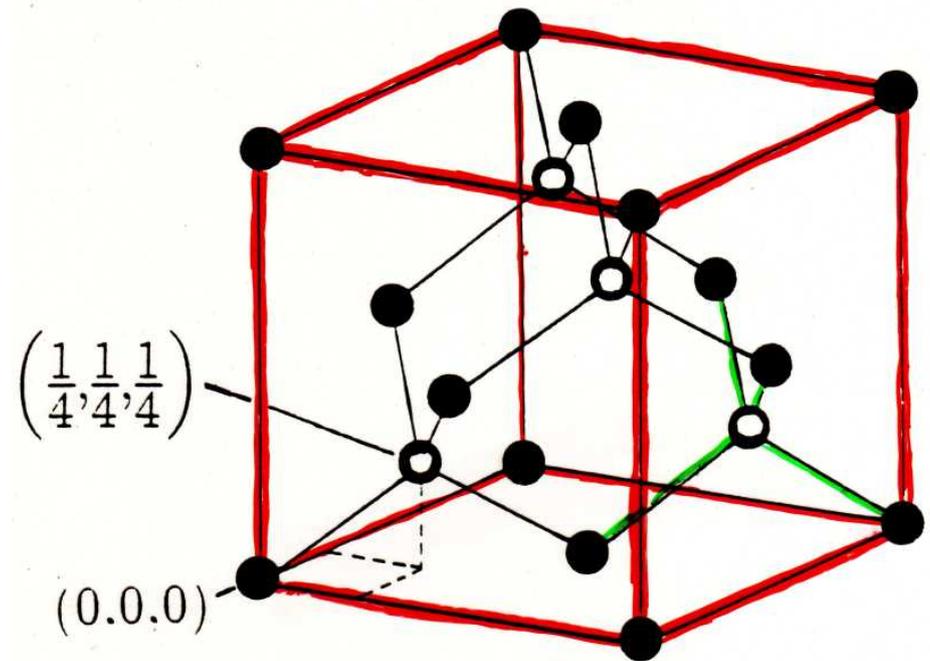
Koordination 4, tetraedrisch

Dichte 34 %

C, Si, Ge, α -Sn, ...

verschiedene Basisatome:

GaAs, GaP, (III-V Halbleiter) ...



II-VI HL wie ZnO, CdS, CdSe, ... oft Wurtzit (hex.)

ELEMENTS WITH THE DIAMOND CRYSTAL STRUCTURE

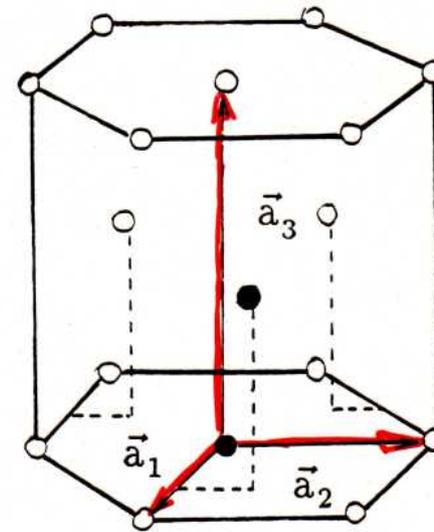
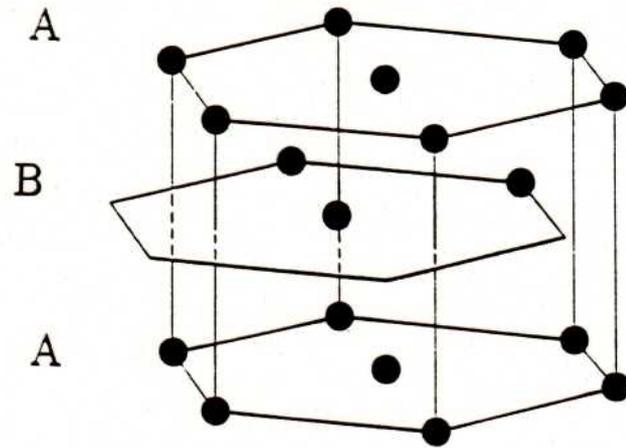
ELEMENT	CUBE SIDE a (Å)
C (diamond)	3.57
Si	5.43
Ge	5.66
α -Sn (grey)	6.49

