

Cluster und Käfige I

Anionische Käfige und Cluster der
Gruppen 13 und 14.

AC-Sonderseminar, 6.2.2006

Verbindungen mit Anionen der 13. und 14. Gruppe

| | | | | | | | |
|----|----|----|----|----|----|----|----|
| H | | | | | | | He |
| Li | Be | B | C | N | O | F | Ne |
| Na | Mg | Al | Si | P | S | Cl | Ar |
| K | Ca | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | Tl | Pb | Bi | Po | At | Rn |




+I

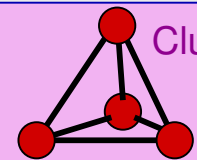
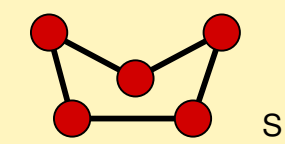
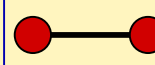

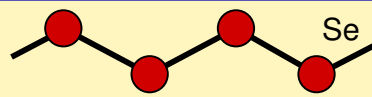
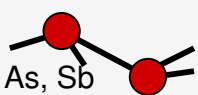
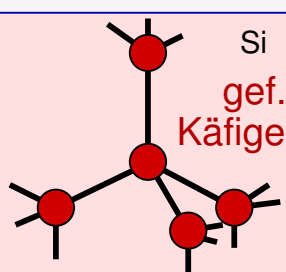
+II

Kovalente Verbindungen

- $\text{VEZ/Atom} \geq 4 \mapsto$ Zahl der VE (N) bestimmt Bindigkeit (8-N-Regel)
 - ◇ $N=8$: Edelgase, Halogenide E(VII)^- , E(VI)^{2-} , E(V)^{3-} , $\text{E(IV)}^{4-} \mapsto$ keine Bindung
 - ◇ $N=7$: elementare Halogene, E(VI)^- , E(V)^{2-} , $\text{E(IV)}^{3-} \mapsto$ einbindig
 - ◇ $N=6$: elementare Chalkogene, E(V)^- , $\text{E(IV)}^{2-} \mapsto$ zweibindig \mapsto Ketten und Ringe
 - ◇ $N=5$: elementare Pentele, E(IV)^- , E(III)^{2-} , $\text{E(VI)}^+ \mapsto$ dreibindig \mapsto Käfige bis Raumnetze
 - ◇ $N=4$: elementare Tetrele, $\text{E(III)}^- \mapsto$ vierbindig \mapsto Raumnetze, Clathrate
- $\text{VEZ/Atom} < 4$ (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 oedicnemus</i> | <i>Turdus torquatus</i> |
| 35 cm | 40 cm | 24 cm |
| goldbraun, im Winter im Sommer schwarz mit dunklen 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-Verbände 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)

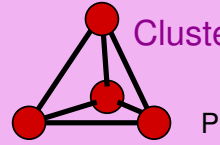
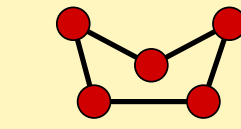
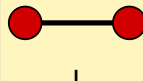

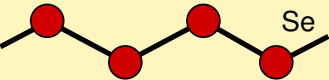
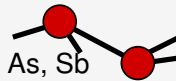
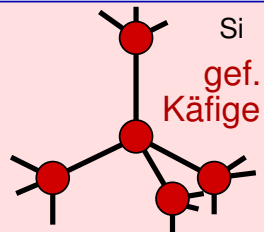


Käfige und Cluster: Anionen mit $N \leq 5$ (Inhaltsübersicht)

- 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




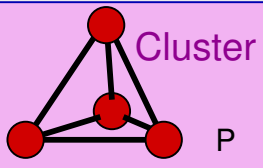
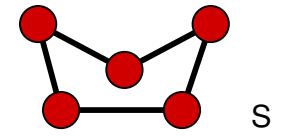
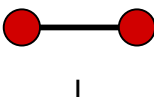

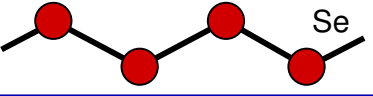
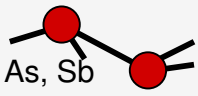
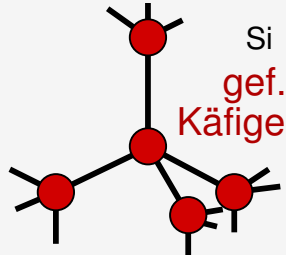
| | N=3 | N=4 | N=5 | N=6 | N=7 | N=8 |
|----------------------|----------------------|------------|----------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|
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| 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 | | | |

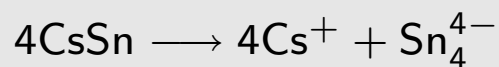
I. elektronenpräzise Käfig-Anionen (N = 5, Pentel-isoster)

