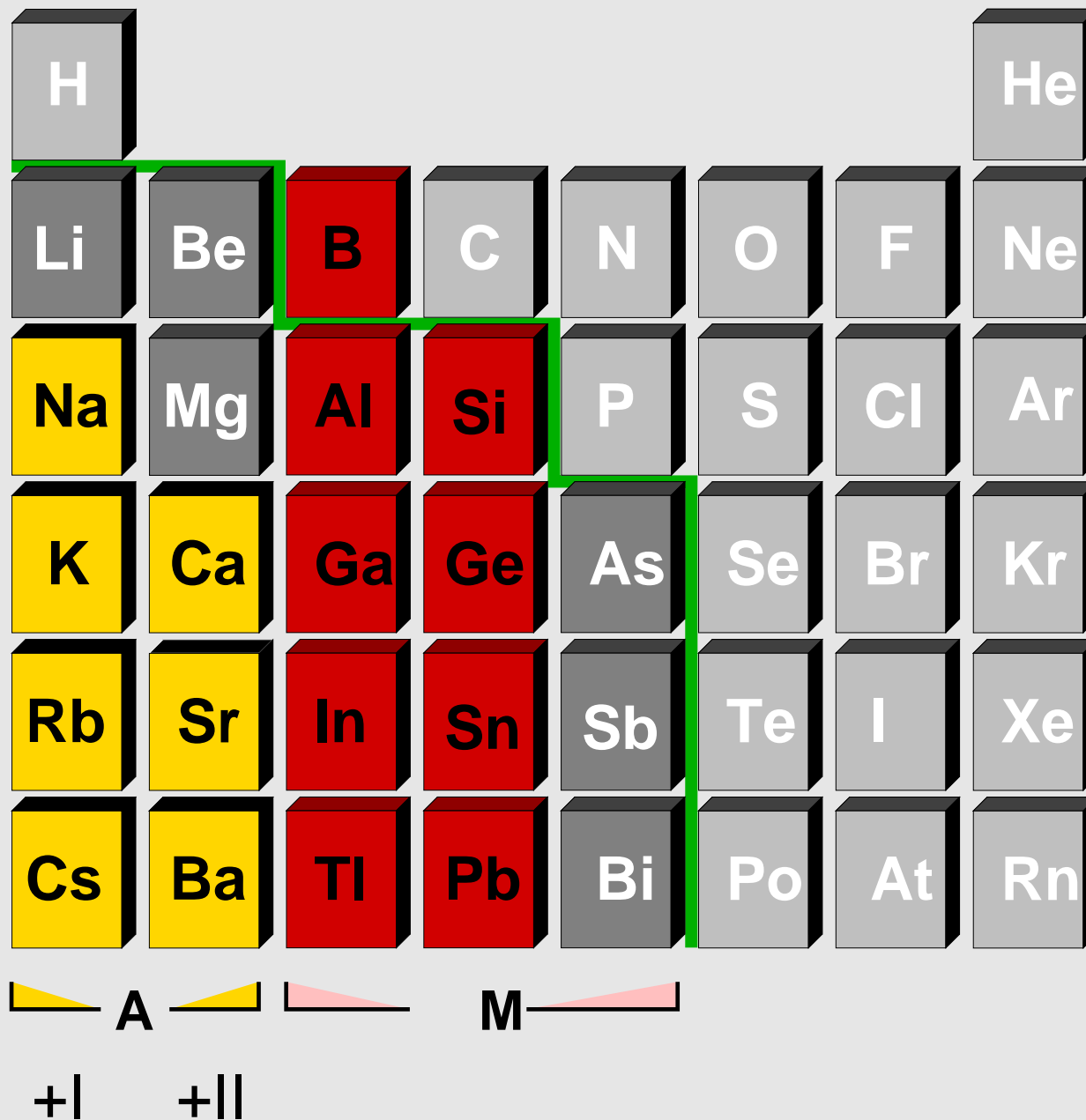


Cluster und Käfige

Anionische Käfige und Cluster der Gruppen 13 und 14

AGP-Begleitvorlesung, 24.11.2009


Verbindungen mit Anionen der 13. und 14. Gruppe

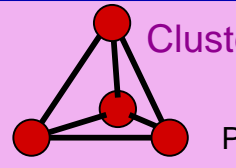
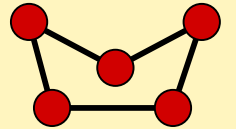
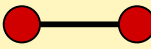

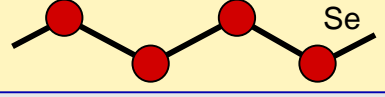
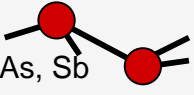
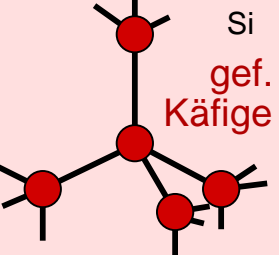


Kovalente Verbindungen

- VEZ/Atom $\geq 4 \mapsto$ Zahl der VE (N) bestimmt Bindigkeit (8-N-Regel)
 - ◇ N=8: Edelgase, Halogenide $E(VII)^-$, $E(VI)^{2-}$, $E(V)^{3-}$, $E(IV)^{4-} \mapsto$ keine Bindung
 - ◇ N=7: elementare Halogene, $E(VI)^-$, $E(V)^{2-}$, $E(IV)^{3-} \mapsto$ einbindig
 - ◇ N=6: elementare Chalkogene, $E(V)^-$, $E(IV)^{2-} \mapsto$ zweibindig \mapsto Ketten und Ringe
 - ◇ N=5: elementare Pentele, $E(IV)^-$, $E(III)^{2-}$, $E(VI)^+ \mapsto$ dreibindig \mapsto Käfige bis Raumnetze
 - ◇ N=4: elementare Tetrele, $E(III)^- \mapsto$ vierbindig \mapsto Raumnetze, Clathrate
- VEZ/Atom < 4 (Triele) \mapsto elektronenarme Verbindungen, Elektronenmangel, Cluster

Zintl-Grenze



	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 Cluster P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige			
			SrSi ₂ -Typ ThSi ₂ -Typ			

Triel ?



Regenpfeifer	Triel	Ringdrossel
<i>Actitis hypoleucos</i>	<i>Burhinus oedicanus</i>	<i>Turdus torquatus</i>
	40 cm	24 cm
goldbraun, im Winter im Sommer schwarz mit weißen Seiten; Nestflüchter; Teilzieher	weiße Flügelbinde, Schnabel gelb und schwarz, Augen groß, gelb; Nestflüchter; Teilzieher	♂ mit weißem, Brustschild, Gefieder schwarz, ♀ brauner; Nesthocker; Teilzieher

(Poly-)Anionen: Bindungskonzepte


- Zintl-Klemm-Konzept
 - ◇ Eduard Zintl (1898-1941) (München, [Freiburg \(1928-1933\)](#), Darmstadt)
 - ◇ Wilhelm Klemm (Münster)
- für polare intermetallische Phasen (Alkali/Erdalkalimetall-(A)-Verbindungen mit Elementen M bis zur 14., z.T. auch 13. Gruppe)
- ionische Zerlegung in Kationen A und (Poly-)Anionen M
- a) M-Verbindungen sind Element-isoster und isostrukturell (Zintl)
- b) Bindigkeit im M-(Poly-)Anion folgt der 8-N-Regel (Klemm)
- c) Erweitertes Zintl-Konzept (Wade-Regeln für das Anion)

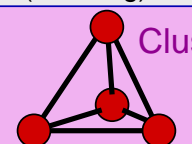
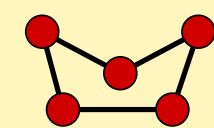


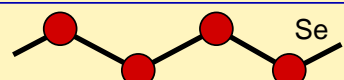
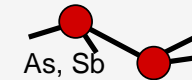
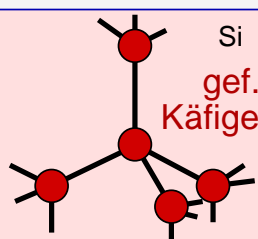


Käfige und Cluster: Anionen mit $N \leq 5$ (Inhaltsübersicht)

- I: elektronenpräzise Käfig-Anionen (8-N-Regel gilt)
 1. isoliert: mehrere Atome mindestens 3-bindig
 2. Konkurrenz: Kondensation zu Schicht oder Raumnetz (vgl. $P_{\text{elementar}}$)
- II: Anionen mit vierbindigen Atomen (8-N-Regel gilt)
 1. einfache Tetraederraumnetze
 2. Raumnetze mit gefüllten Käfigen
- III: echte Cluster (8-N-Regel gilt nicht, Elektronenmangel, Wade-Mingos-Regeln)
 1. isolierte Cluster
 2. kondensierte Cluster

Zintl-Grenze




	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 Cluster P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige			
			SrSi ₂ -Typ ThSi ₂ -Typ			

I. elektronenpräzise Käfig-Anionen (N = 5, Pentel-isoster)

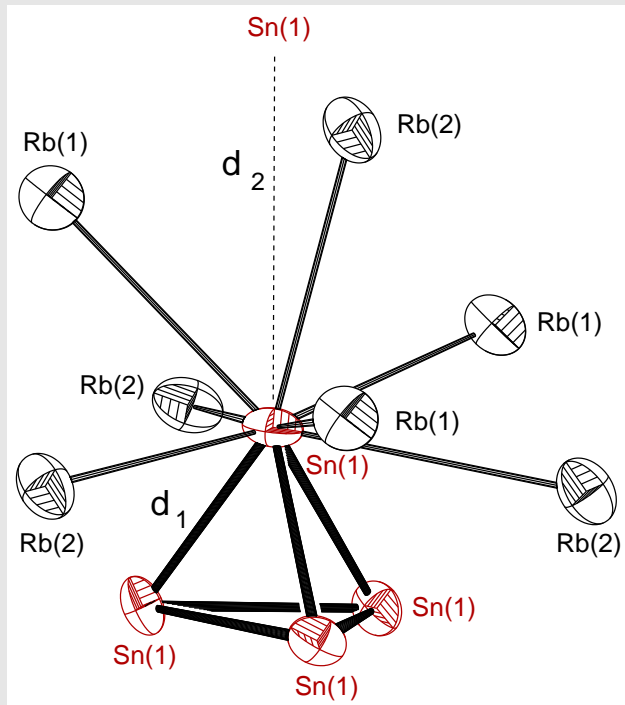
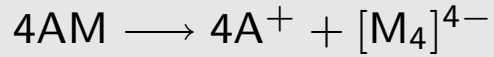
- Alkalimetall-Tetrelide $A^I M^{IV}$ (Bsp: $M^{IV} = Sn$)
- Alkalimetall-Triellide $A_2^I M^{III}$ (Bsp.: $M^{III} = In$)
- Erdalkalimetalle-Tetrelide $A^{II} M_2^{IV}$ (Bsp.: $M^{IV} = Si$)

Zintl-Grenze



	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		Cluster P	S	I	Ar
1-dim. (Kette)				Se		
2-dim. (Schicht)			As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster					
		Si gef. Käfige	SrSi ₂ -Typ ThSi ₂ -Typ			

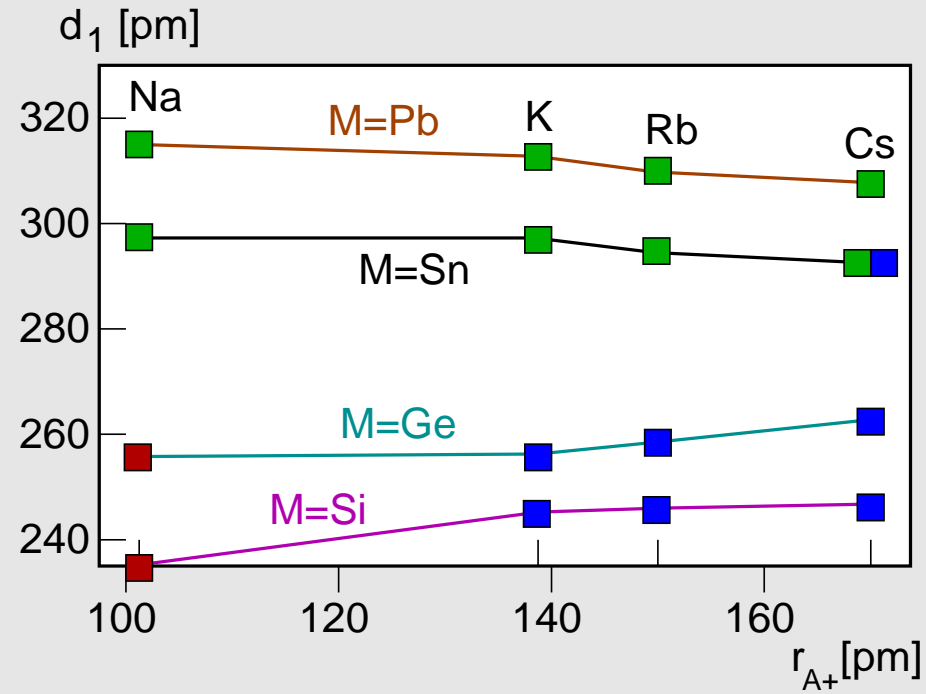
Verbindungen $A^I M^{IV}$



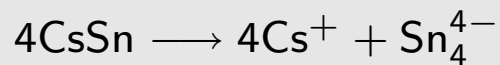
	Si	Ge	Sn	Pb
Na				
K				
Rb				
Cs				

Anionenpackung

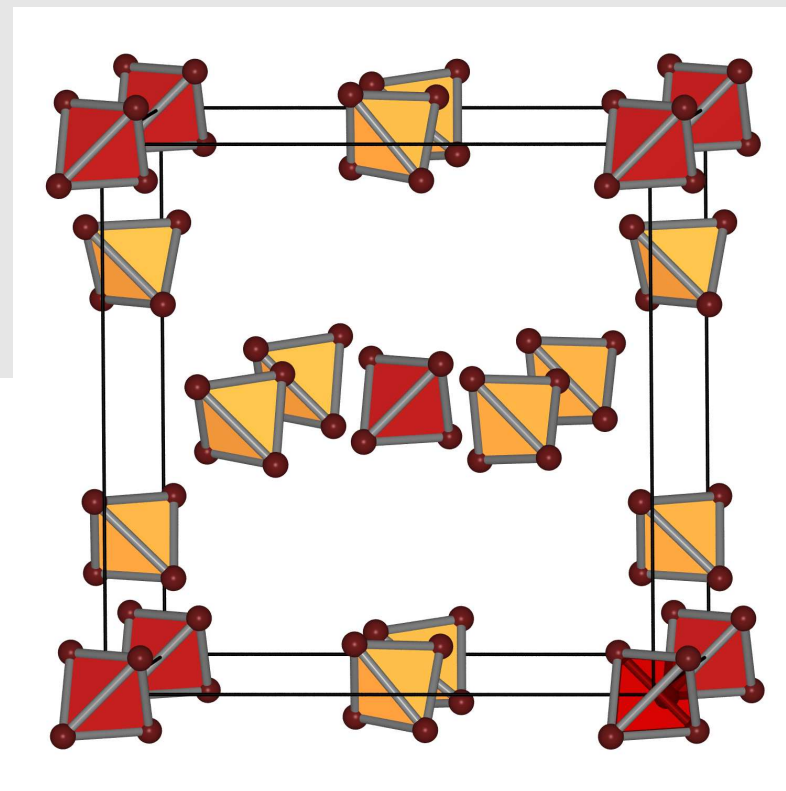
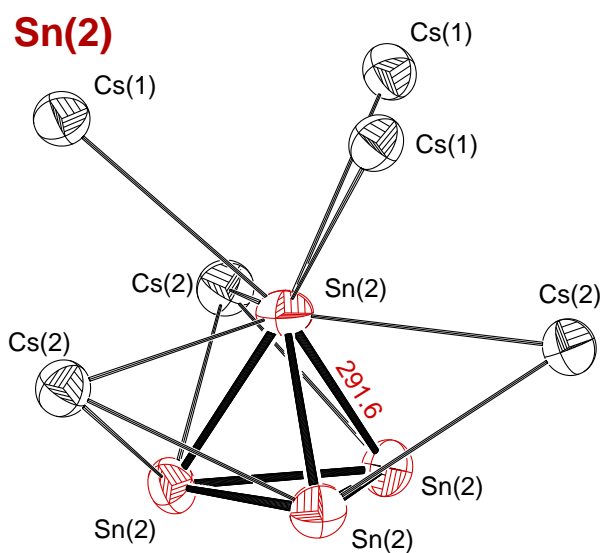
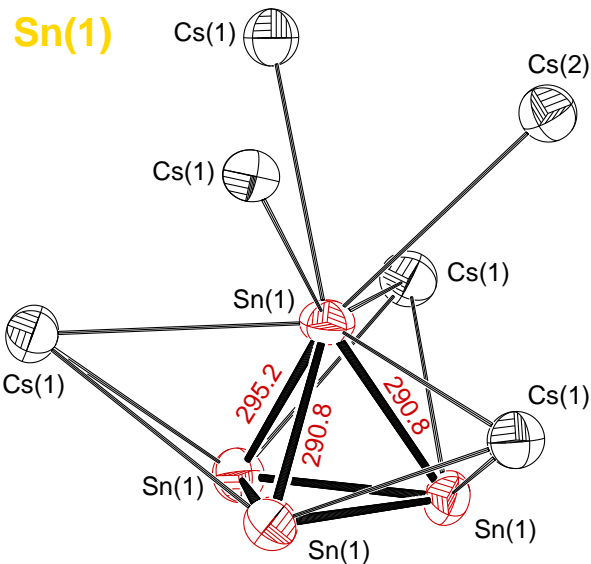
- NaSi-Typ f.c.c.
- KGe-Typ Cr_3Si
- NaPb-Typ b.c.c.