Diamond structure with 2 different species:

SOME COMPOUNDS WITH THE ZINCBLLENDE STRUCTURE

CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
CuF	4.26	ZnS	5.41	AlSb	6.13
CuCl	5.41	ZnSe	5.67	GaP	5.45
CuBr	5.69	ZnTe	6.09	GaAs	5.65
CuI	6.04	CdS	5.82	GaSb	6.12
AgI	6.47	CdTe	6.48	InP	5.87
BeS	4.85	HgS	5.85	InAs	6.04
BeSe	5.07	HgSe	6.08	InSb	6.48
BeTe	5.54	HgTe	6.43	SiC	4.35
MnS (red)	5.60	AlP	5.45		
MnSe	5.82	AlAs	5.62		

Hexagonales Gitter – hexagonal close packed (hcp)



Grundfläche hexagonal dichtgepackt

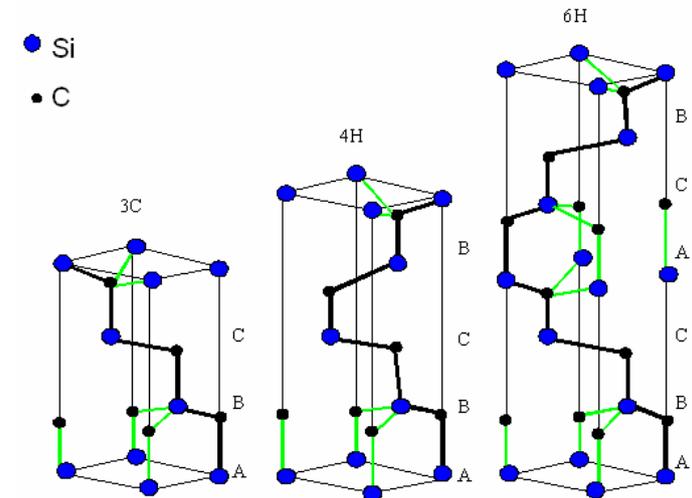
Stapelfolge ABAB...

2 Atome / EZ $(0,0,0)$, $(2/3, 1/3, 1/2)$

Packungsdichte 74 %

Koordination 12

Zn, Cd, Be, Mg, ...



Es gibt auch zufällige Stapelungen oder große EZ, z. B. SiC

ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α -Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62		—	—	
Nd	3.66	5.90	1.61	"Ideal"			1.63

Was ist "besser",

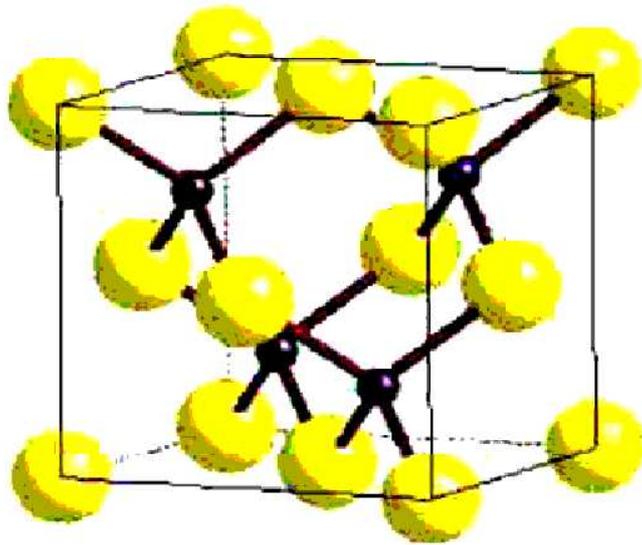
NaCl oder CsCl oder Wurtzit ?

- Wettbewerb um optimalen Ionenabstand:

Madelungenergie ↓ - Ionenradien ↑

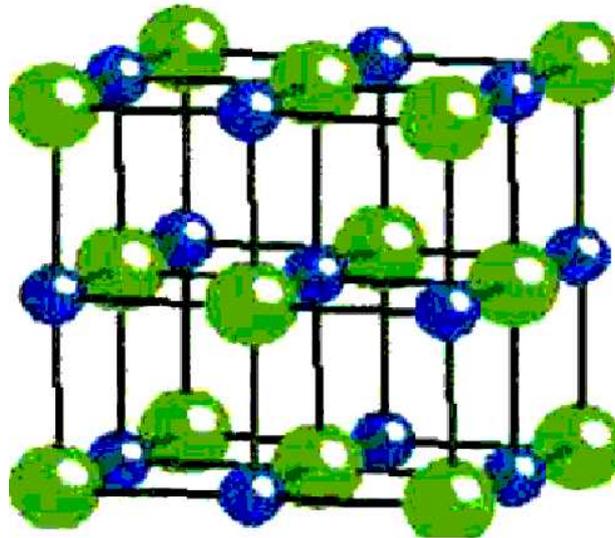
- Madelungenergie (Coulomb) begünstigt maximale Koordination