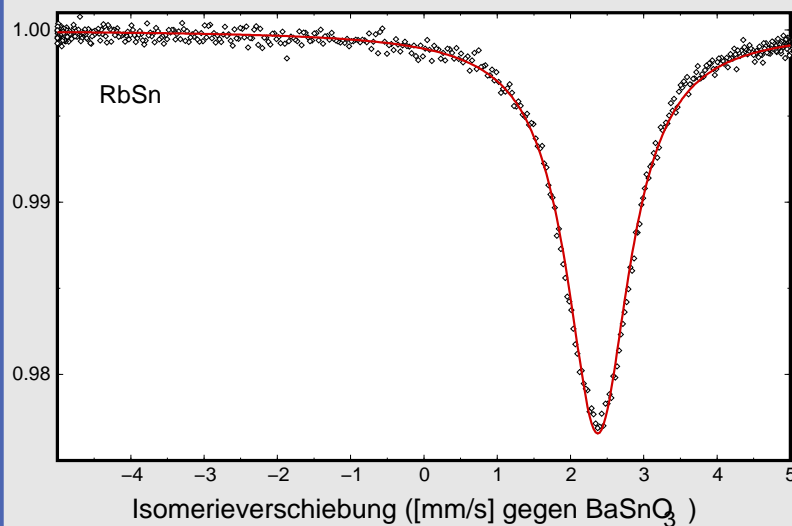
β -CsSn (VE/M=5)



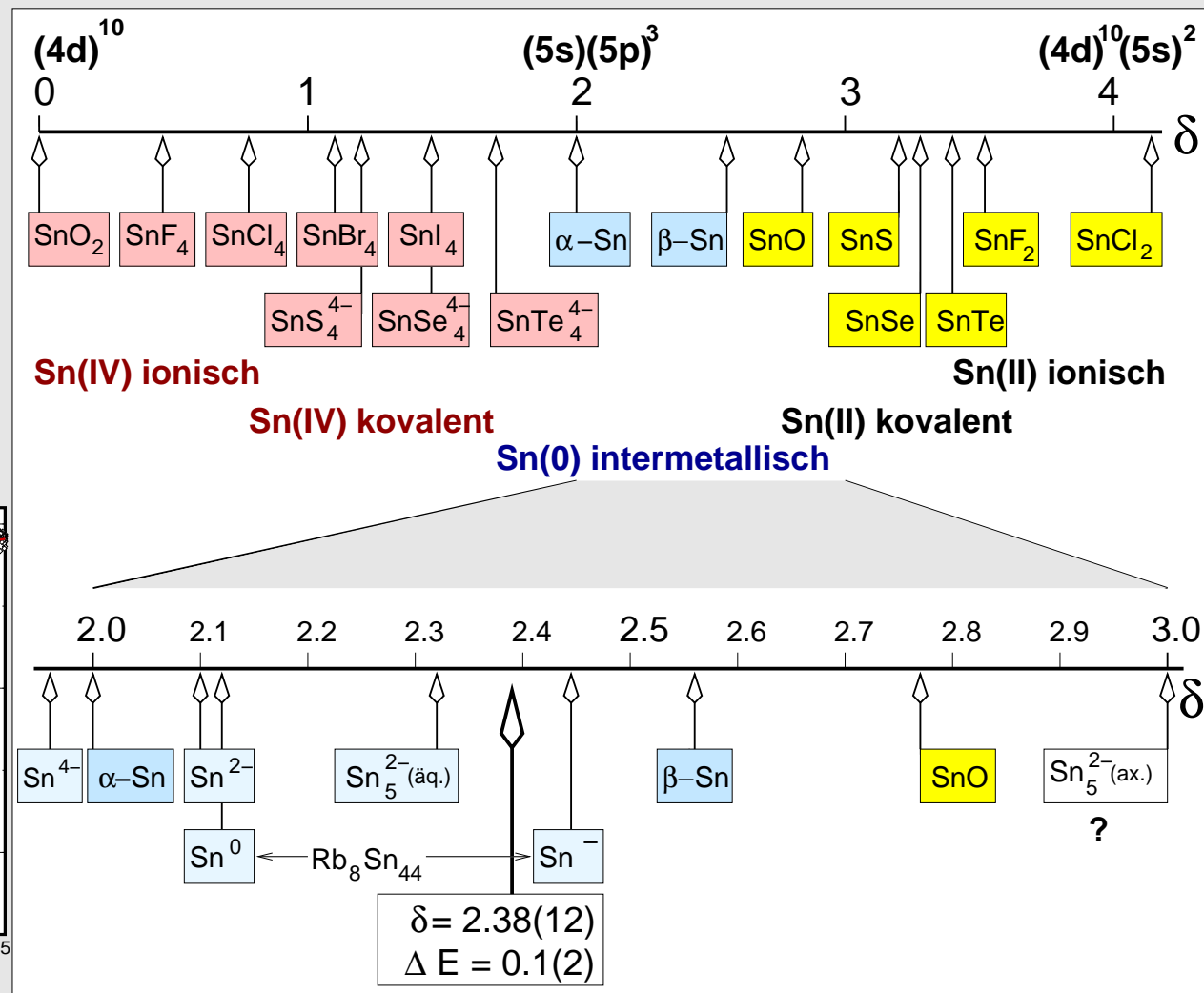
Strukturtyp		KGe
Kristallsystem		kubisch
Raumgruppe		$P\bar{4}3n$, Nr. 218
Gitterkonstante [pm]	a	1444.74
Z		32
R-Werte	R1	0.0395
	wR2	0.0709
$d_{\text{Sn}-\text{Sn}}$ [pm]		291 - 295



RbSn: ^{119}Sn -Mößbauer-Spektrum

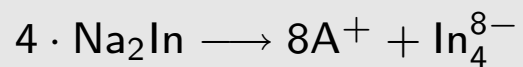


Spektrum von RbSn

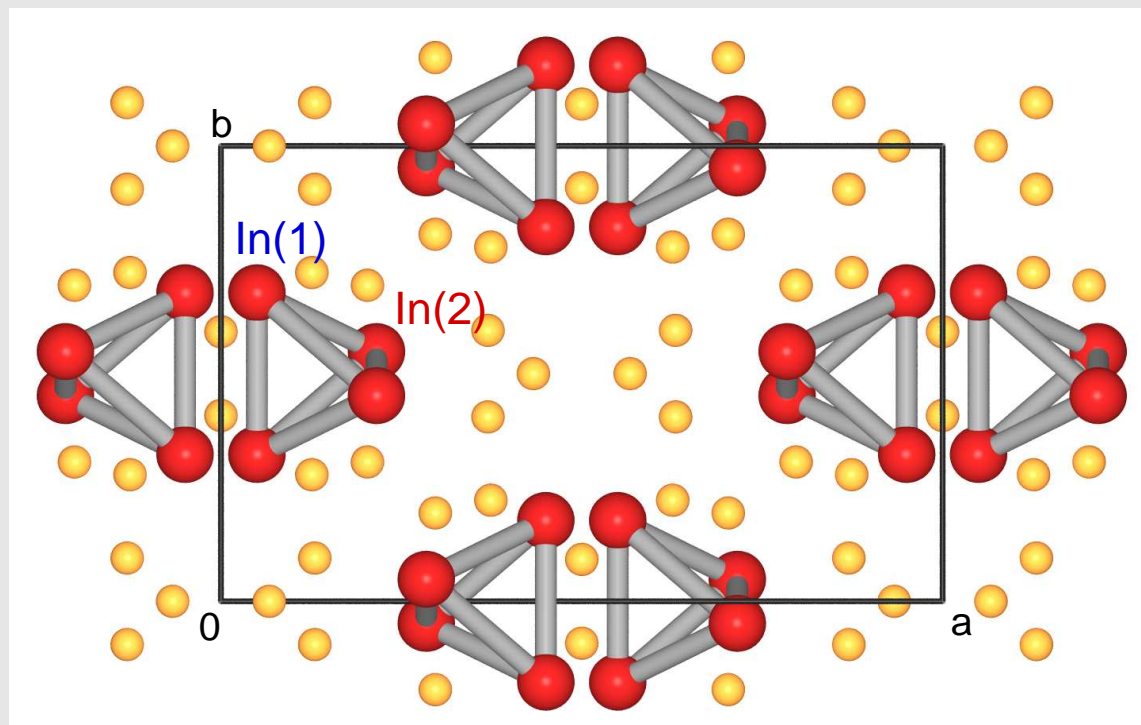


Skala der ^{119m}Sn -Isomerieverschiebungen

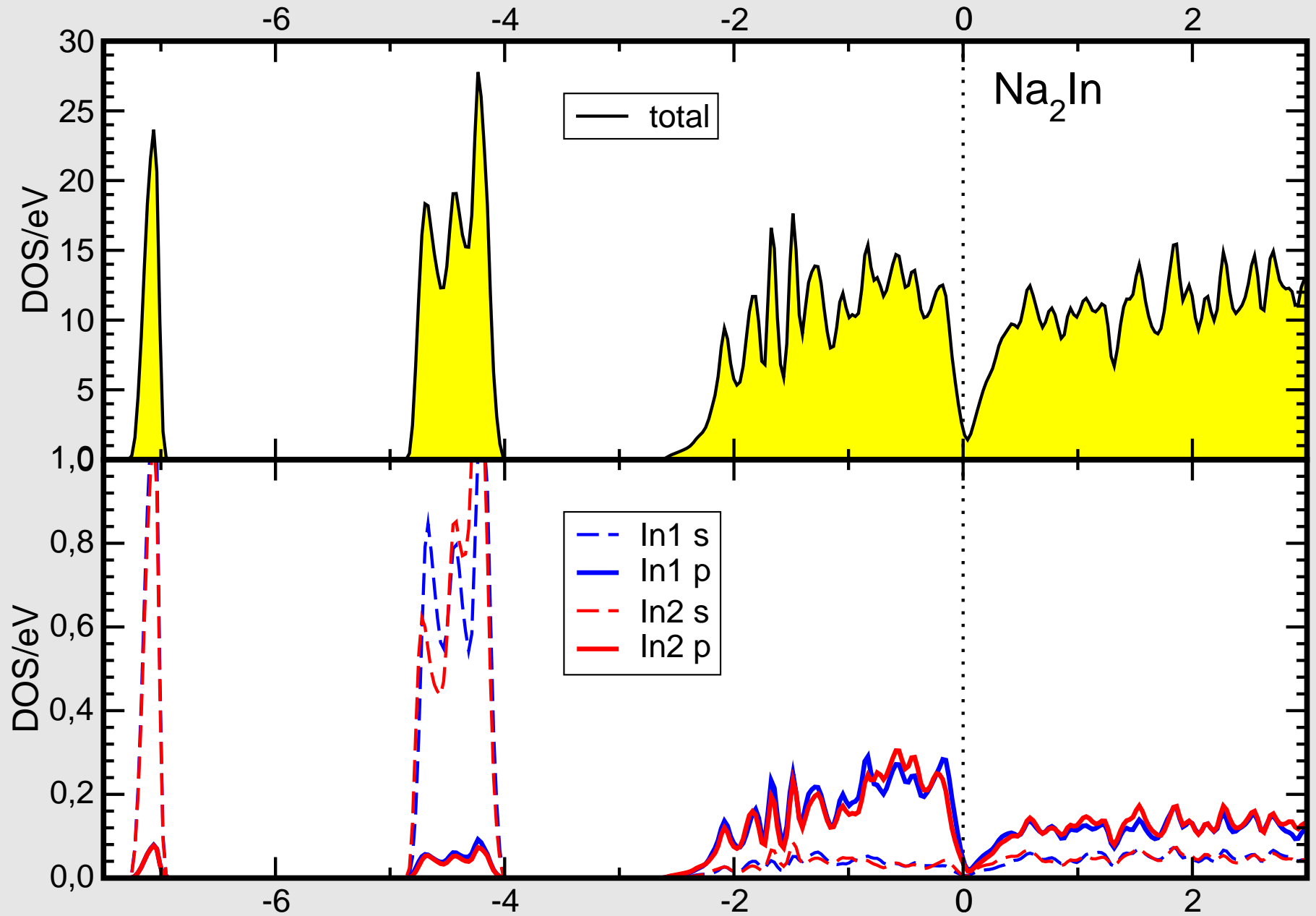
Na₂In (VE/M=5)



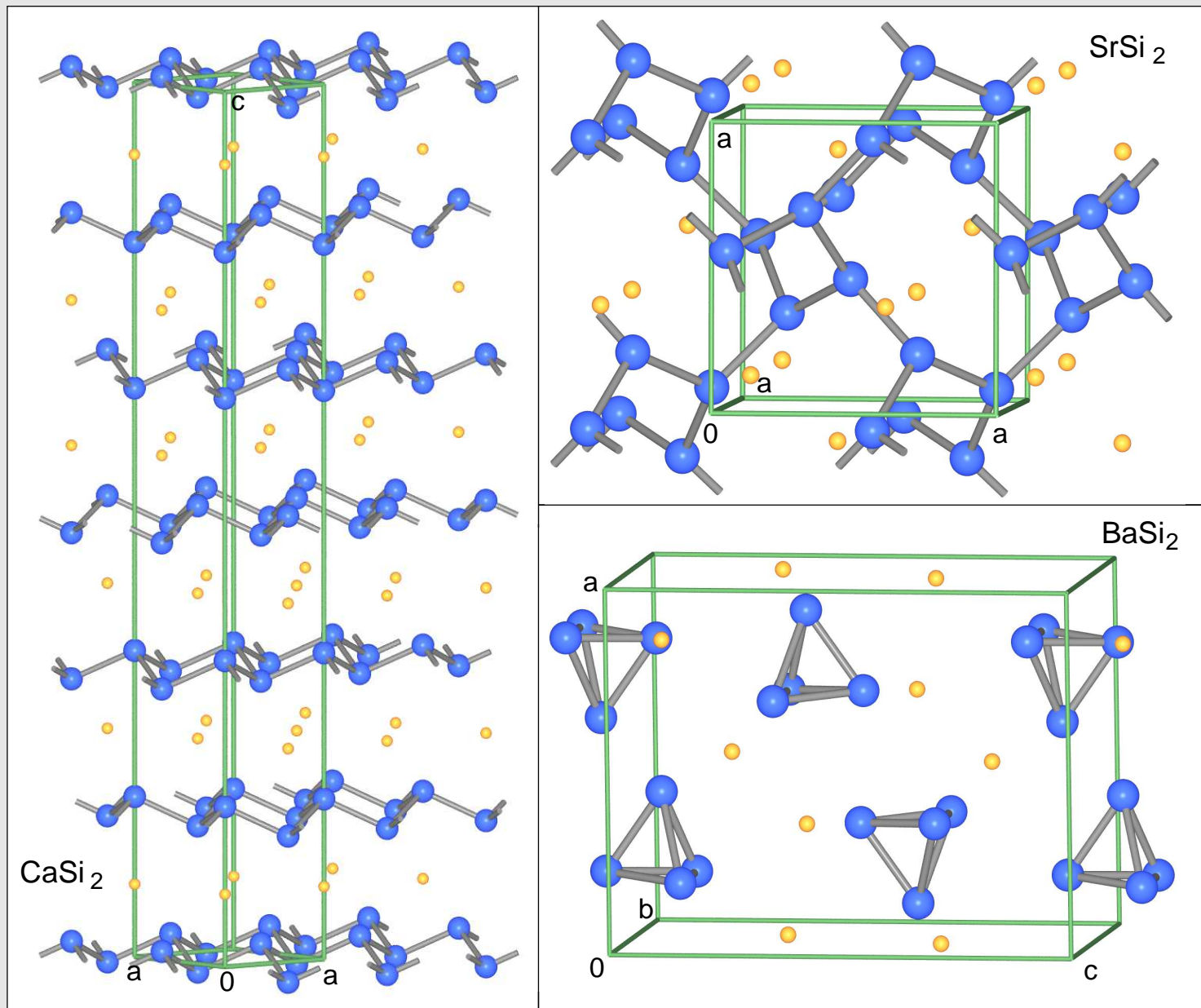
Strukturtyp		Na ₂ Tl
Kristallsystem		orthorhombisch
Raumgruppe		C 2 2 2 ₁
Gitter-	a	883.3
konstanten	b	1385.0
[pm]	c	1175.8
d _{In-In} [pm]		307-315



Na₂In : Totale und partielle In Zustandsdichte



Strukturen der Erdalkalimetall-Disilicide $A^{II}Si_2$ (VE/M=5)

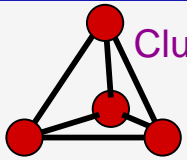
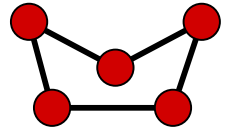



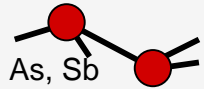
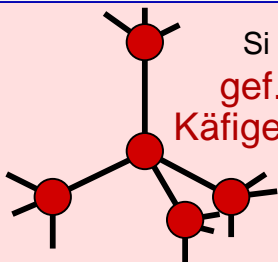


II. Polyanionen mit $N = 4$ (elektronenpräzise, Tetrel-isoster)

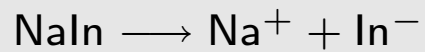
- Alkalimetall-Trielide $A^I M^{III}$ (Bsp.: $M^{III} = \text{In}$)
- Erdalkalimetalle-Trielide $A^{II} M_2^{III}$ (Bsp.: $M^{III} = \text{In}$)
- Clathrate $A_x^I M^{IV}$ ($x \ll 1$) (Bsp.: $M^{IV} = \text{Sn}$)

Zintl-Grenze

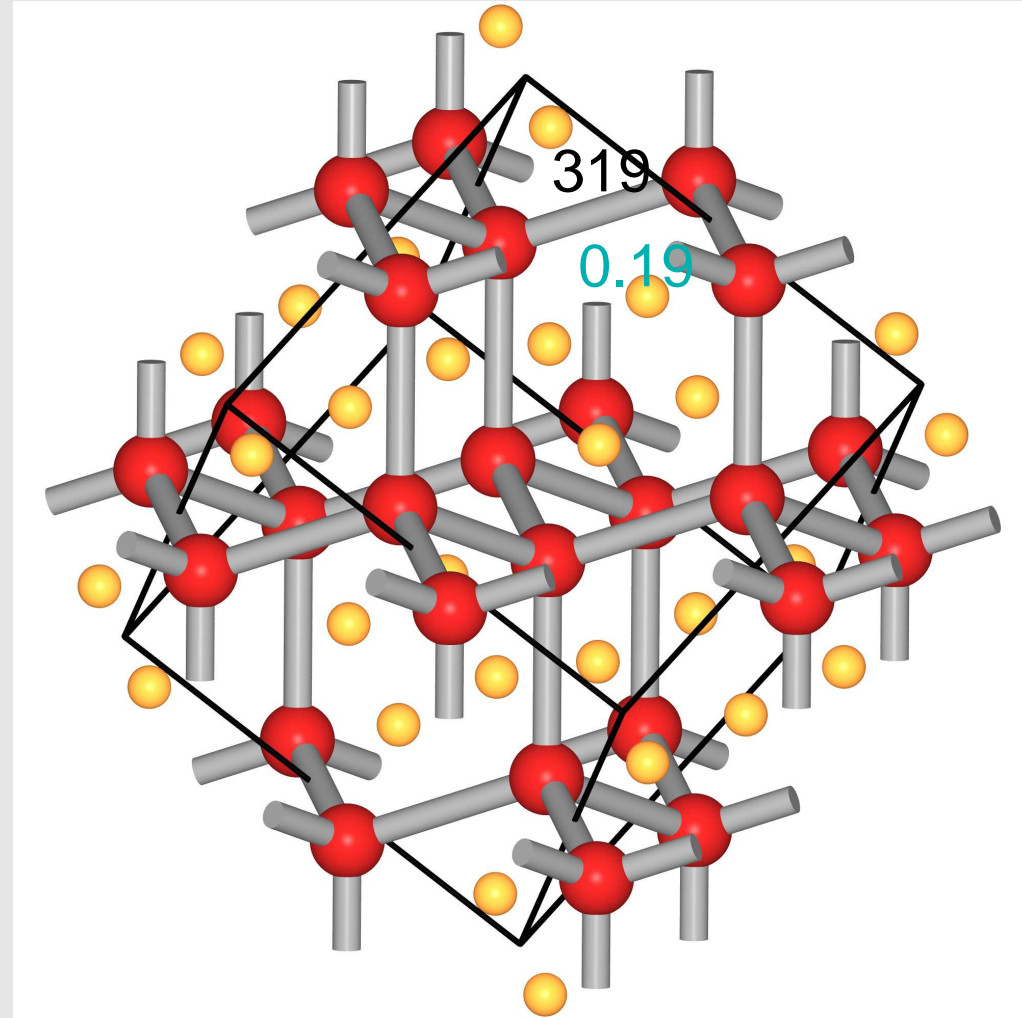
↓

	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 Cluster P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige SrSi ₂ -Typ ThSi ₂ -Typ			