ZnS-Struktur



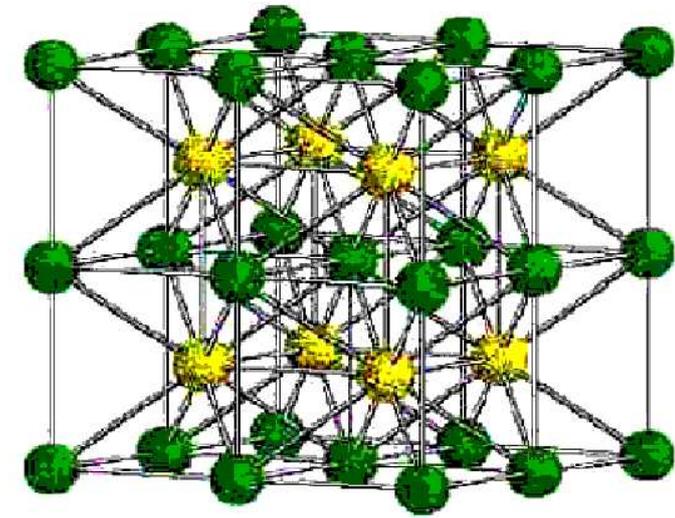
$$a = 1.6381$$

NaCl-Struktur



$$\alpha = 1.747565$$

CsCl-Struktur



$$\alpha = 1.762675$$

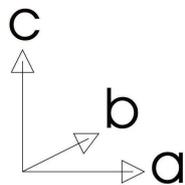
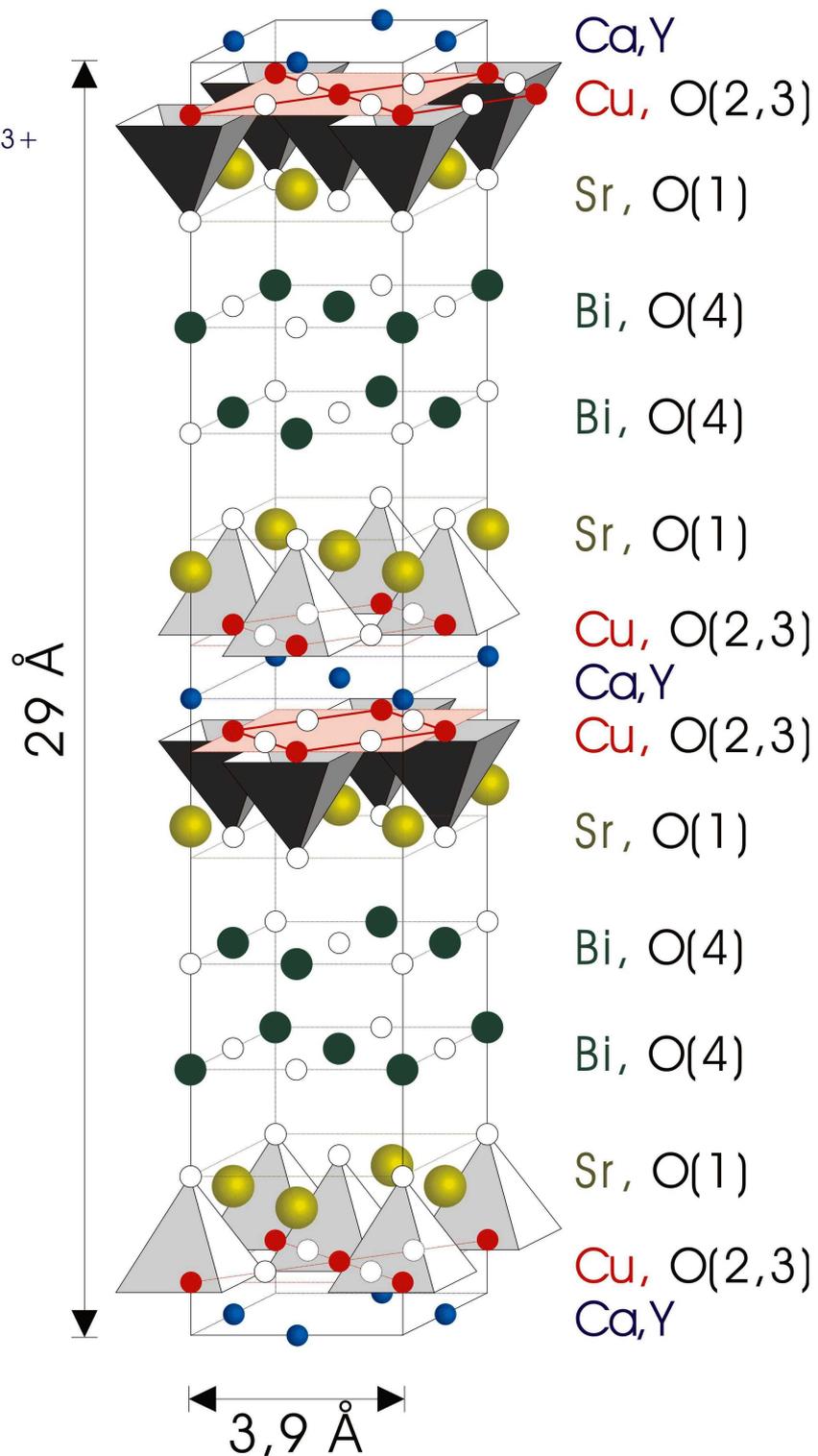
Mögliche Strukturtypen für binäre Verbindungen XY
(r_+ Radius des positiven Ions, r_- Radius des negativen Ions)

$\frac{r_+}{r_-}$	Koordinationszahl	Anordnung der Ionen	Strukturtyp
$0,225 \leq \frac{r_+}{r_-} < 0,414$	4	jedes Kation ist von vier Anionen tetraedrisch umgeben	Zinkblende Wurtzit
$0,414 \leq \frac{r_+}{r_-} < 0,732$	6	jedes Kation ist von sechs Anionen umgeben	Natriumchlorid
$\frac{r_+}{r_-} > 0,732$	8	jedes Kation ist von acht Anionen umgeben	Cäsiumchlorid

- Bi
- Sr
- $\text{Ca}^{2+}, \text{Y}^{3+}$
- Cu^{2+}
- O^-



Bi-2212



Es gibt mehr als Kristalle ...

Nobelpreis 2011: Dan Shechtman

Ikosaeder: Cluster, Quasikristalle

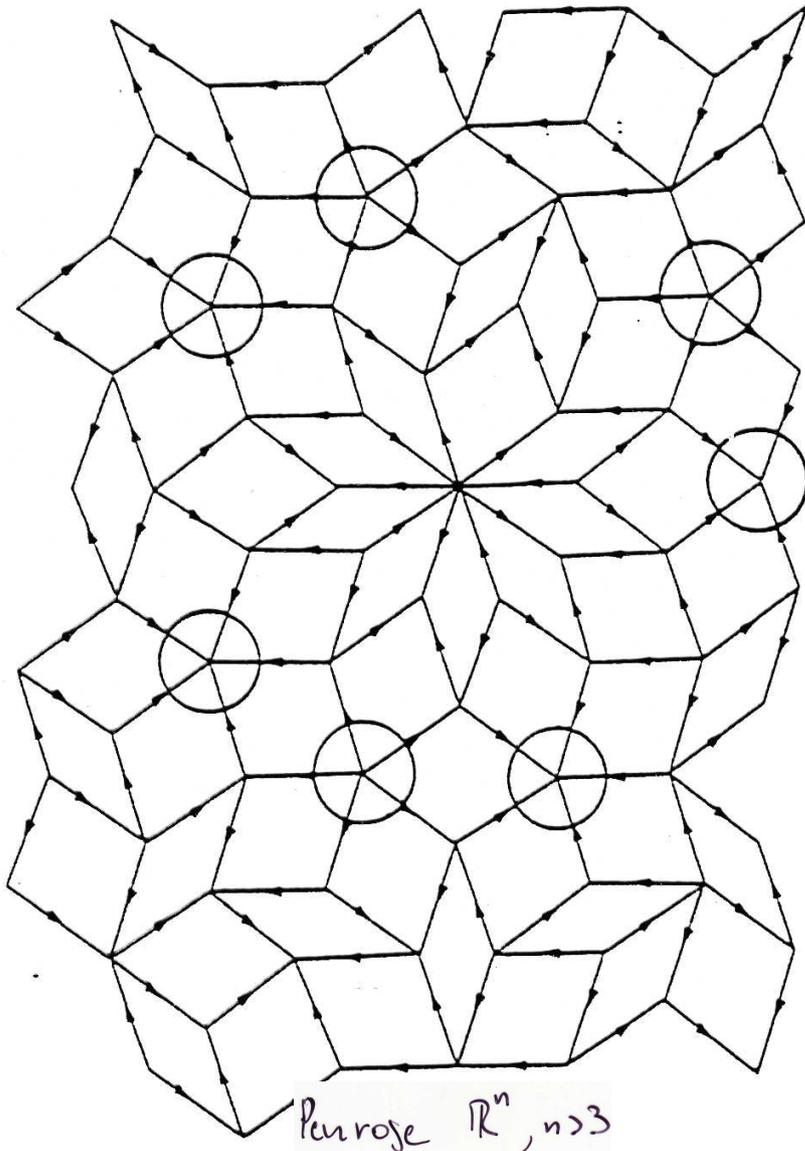
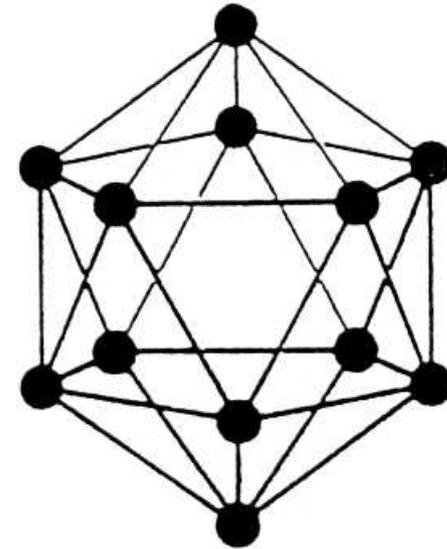


Abb. 4.58
Penrose-Muster



Quasikristalle

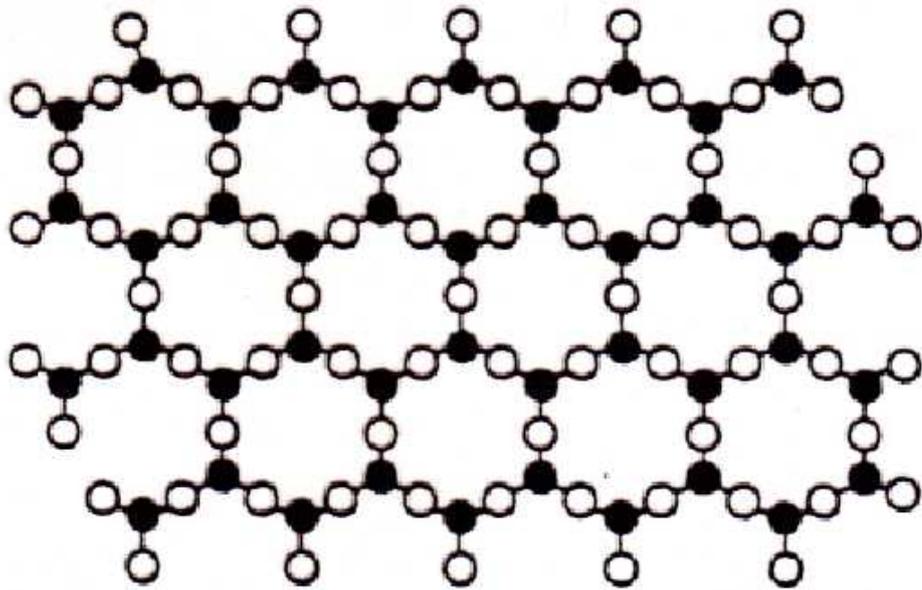
keine Translationsinvarianz
aber Orientierungsordnung
mit ∞ Reichweite