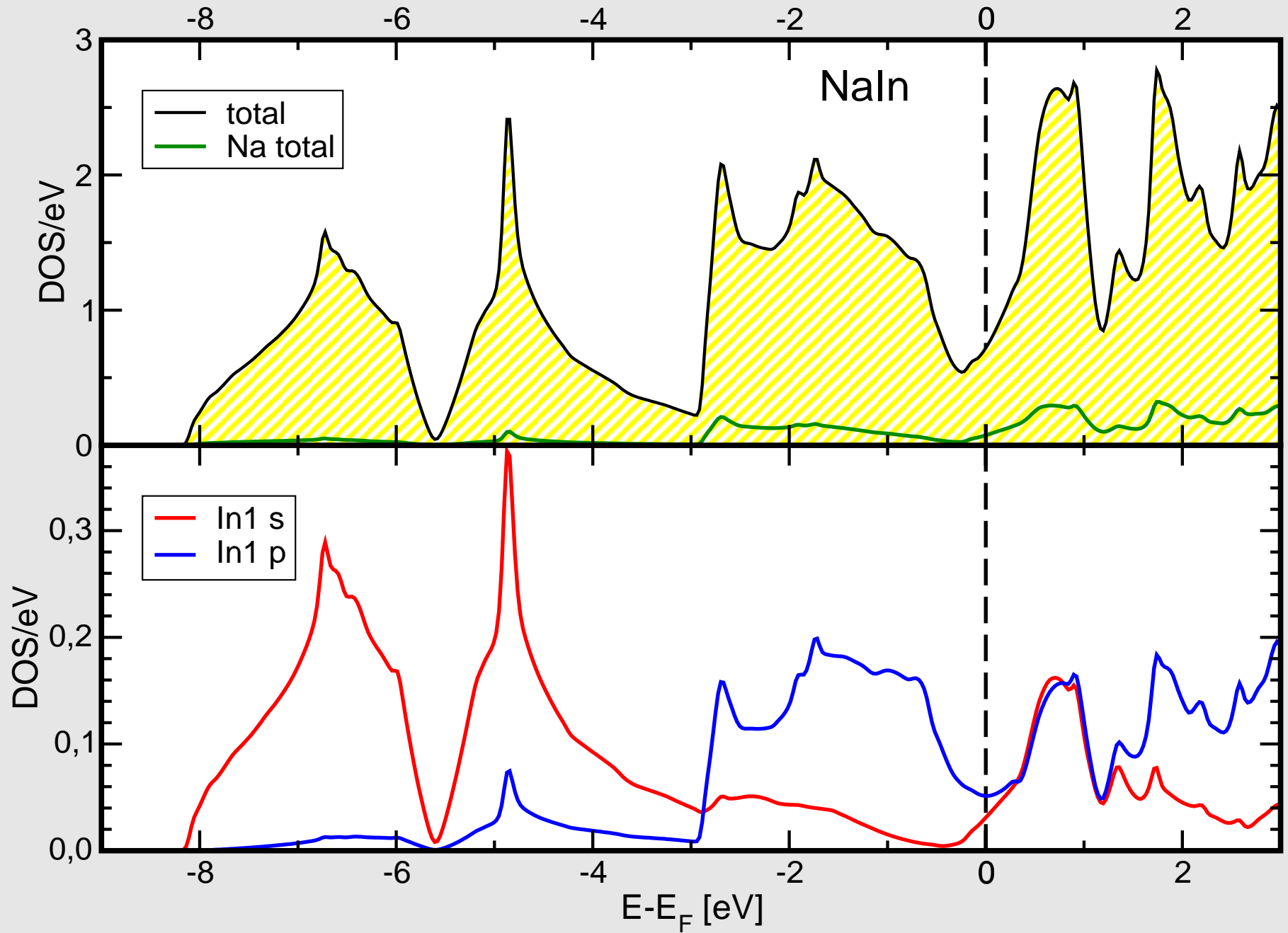
NaIn (VE/M=4): Struktur



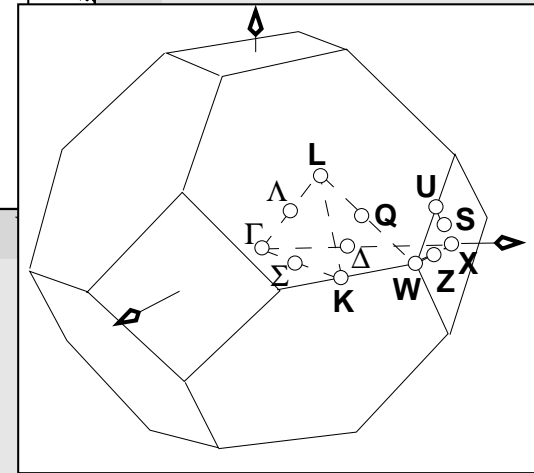
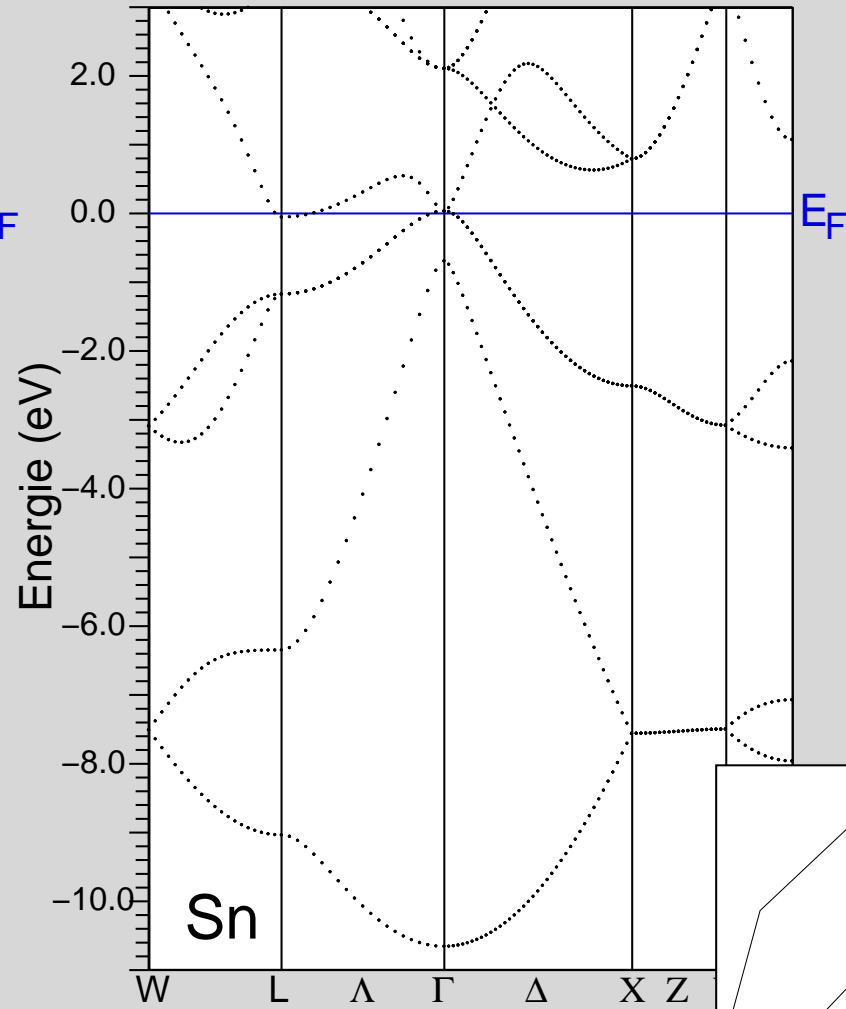
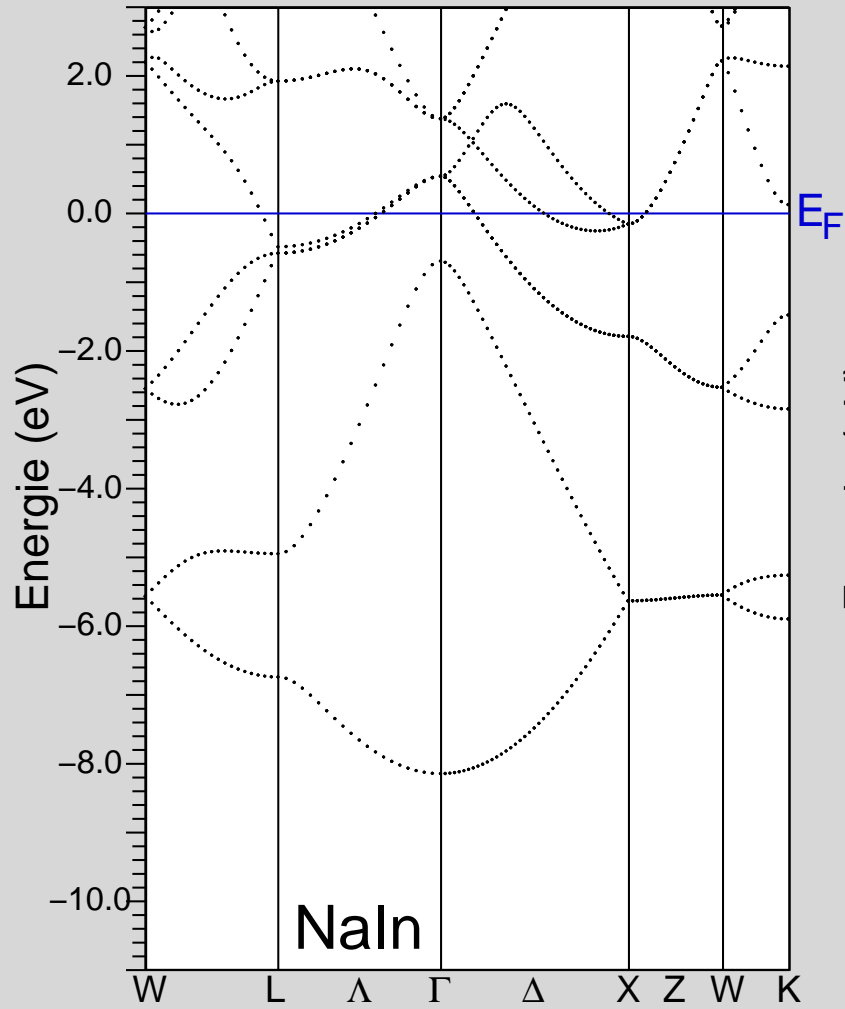
Strukturtyp	NaTl
Kristallsystem	kubisch
Raumgruppe	F d $\bar{3}$ m
$d_{\text{In-In}}$ [pm]	319
Bader-Ladung	In: -0.744
ρ_{BCP} [10^{-6} pm ³]	0.186



NaIn: Totale und partielle In Zustandsdichte



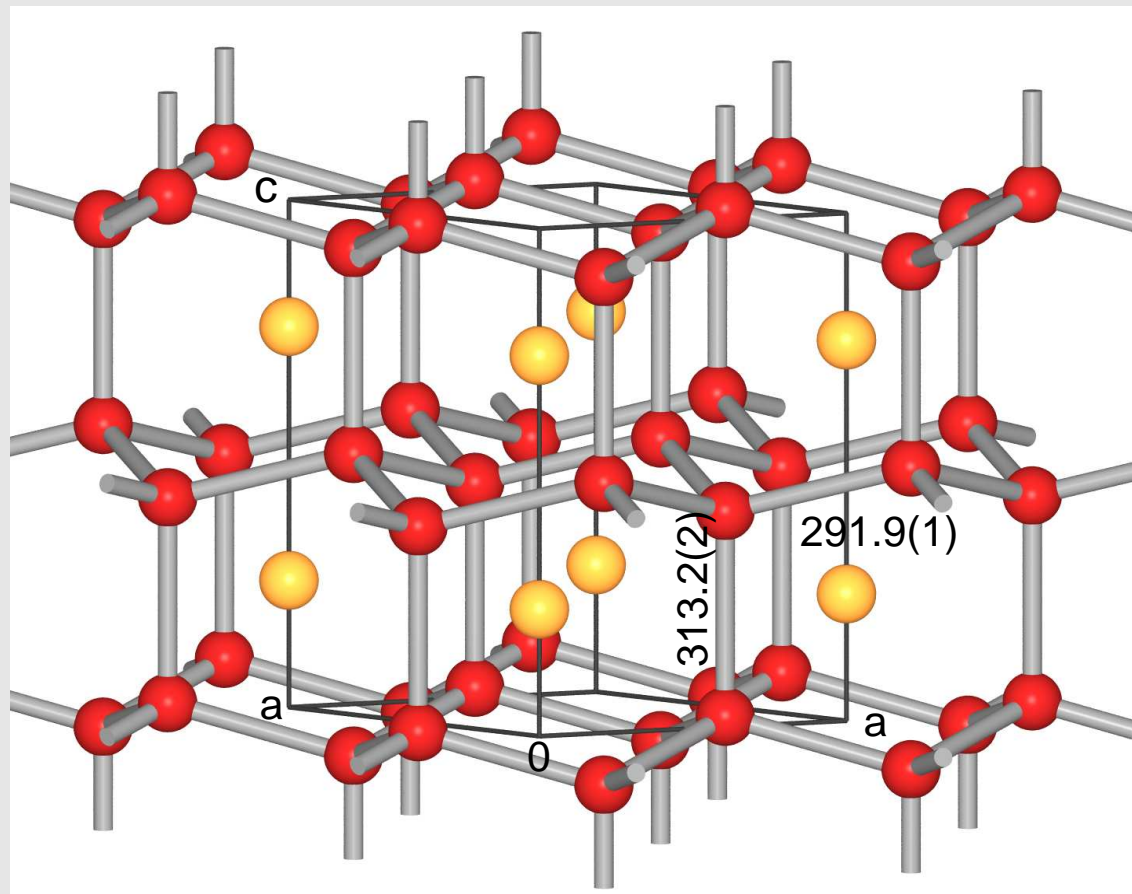
Naln und α -Sn: Vergleich der Bandstrukturen