5-zählige Achsen

z.B. $\text{Al}_{11}\text{Mn}_{89}$

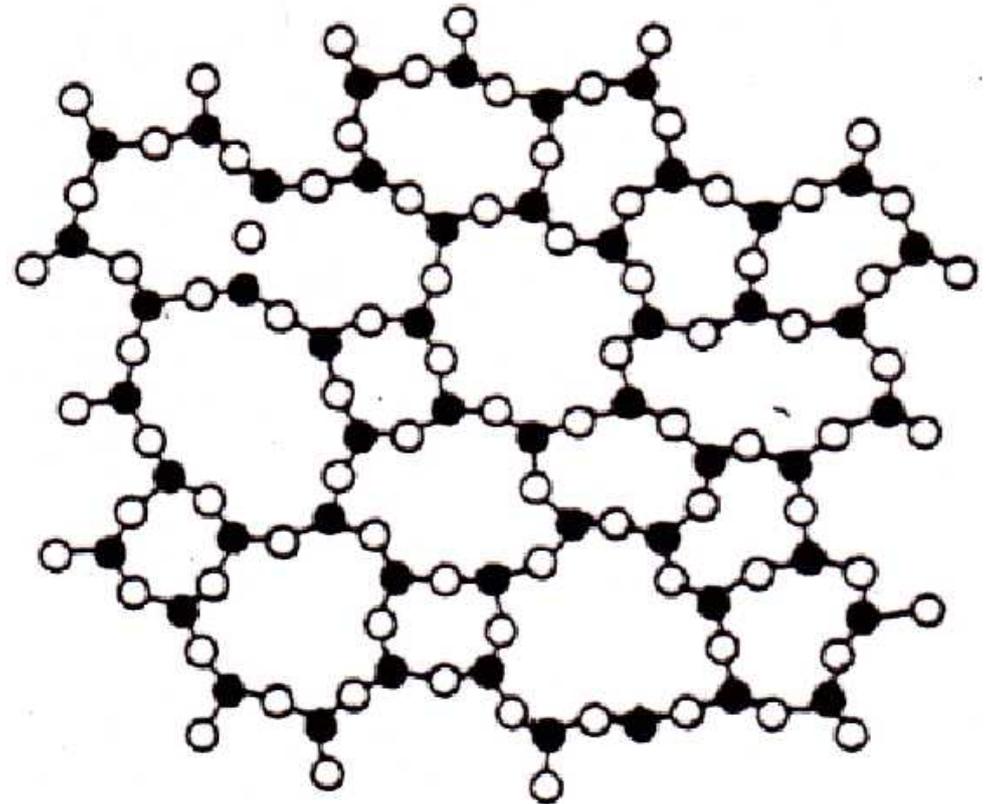
Amorphe Materialien am Beispiel SiO_2

kristallin



2,65 g/cm³

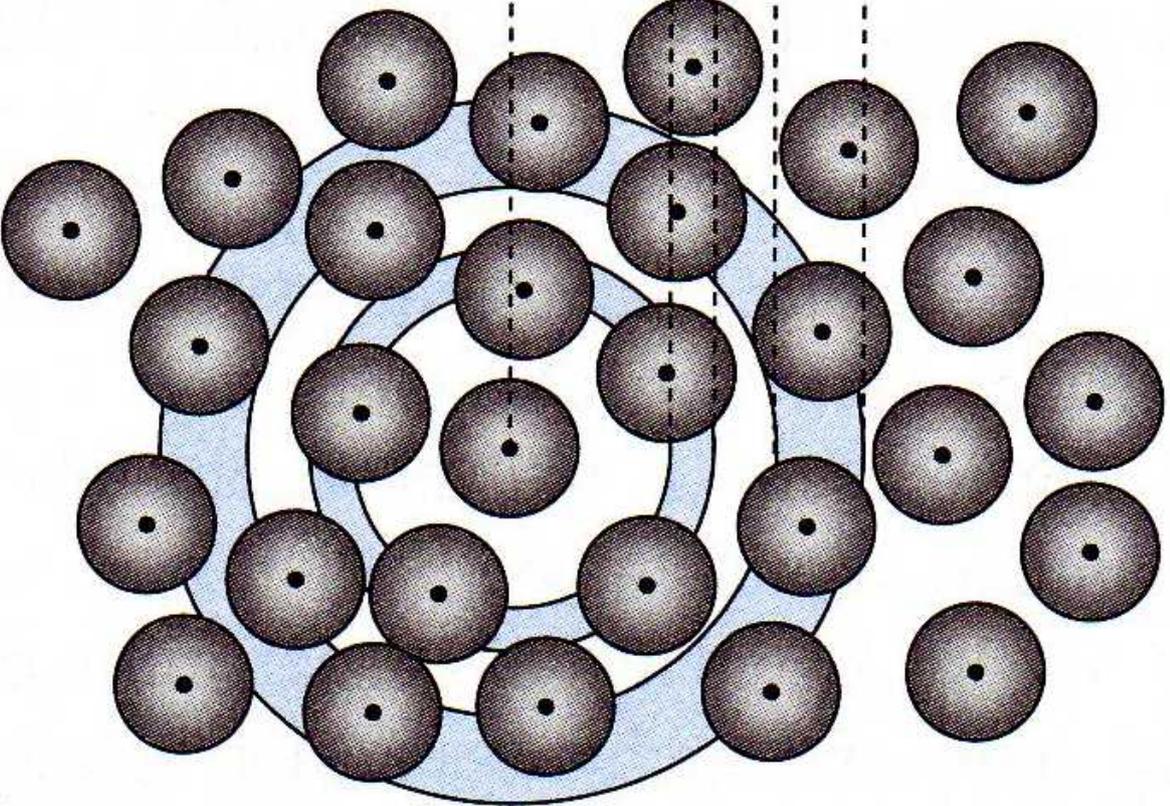
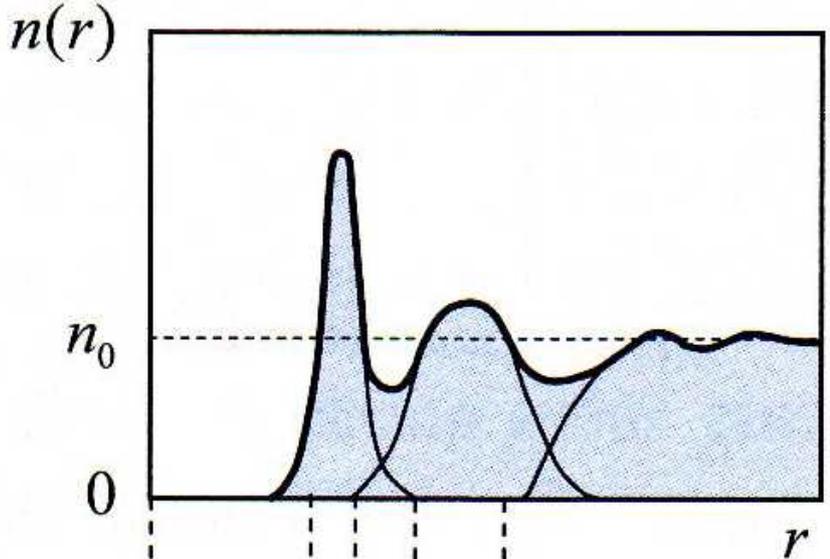
amorph