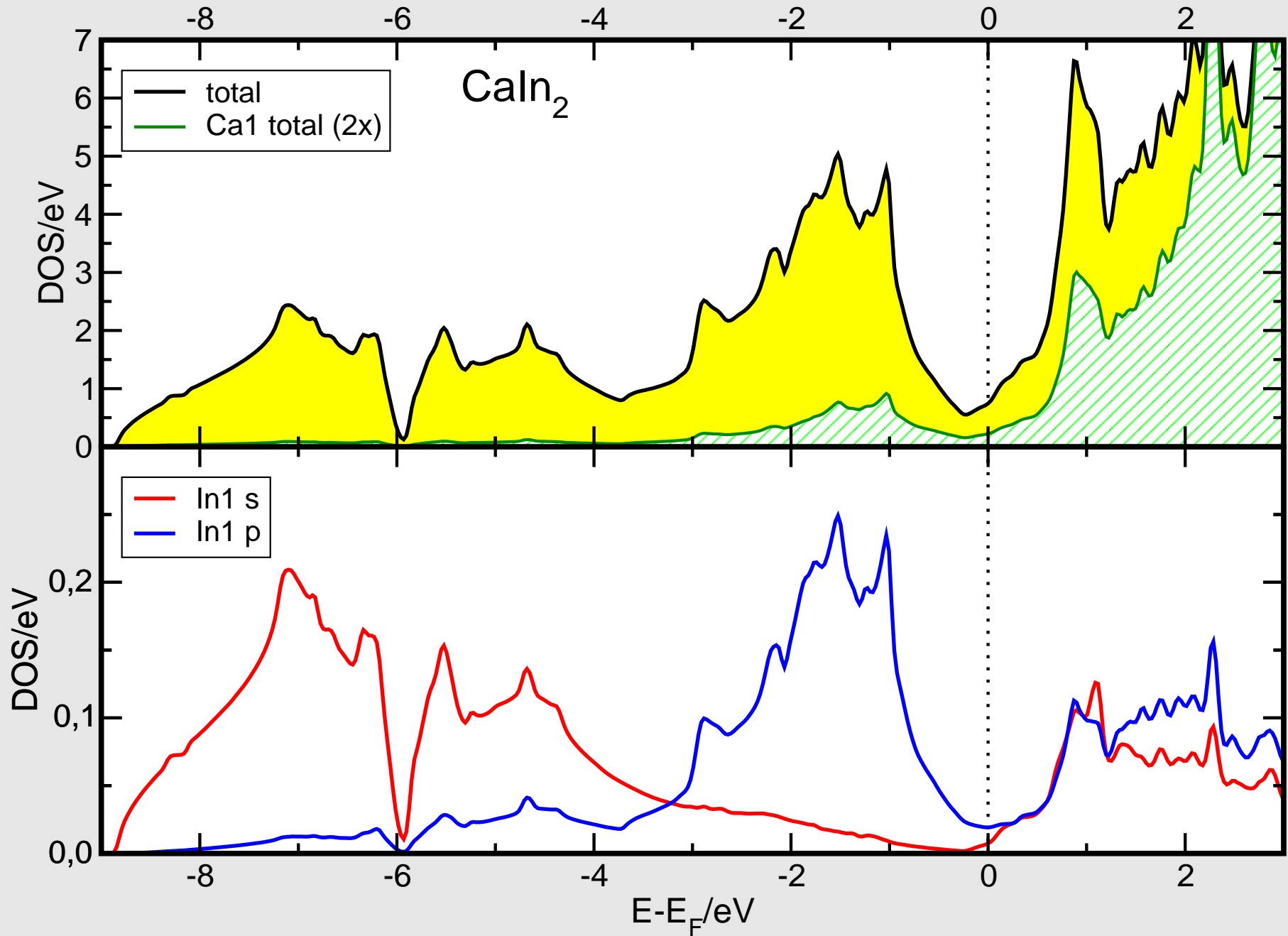
CaIn₂ (VE/M=4): Struktur



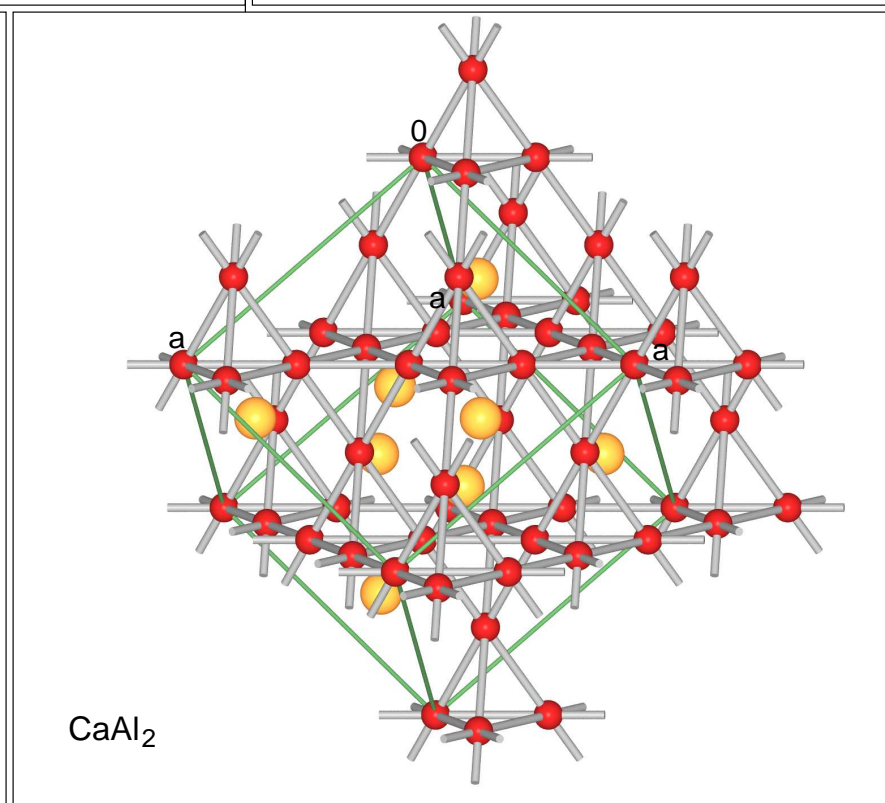
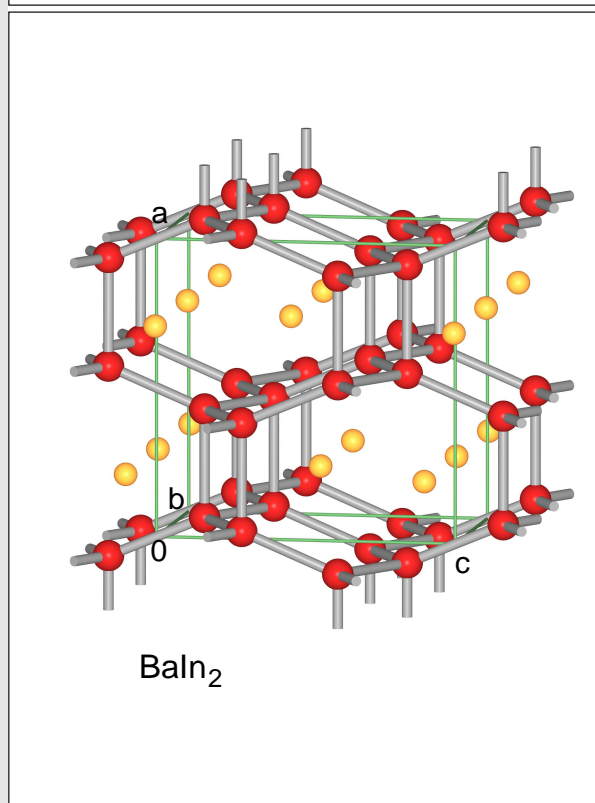
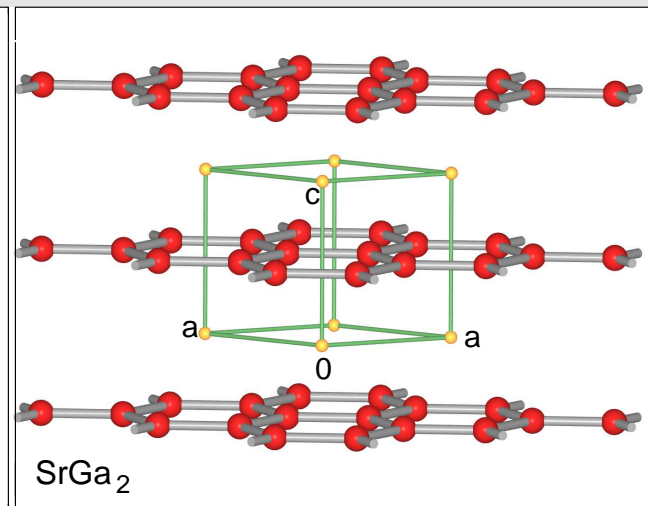
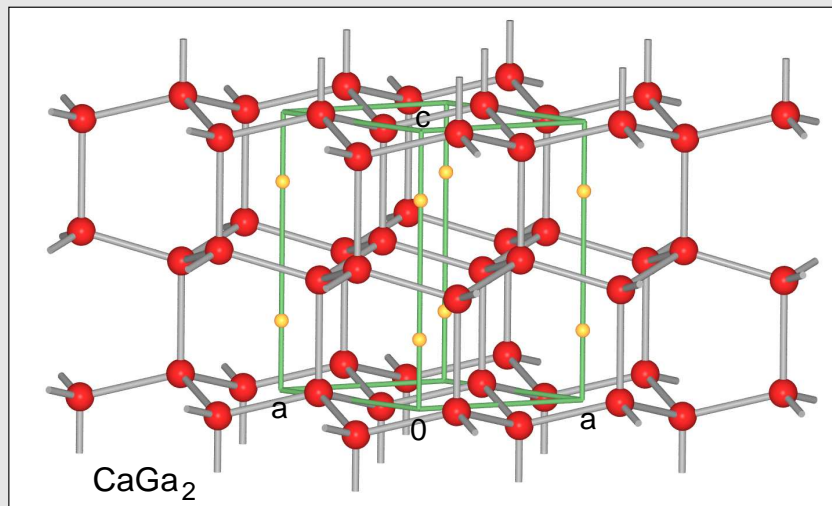
		CaIn ₂	SrIn ₂
Strukturtyp		CaGa ₂	
Kristallsystem		hexagonal	
Raumgruppe		P6 ₃ /mmc, Nr. 194	
Gitter-	a	489.2	500.9
konstanten	c	773.9	803.6
[pm]			
VEZ [10 ⁶ pm ³]		160.4	174.6
Z		2	
R-Wert	R1	0.0254	0.0277



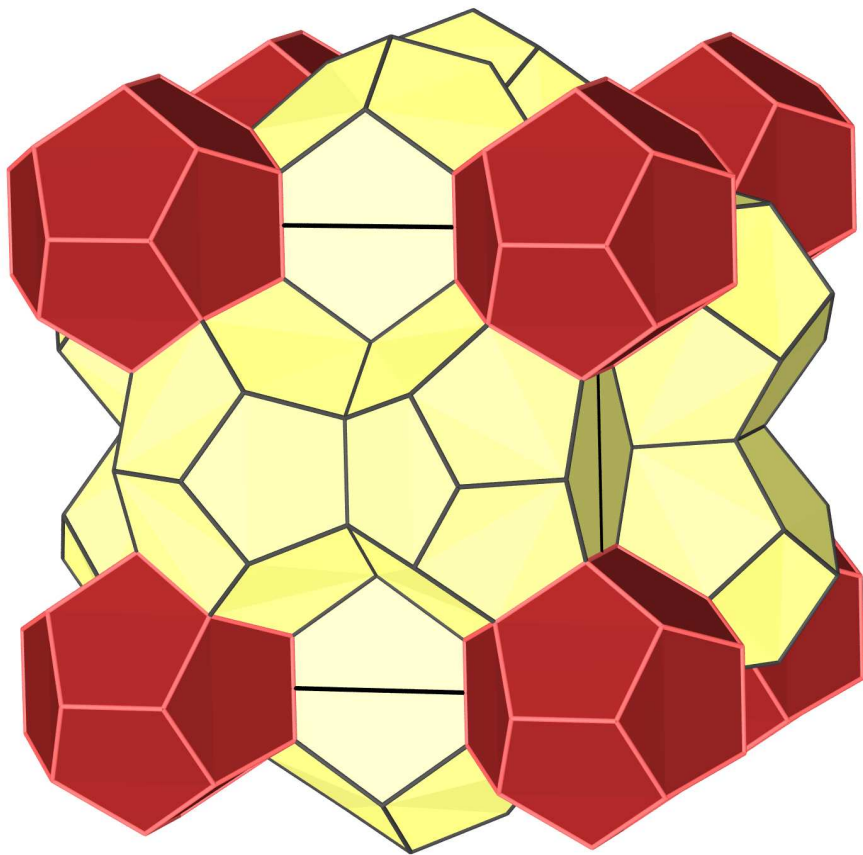
CaIn₂: Totale und partielle In Zustandsdichte



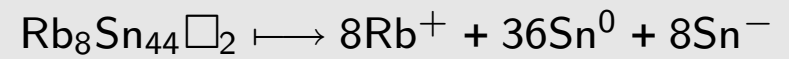
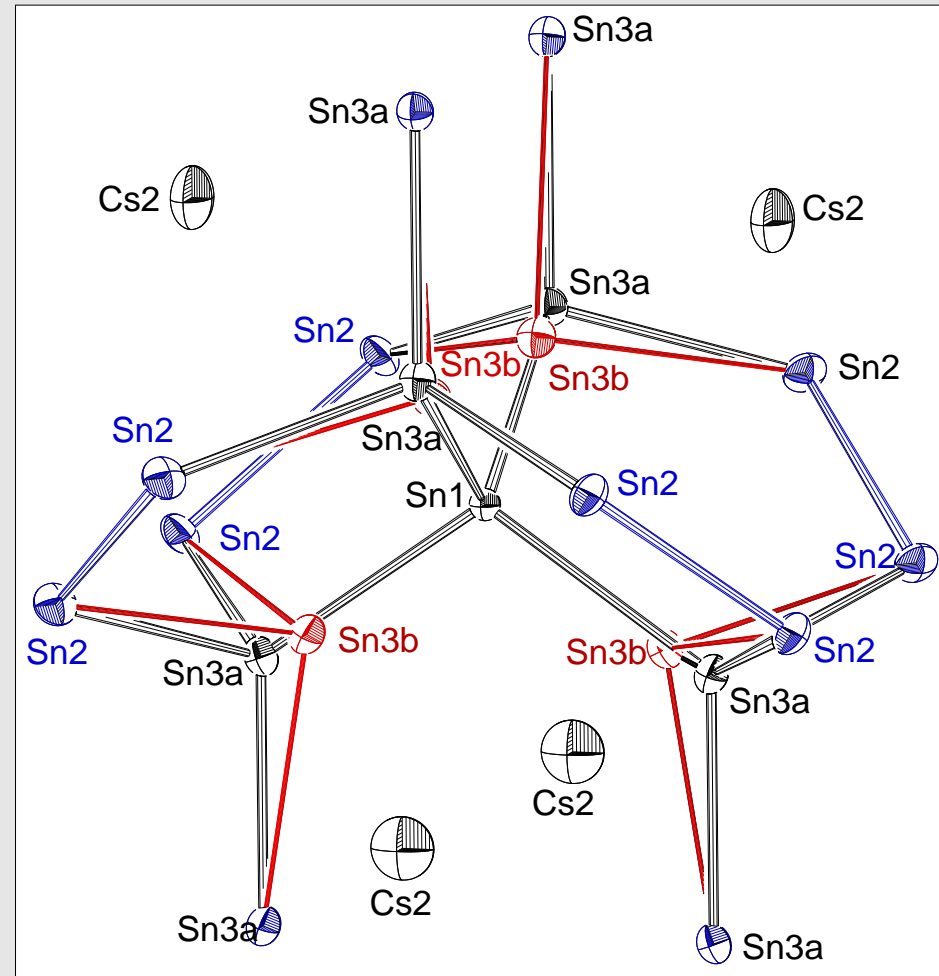
Strukturen der Erdalkalimetall-Ditrielide $A^{II}M_2^{III}$ (VE/M=4)



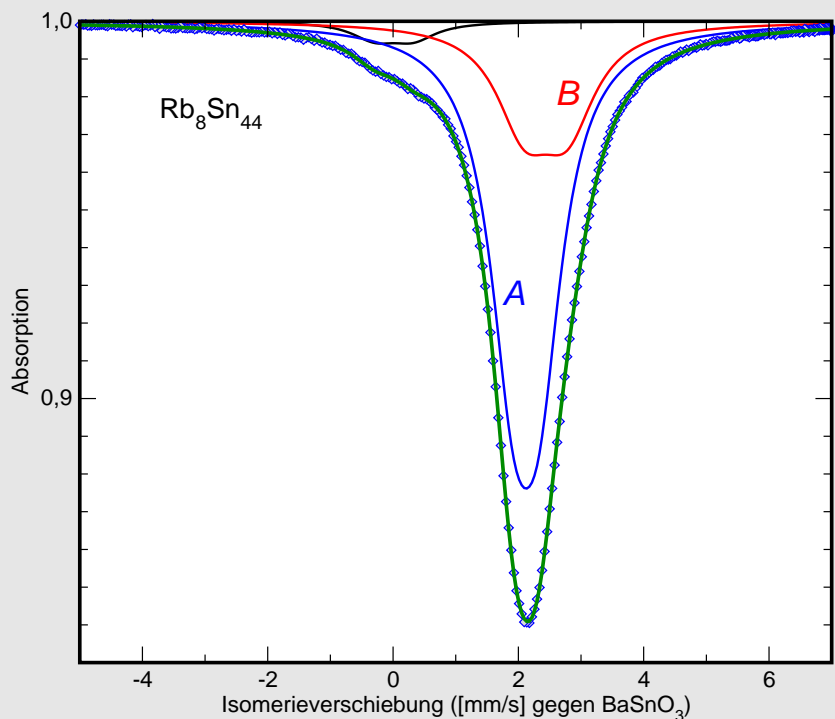
Strukturen von $A_8Sn_{44}\square_2$ (A=Rb, Cs) (VE/M=4.18)



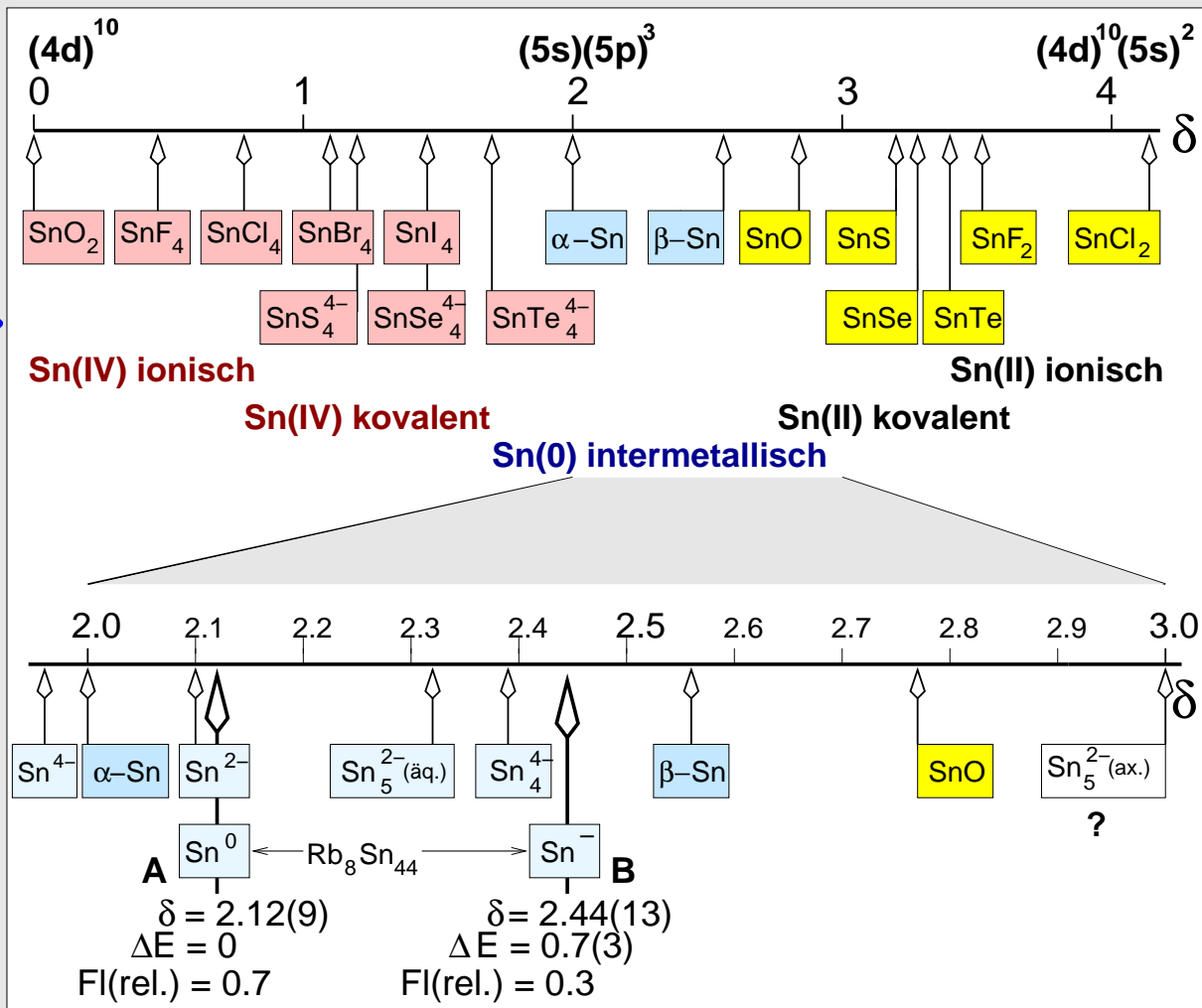
Clathrat-I-Struktur



Rb₈Sn₄₄: ¹¹⁹Sn-Mößbauer-Spektrum



Spektrum von Rb₈Sn₄₄




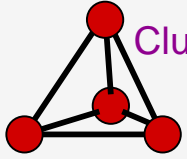
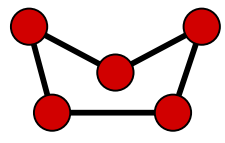
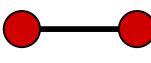

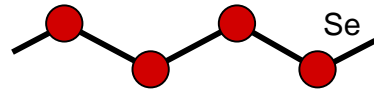
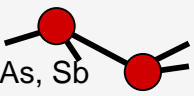
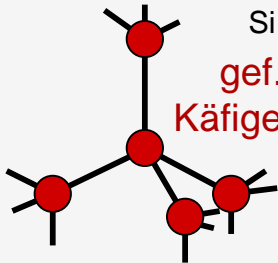
Skala der ^{119m}Sn-Isomerieverschiebungen

III. Polyanionen mit $N < 4$

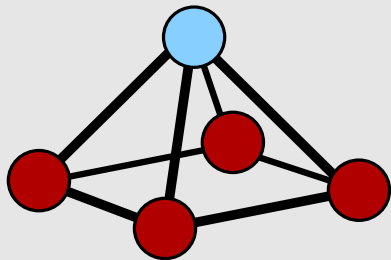
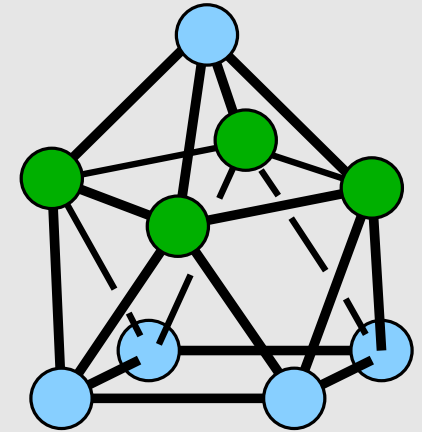
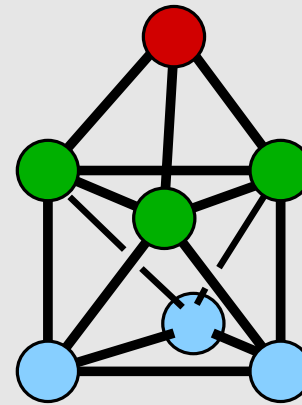
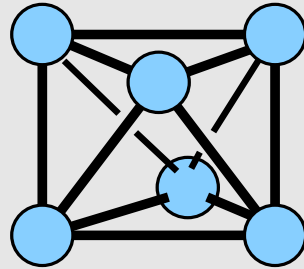
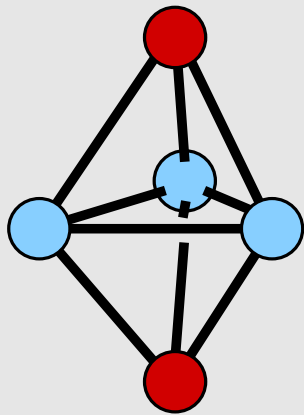
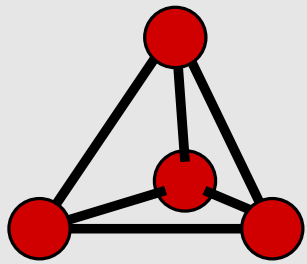
- Elektronenmangelverbindungen (vgl. Borane)
- 3-Zentren-2-Elektronen-Bindung
- Wade-Mingos-Regeln für Clusterstabilitäten
 - ◇ $N+1$ e^- -Paare: Closo-Cluster
 - ◇ $N+2$ e^- -Paare: Nido-Cluster
 - ◇ $N+3$ e^- -Paare: Arachno-Cluster