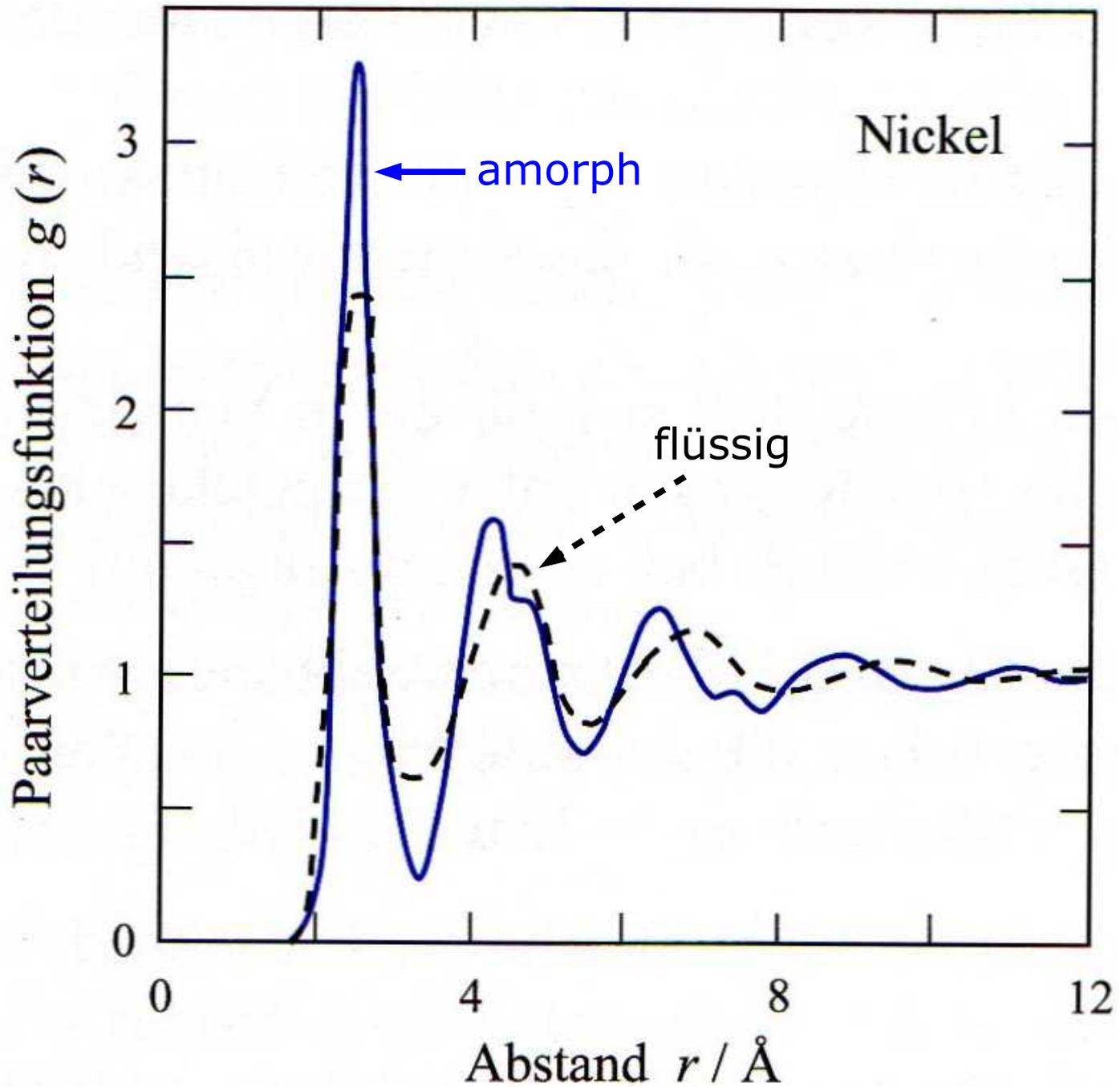
2,1 g/cm³

Metalle vs. Si

Zusammenhang zwischen Struktur
und Teilchenzahldichte $n(r)$ im 2d Fall.
(Beitrag des Aufatoms weggelassen).



Experimentelle Paarverteilungsfunktionen von Nickel



Lattice planes "Balsac":

<http://www.fhi-berlin.mpg.de/~hermann/Balsac/index.html>

oder FHI, Prof. Klaus Hermann

Crystals:

<http://www.ibiblio.org/e-notes/Cryst/Cryst.htm>

<http://cst-www.nrl.navy.mil/lattice/spcgrp/>

VRML viewer plugin:

<http://www.parallelgraphics.com/products/cortona/>