Zintl-Grenze



	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige	SrSi ₂ -Typ ThSi ₂ -Typ		

Ausgewählte Cluster: Formen und Bindigkeiten

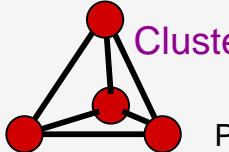
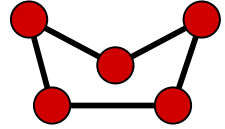



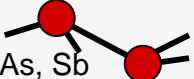
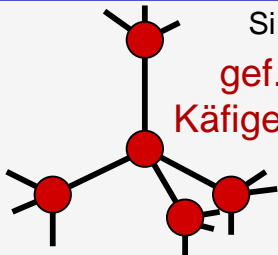


1. Isolierte Cluster

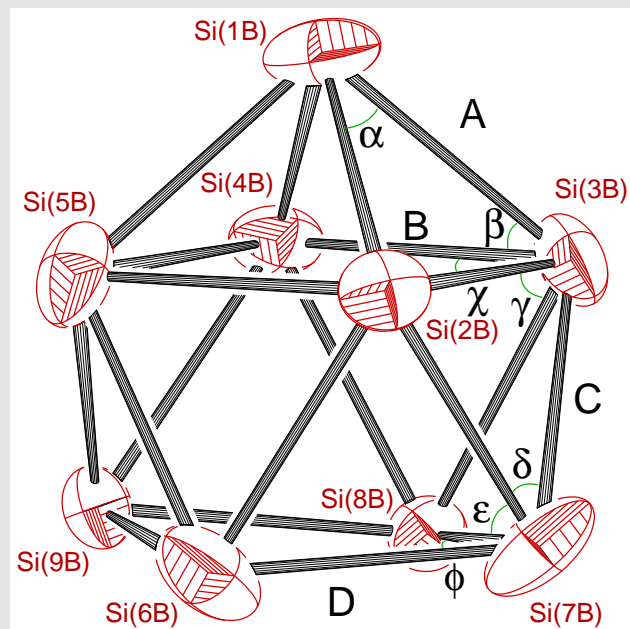
- Alkalimetall-Tetrelide $A_4^I M_9^{IV}$, $A_{12}^I M_{17}^{IV}$ und $A_{52}^I M_{82}^{IV}$ (Bsp: $M^{IV} = Sn$)
- Alkalimetall-Triellide $A^I M^{III}$ (Bsp.: KTI)

Zintl-Grenze

↓

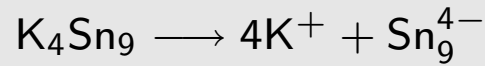
	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 Cluster P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige	SrSi ₂ -Typ ThSi ₂ -Typ		

Wade-Cluster M_9

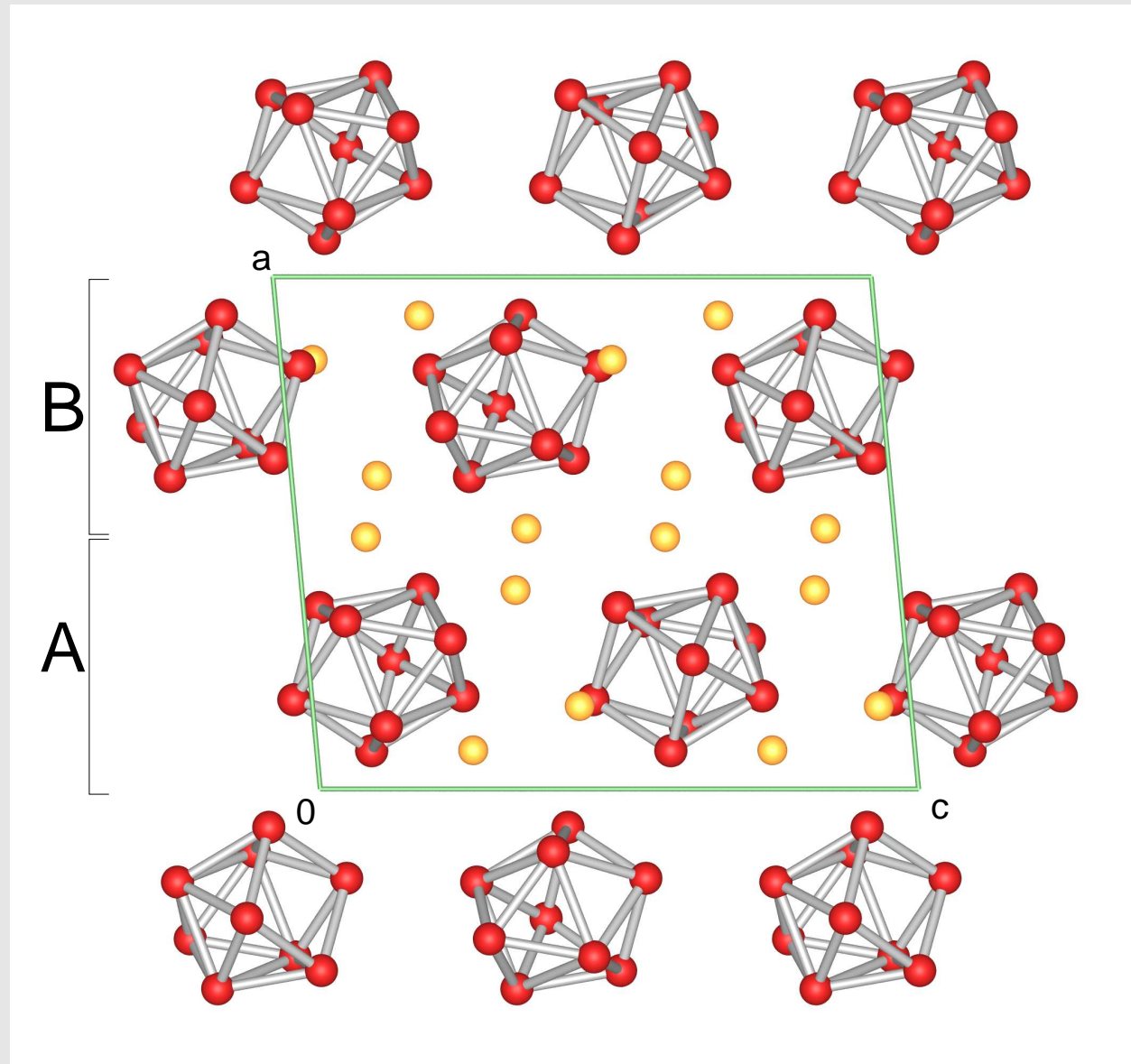
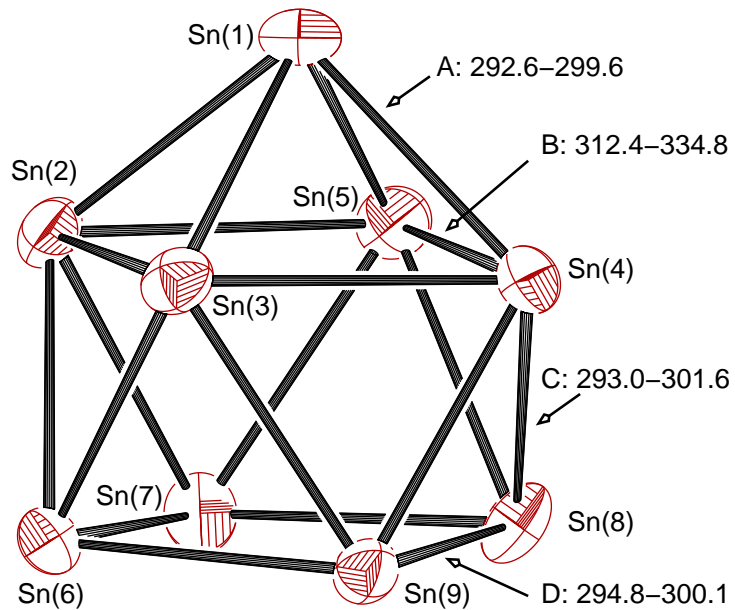


N	Cluster	Gesamtzahl an		Exo-e ⁻ - Paare	Gerüst- e ⁻ -Paare	Wade- Cluster
		Elektronen	e ⁻ -Paaren			
9	[Sn ₉] ⁴⁻	(4*9)+4=40	20	9	11 = N + 2	nido
9	[Bi ₉] ⁵⁺	(5*9)-5=40	20	9	11 = N + 2	nido
9	[Sn ₉] ²⁻	(4*9)+2=38	19	9	10 = N + 1	closo
8	[Bi ₈] ²⁺	(5*8)-2=38	19	8	11 = N + 3	arachno

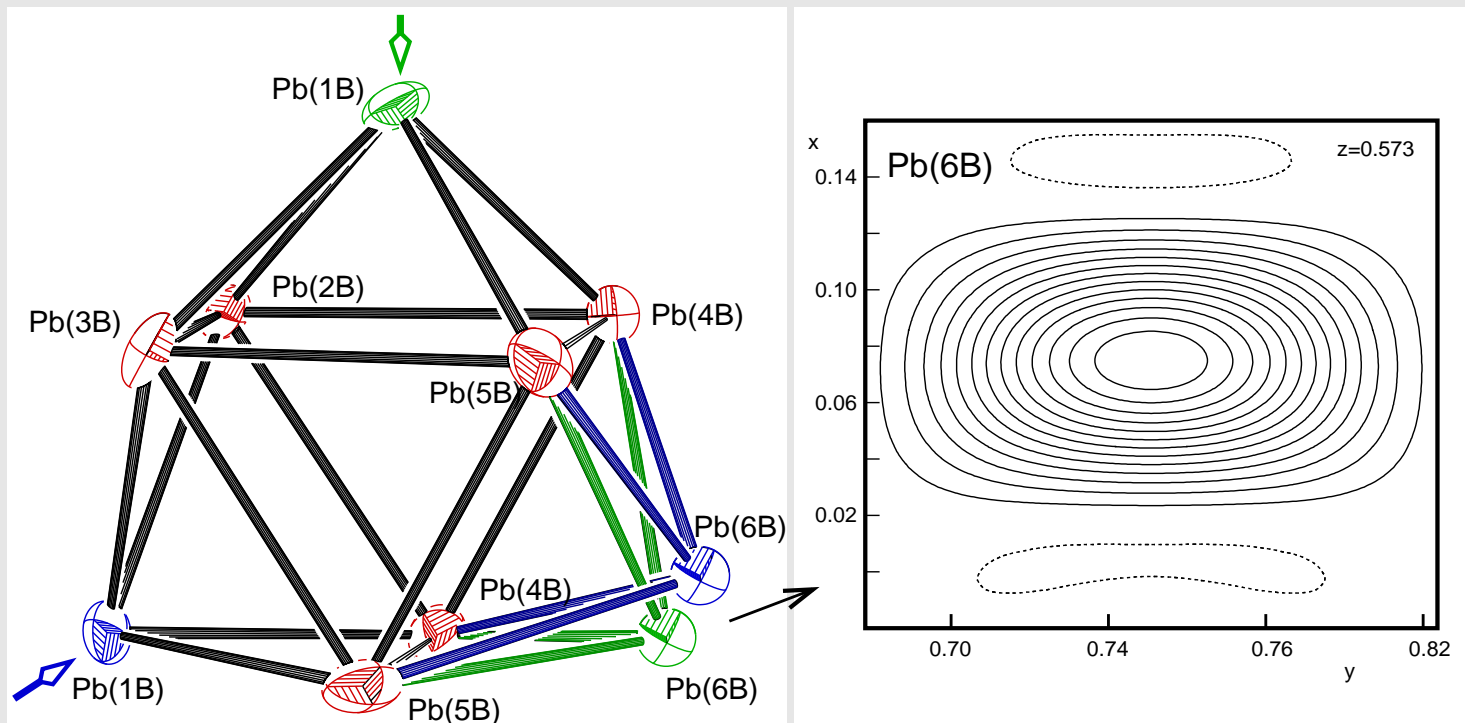
K_4Sn_9 (VE/M=4.44)



Kristallsystem	monoklin	
Raumgruppe	$P2_1/c$, Nr. 14	
Gitterkonstanten	a	1423.8(2)
[pm, °]	b	835.5(1)
	c	1648.7(3)
	β	95.261(3)
Z	4	
R-Wert	R1	0.027



A₄Pb₉ (A=K, Rb): Fehlordnung der Cluster B

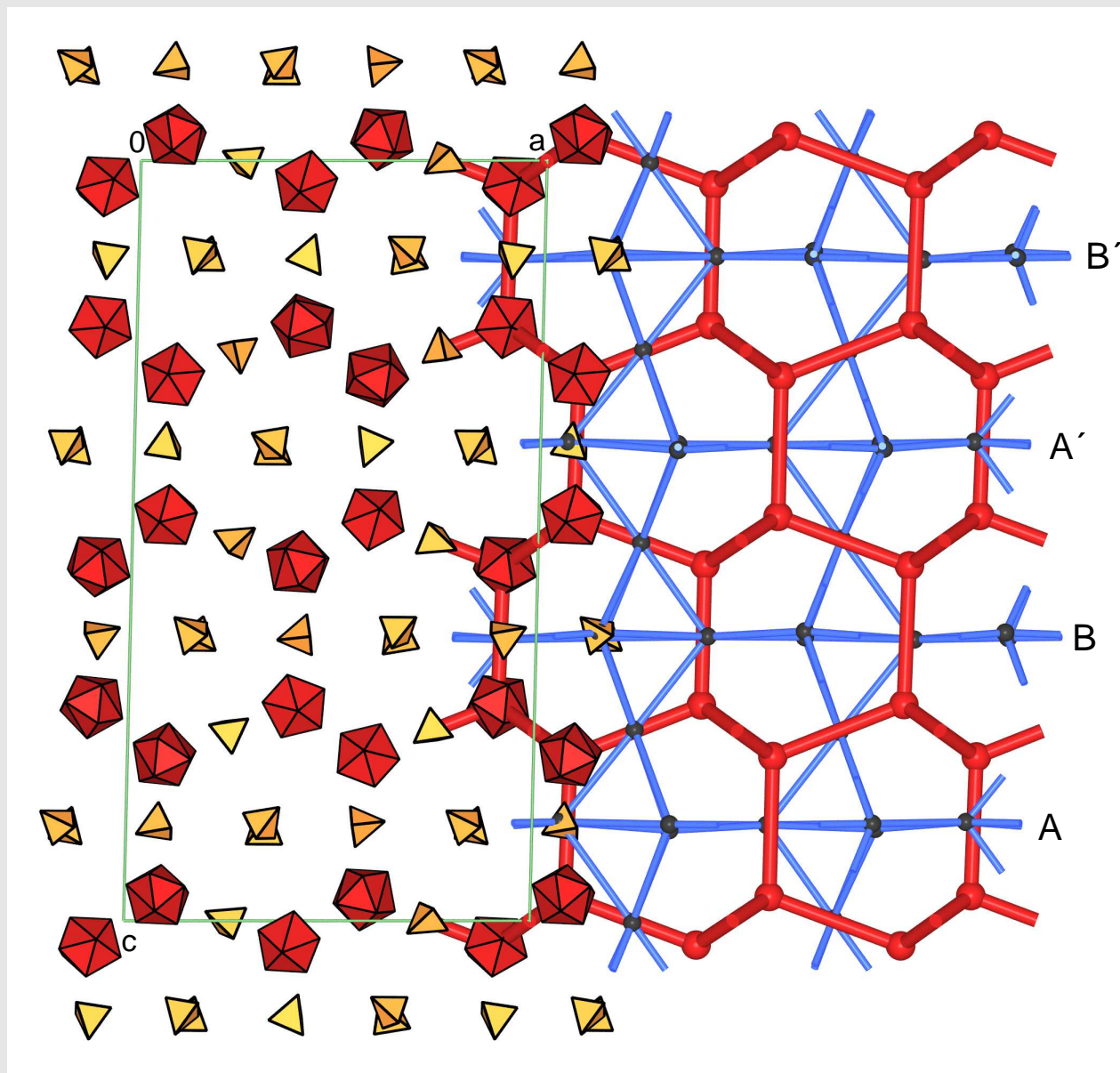
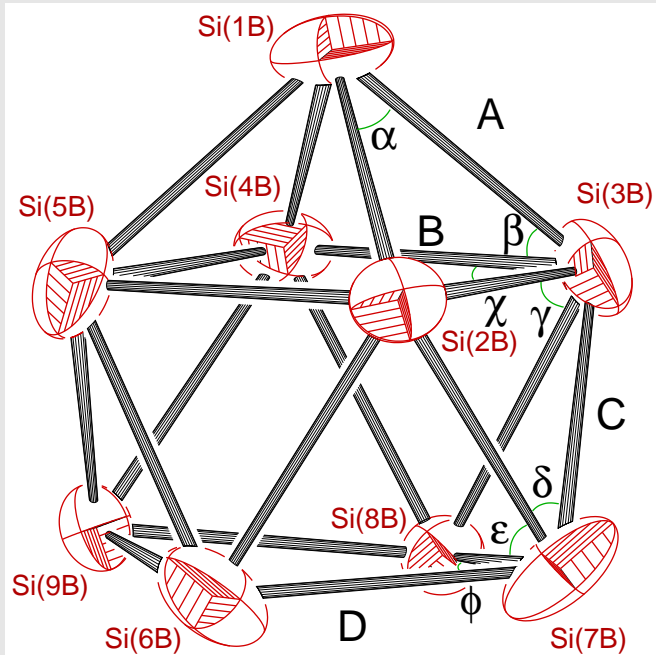


Abstand	Cluster A		Cluster B	
	Bereich [pm]	Mittelwert [pm]	Bereich [pm]	Mittelwert [pm]
A	307.1 - 312.5	310.0	307.6 - 318.1	312.9
B	335.4 - 370.3	346.9	321.8 - 390.4	333.0
C	300.3 - 326.7	313.4	307.9 - 332.7	317.0
D	307.0 - 315.1	311.8	293.8 - 323.5	310.9

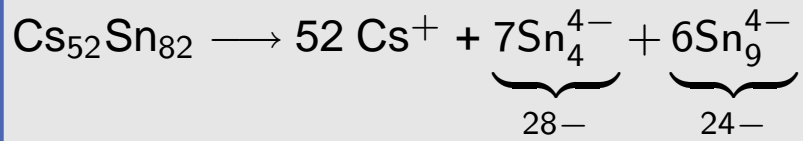
K₁₂Si₁₇



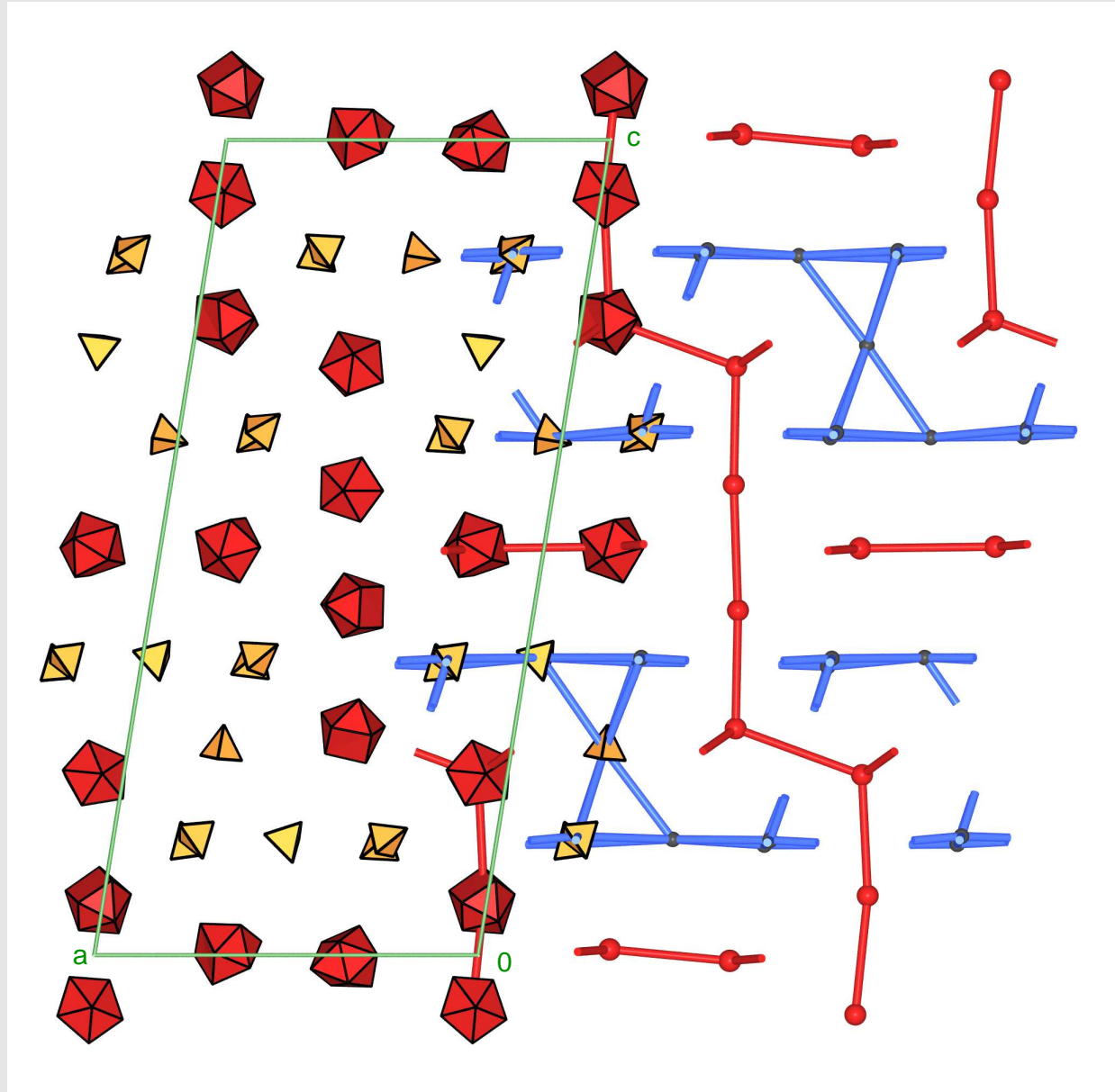
Kristallsystem		monoklin
Raumgruppe		P2 ₁ /c, Nr. 14
Gitterkonstanten	a	2413.1
	b	1371.4
	c	4500.1
[pm, °]	β	91.69
Z		4
R-Wert	R1	0.089



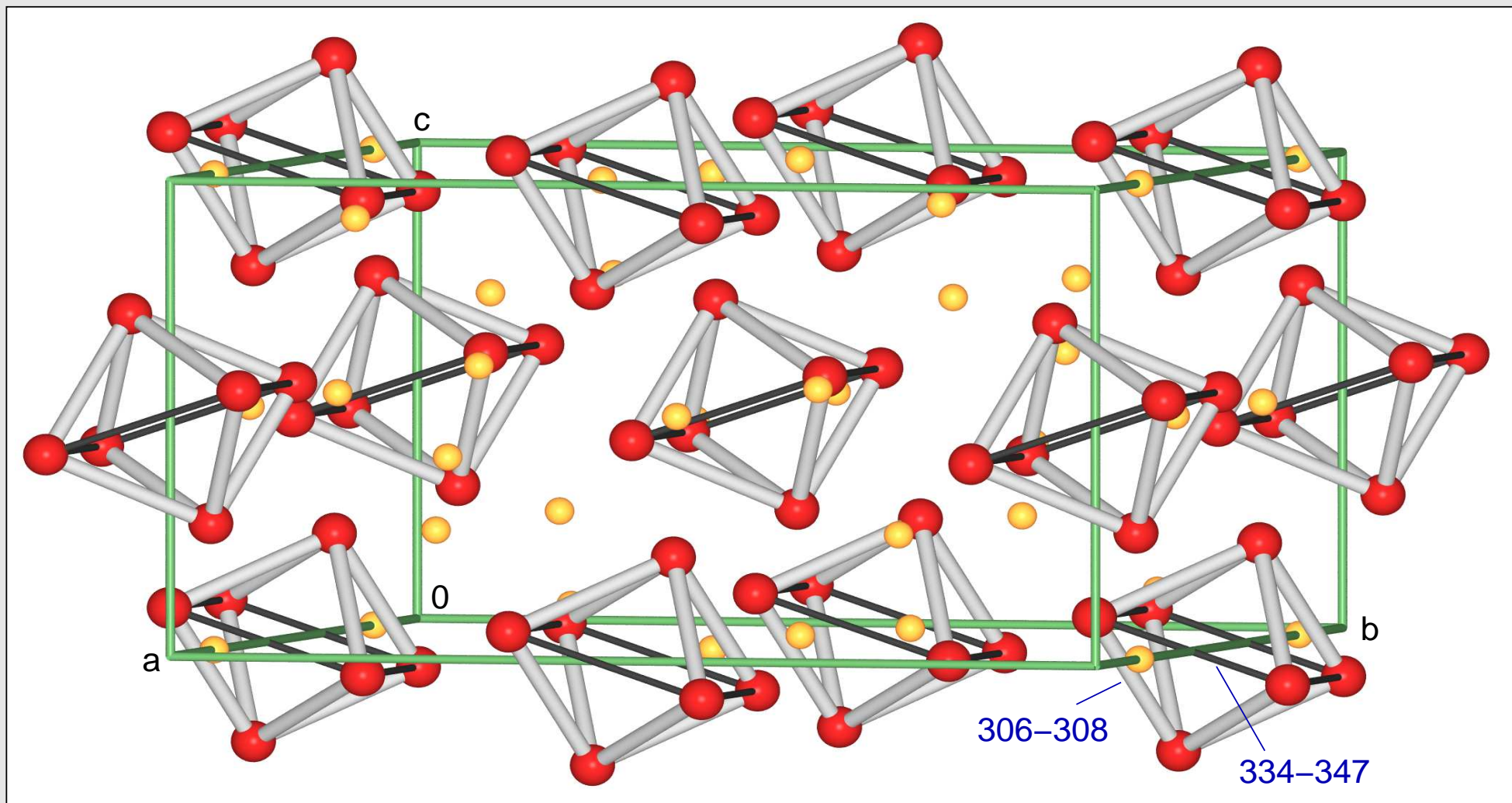
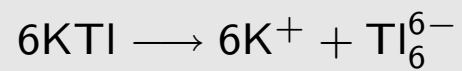
Cs₅₂Sn₈₂ (VE/M=4.63)



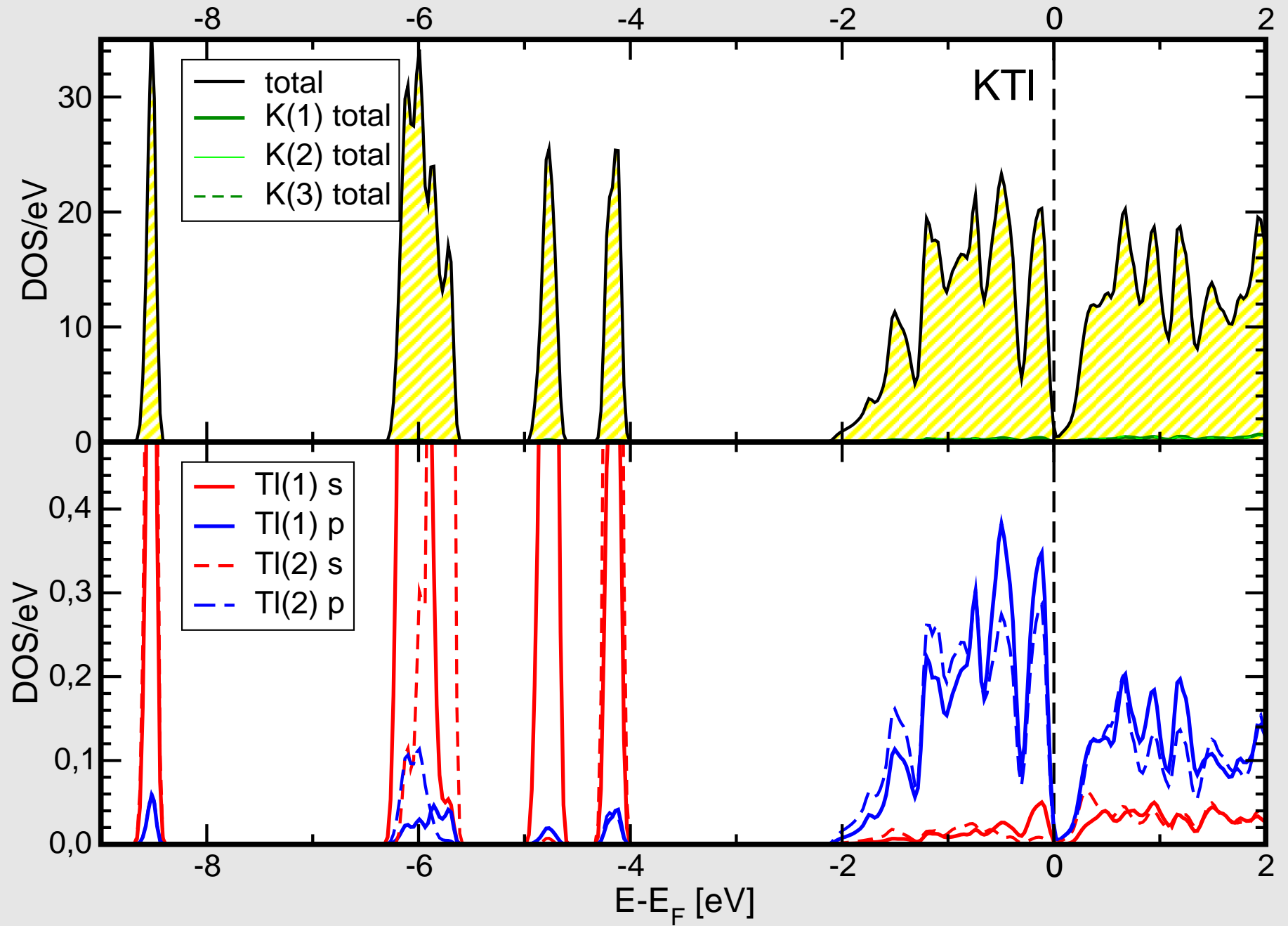
Kristallsystem	monoklin	
Raumgruppe	P2 ₁ /c, Nr. 14	
Gitter-	a	2730.4
konstanten	b	1556.5
[pm, °]	c	5905.0
	β	99.193
Z	4	
R-Wert	R1	0.138



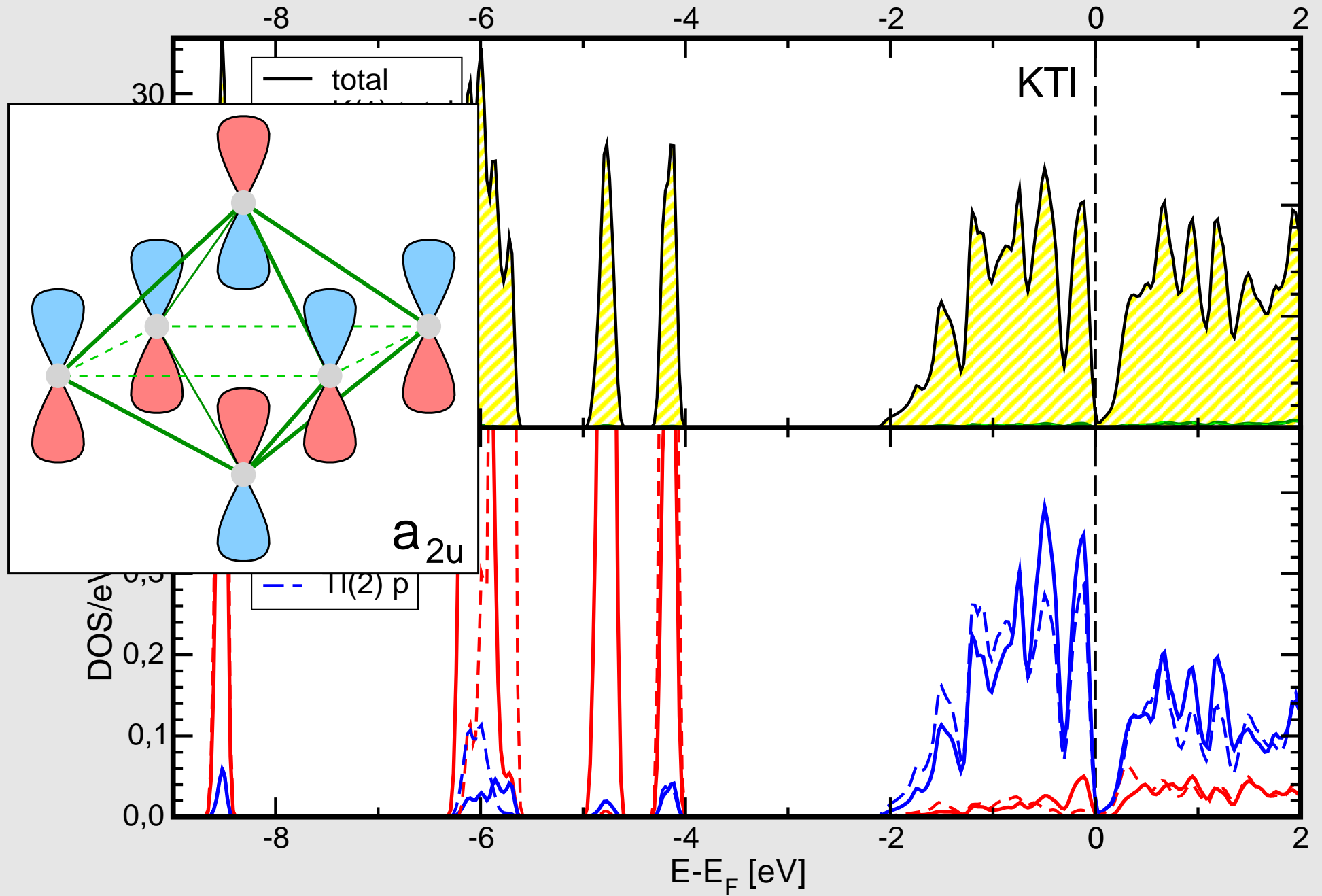
KTI: Struktur



KTI: Totale und partielle TI Zustandsdichten




KTI: Totale und partielle TI Zustandsdichten

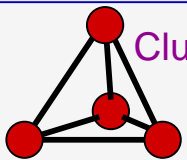
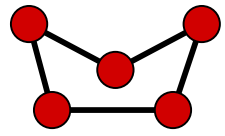


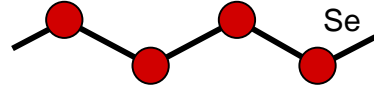
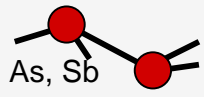
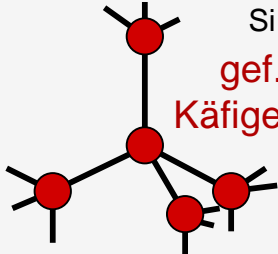


2. Kondensierte Cluster

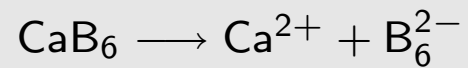
- Boride (Bsp.: CaB_6)
- Indide (Bsp.: AlIn_3 , Al_2In_3)
- Übergang zu echten Metallen (Bsp.: BaIn_4)

Zintl-Grenze



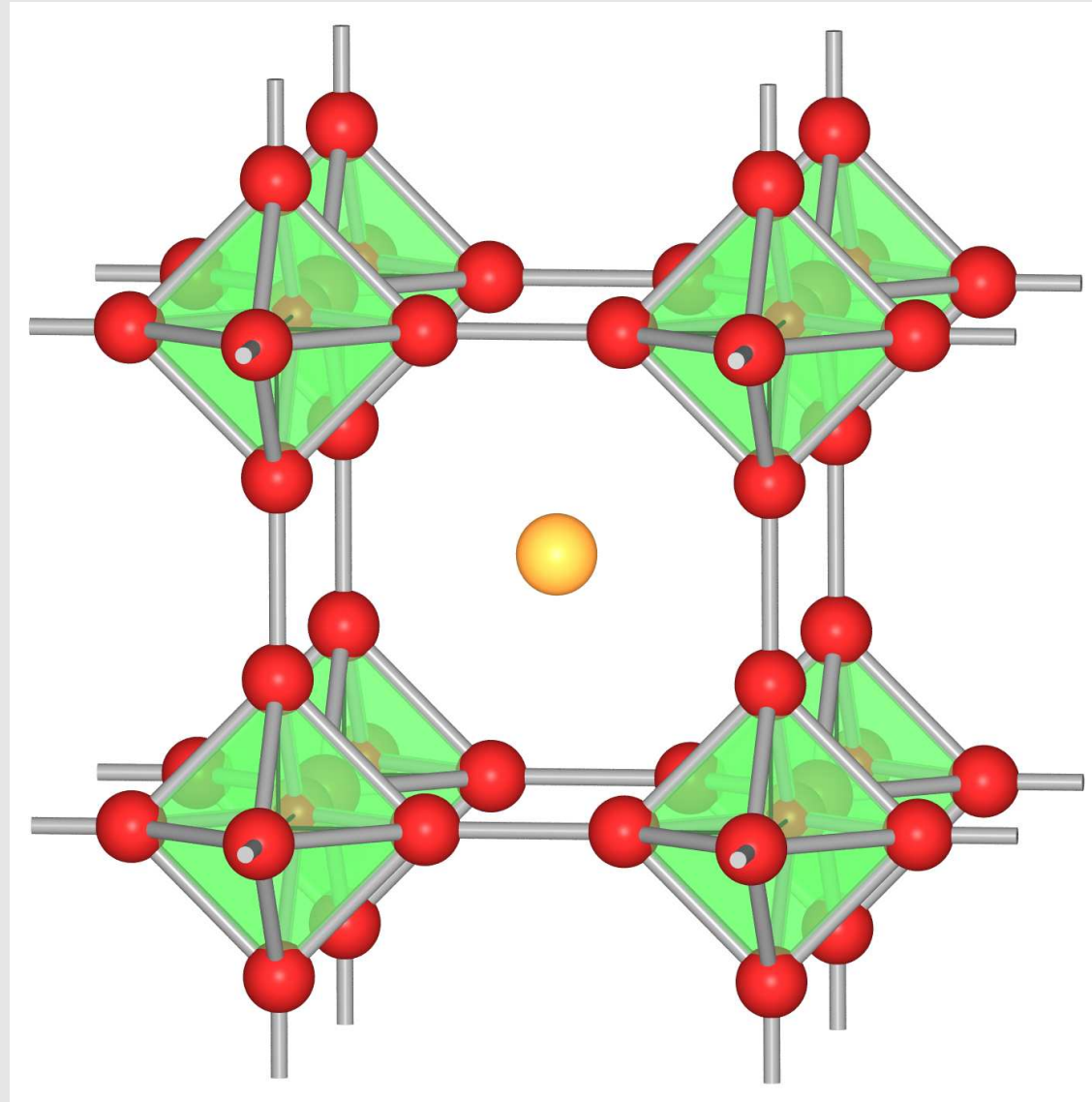
	N=3	N=4	N=5	N=6	N=7	N=8
	?	(4-bindig)	(3-bindig)	(2-bindig)	(1-bindig)	(0-bindig)
0-dim. (Molekül)	isolierte Cluster		 P	 S	 I	 Ar
1-dim. (Kette)				 Se		
2-dim. (Schicht)			 As, Sb			
3-dim. (Raumnetz)	kondensierte Cluster		 Si gef. Käfige	SrSi ₂ -Typ ThSi ₂ -Typ		

Kondensierte Closo-Cluster: CaB₆

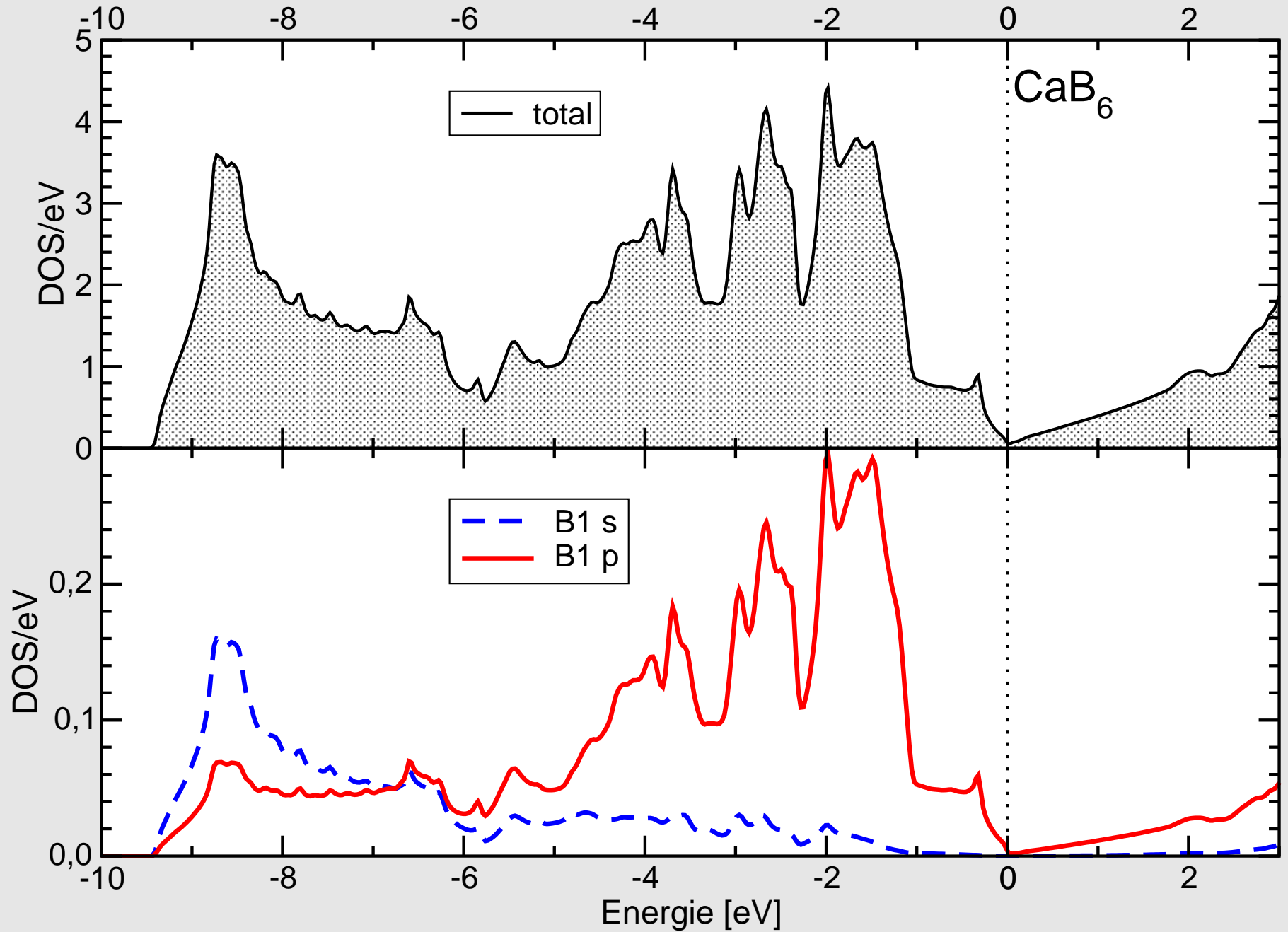


Cluster-Elektronen:

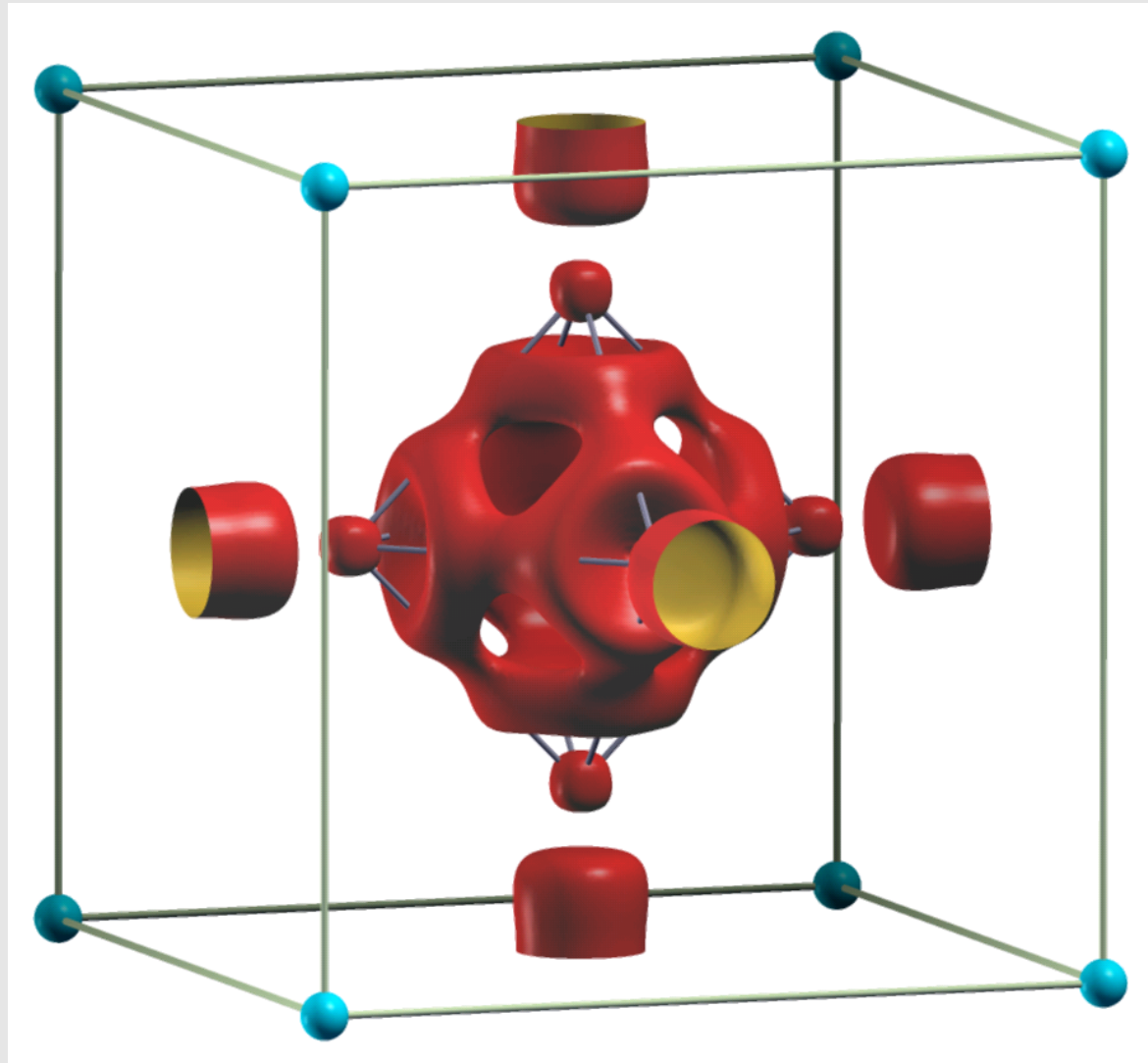
$$\underbrace{6 \cdot 3}_{\text{von B}} + \underbrace{2}_{\text{Ladung}} - \underbrace{6}_{\text{exo-b}} = 14 = 2N+2$$



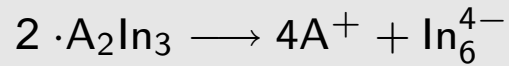
CaB₆ : Totale und partielle B-Zustandsdichte



CaB₆ : berechnete Elektronendichte



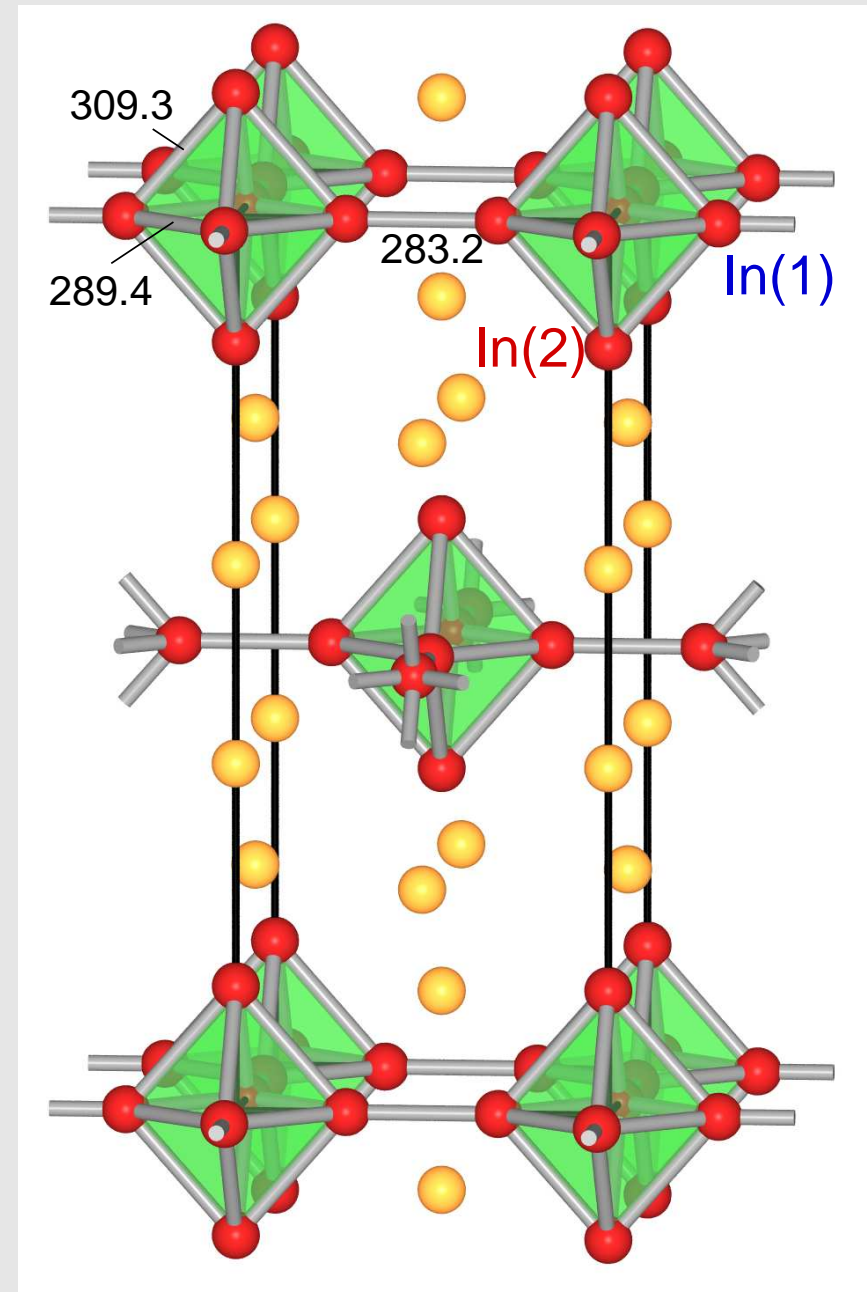
Cs₂In₃ (VE/M=3.67)



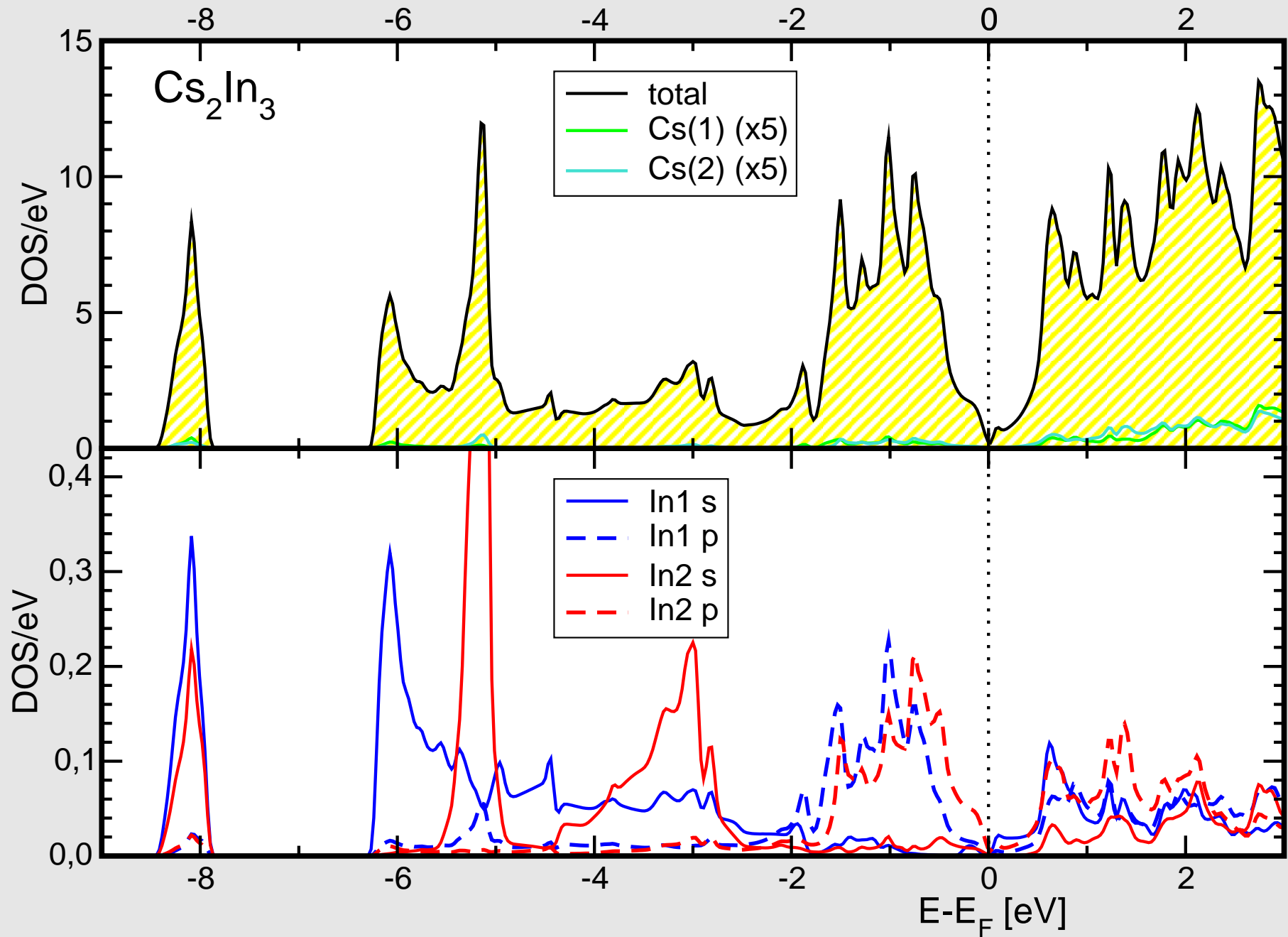
Cluster-Elektronen:

$$\underbrace{6 \cdot 3+}_{\text{von In}} \underbrace{4}_{\text{Ladung}} - \underbrace{4}_{\text{exo-b}} - 2 \cdot \underbrace{2}_{\text{nicht-b.}} = 14 e^- \mapsto 7 EP = N + 1$$

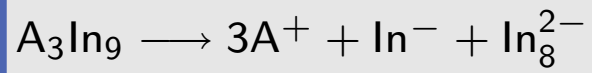
Kristallsystem		tetragonal
Raumgruppe		I4/mmm, Nr. 139
Gitter-	a	692.5(1)
konstanten	c	1663.2(5)
[pm]		
VEZ [10 ⁶ pm ³]		932.3
Z		4
R-Wert	R1	0.142



Cs₂In₃ : Totale und partielle In Zustandsdichte



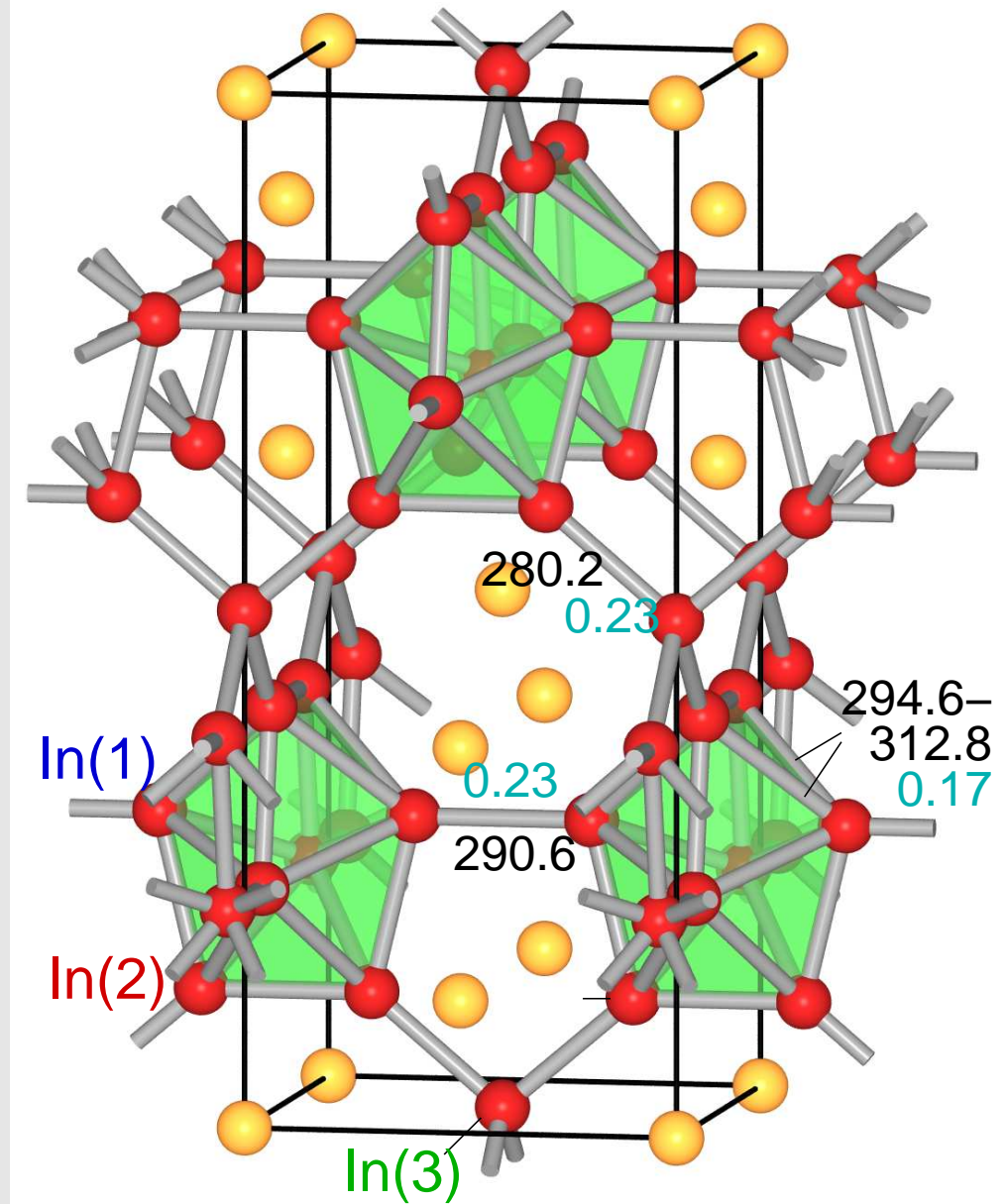
CsIn₃: Struktur



Cluster-Elektronen:

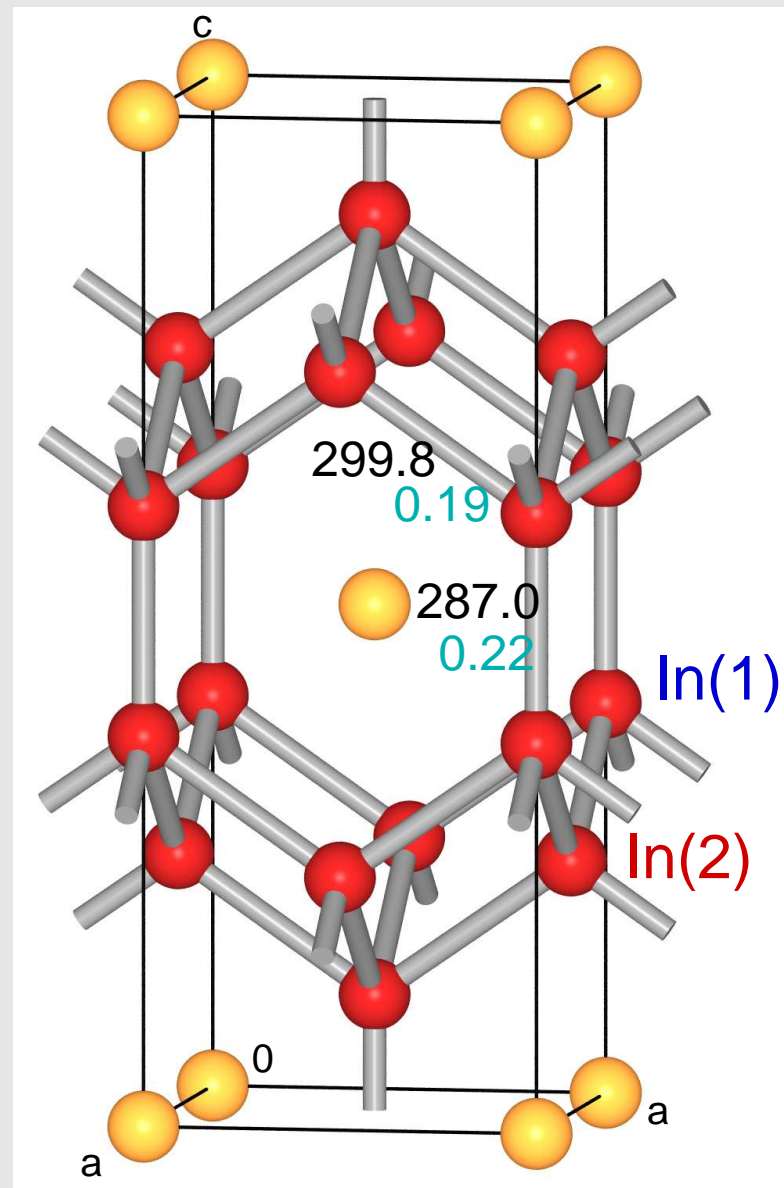
$$8 \cdot 3 + 2_{\text{Ladung}} - 8_{\text{exo-b}} = 18 = 2N + 2$$

Kristallsystem		tetragonal
Raumgruppe		$I\bar{4}m2$, Nr. 119
Gitterkonstanten	a	704.2(2)
	c	1678.3(5)
		[pm]
VEZ [10 ⁶ pm ³]		832.3
Z		4
R-Wert	R1	0.033

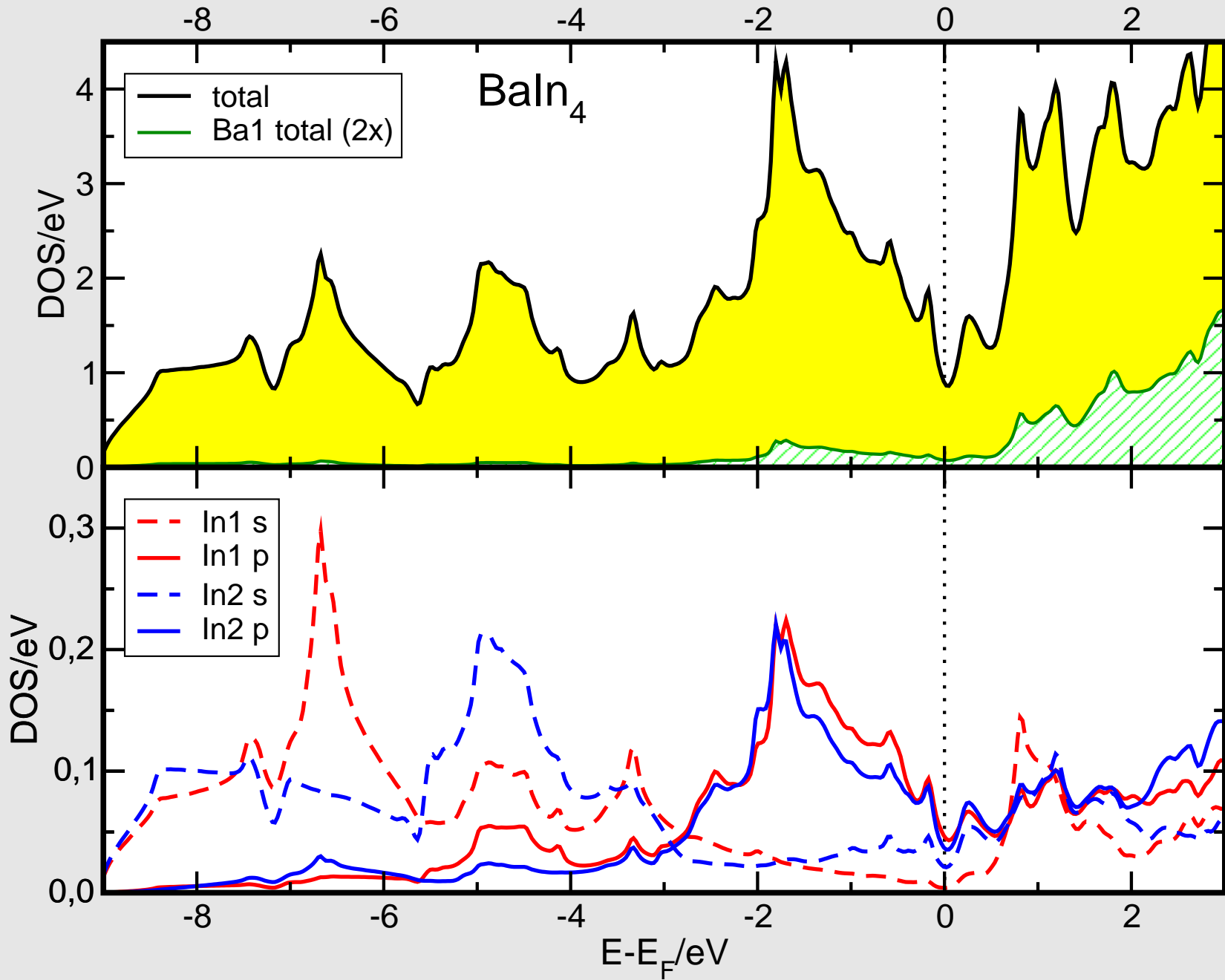


Aln₄

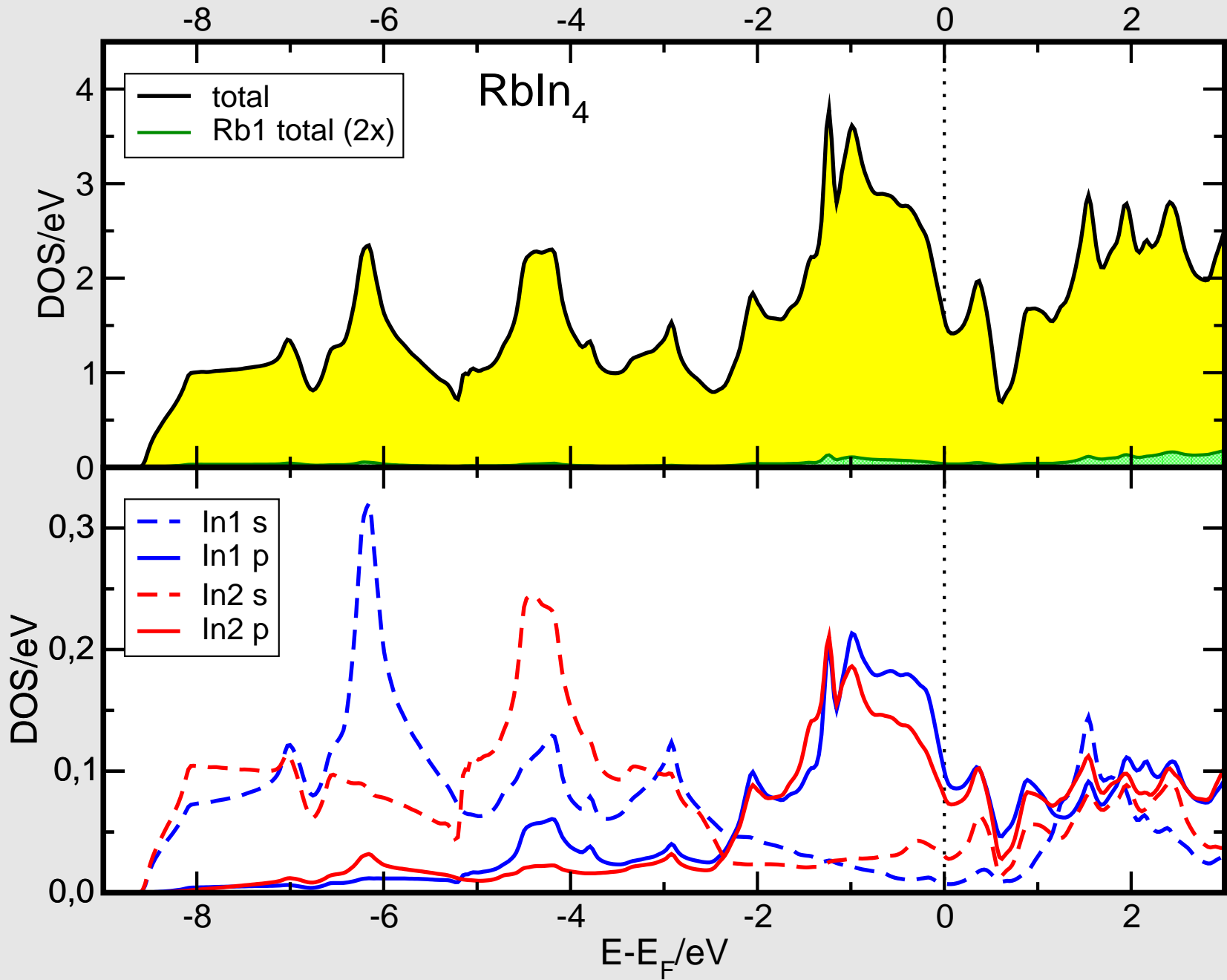
	A	K	Rb	Ba
Strukturtyp			BaAl ₄	
Kristallsystem			tetragonal	
Raumgruppe			I4/mmm, Nr. 139	
Gitterkonstanten a	483.97(4)	492.8(3)	497.0(2)	
[pm]				
c	1256.37(3)	1257.5(4)	1198.3(5)	
VEZ [10 ⁶ pm ³]	294.3	305.4	296.0	
c/a-Verhältnis	2.596	2.552	2.411	
Z		2		
R-Werte		R _p =0.129	R1=0.0288	R1=0.0187
d _{In(1)–In(1)} [pm]		286.9	287.0	279.7
d _{In(1)–In(2)} [pm]		298.2	299.8	295.4
d _{In(2)–In(2)} [pm]		342.2	348.5	351.4



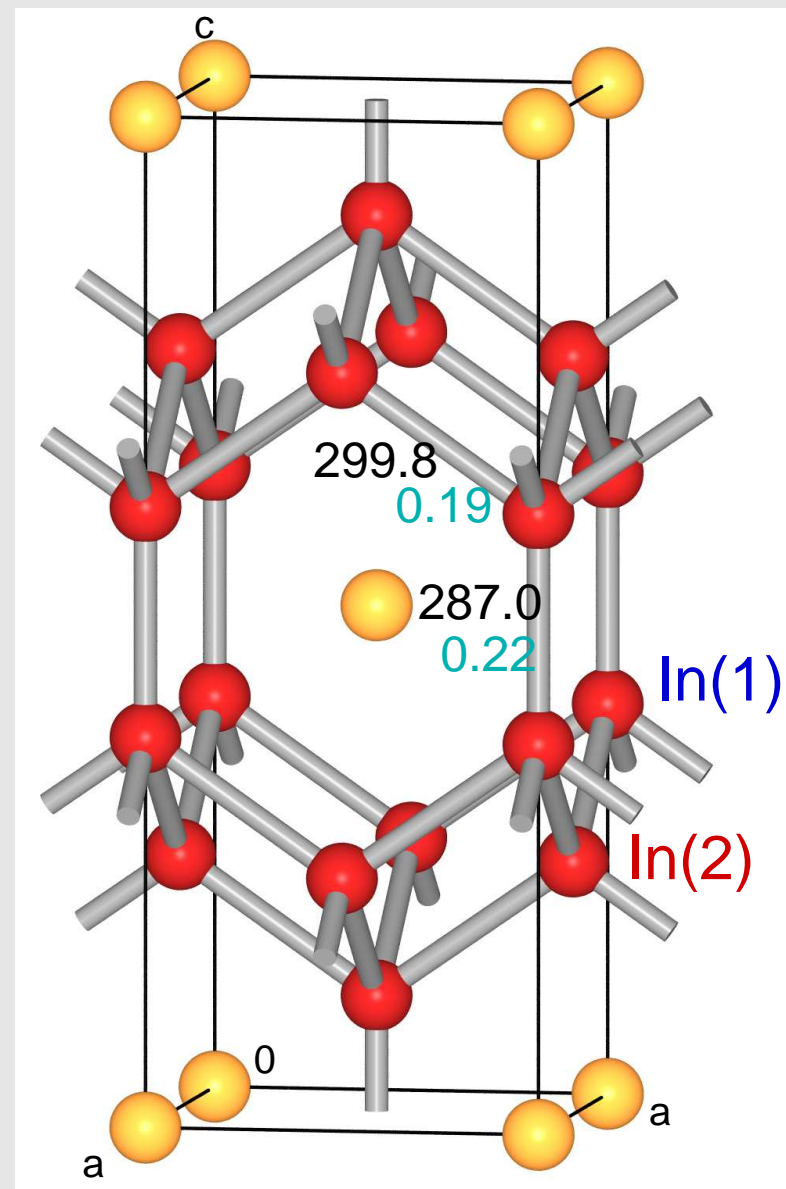
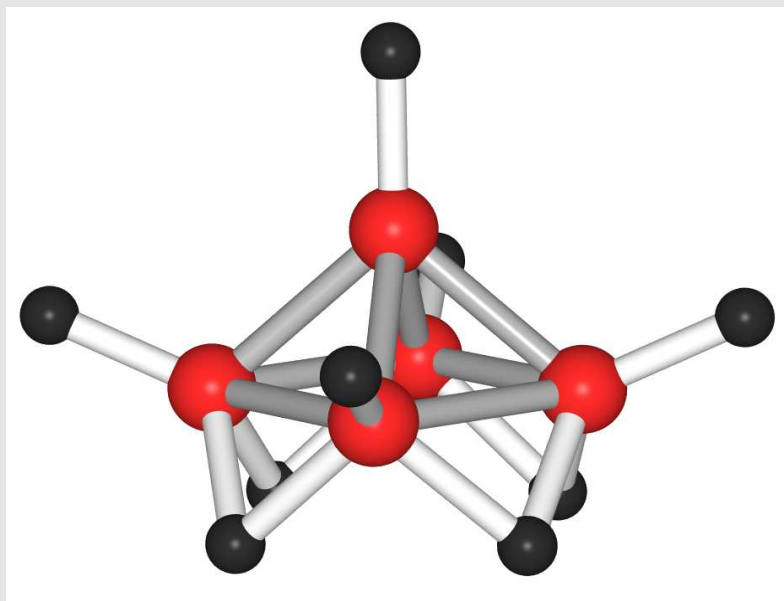
BaIn₄ : Totale und partielle In Zustandsdichte



RbIn₄ : Totale und partielle In Zustandsdichte



Analogie $BaAl_4$ – Typ und B_5H_9



Zusammenfassung

- Polyanionen der 13. und 14. Gruppe mit Alkali/Erdalkalimetallen als Bindungspartner
- häufig elektronenpräzise Anionenbauverbände nach ionischer Zerlegung (Zintl-Konzept)
- elektronenpräzise M_4 -Tetraeder-Käfige bei Si bis Pb sowie In und Tl (nur bei ausreichender Zahl/Volumen der Kationen)
- Tetraederraumnetze bei Trieliden $A^I M^{III}$ (kub. Diamant) und $A^{II} M_2^{III}$ (hex. Diamant)
- Clathrate mit gefüllten Käfigen (Pentagondodekaeder, Hexakaidekaeder) bei Tetrel-reichen A^I -Tetreliden
- Tetrel-Cluster M_9^{4-} (nido-Cluster, nach Wade erklärbar)
- Boride und Indide mit kondensierten Clustern
- trotz fehlender Bandlücken z.T. noch gültige Wade-Regeln bei weniger polaren metallischen Systemen
- !! zusätzlich: viele Ausnahmen von diesen Elektronenzählregeln, umso häufiger, je weiter links und unten im PSE M steht (d.h. je metallischer M ist) !!