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

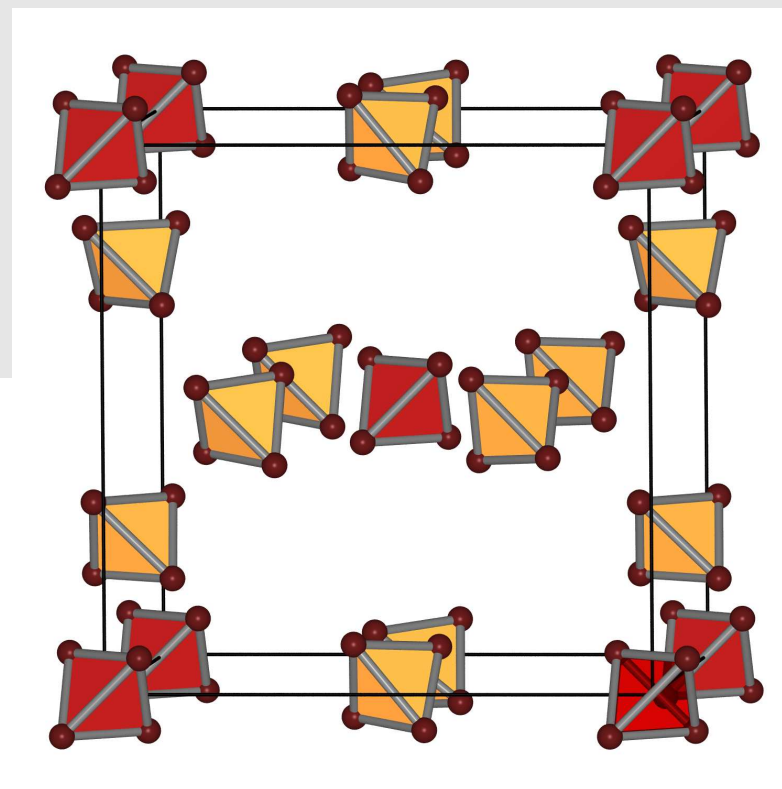
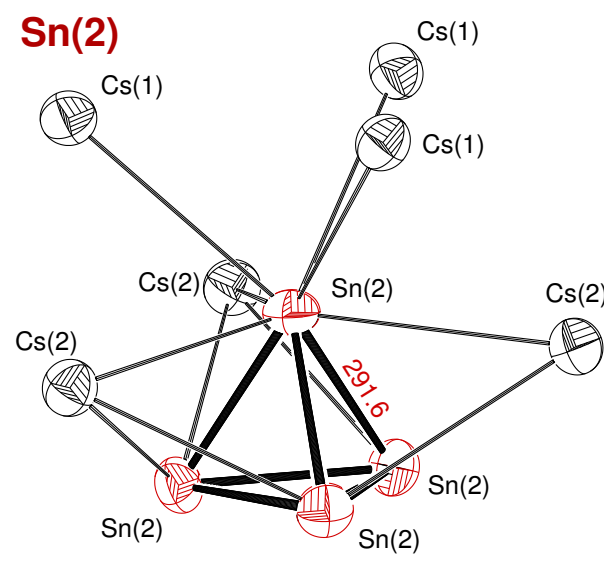
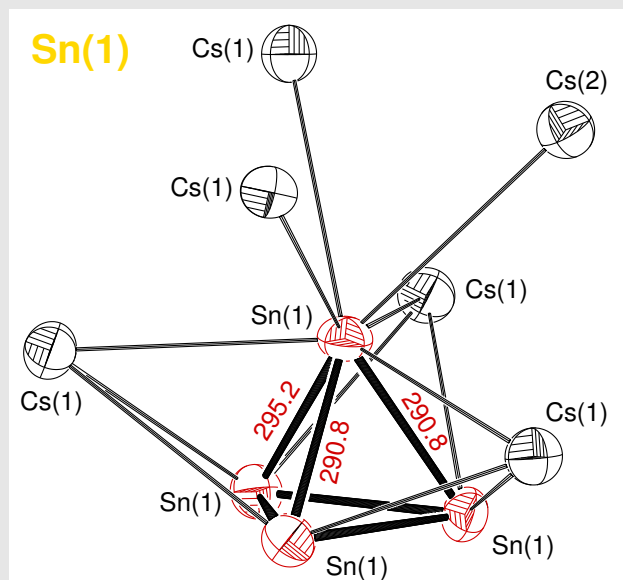
Zintl-Grenze



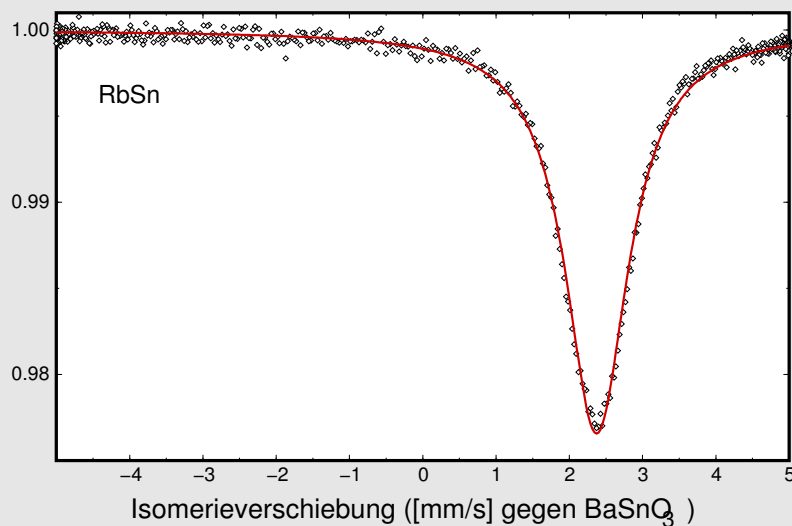
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| 0-dim. (Molekül) | isolierte Cluster | |  Cluster P |  S |  I |  Ar |
| 1-dim. (Kette) | | | |  Se | | |
| 2-dim. (Schicht) | | |  As, Sb | | | |
| 3-dim. (Raumnetz) | kondensierte Cluster | |  Si gef. Käfige | SrSi ₂ -Typ ThSi ₂ -Typ | | |



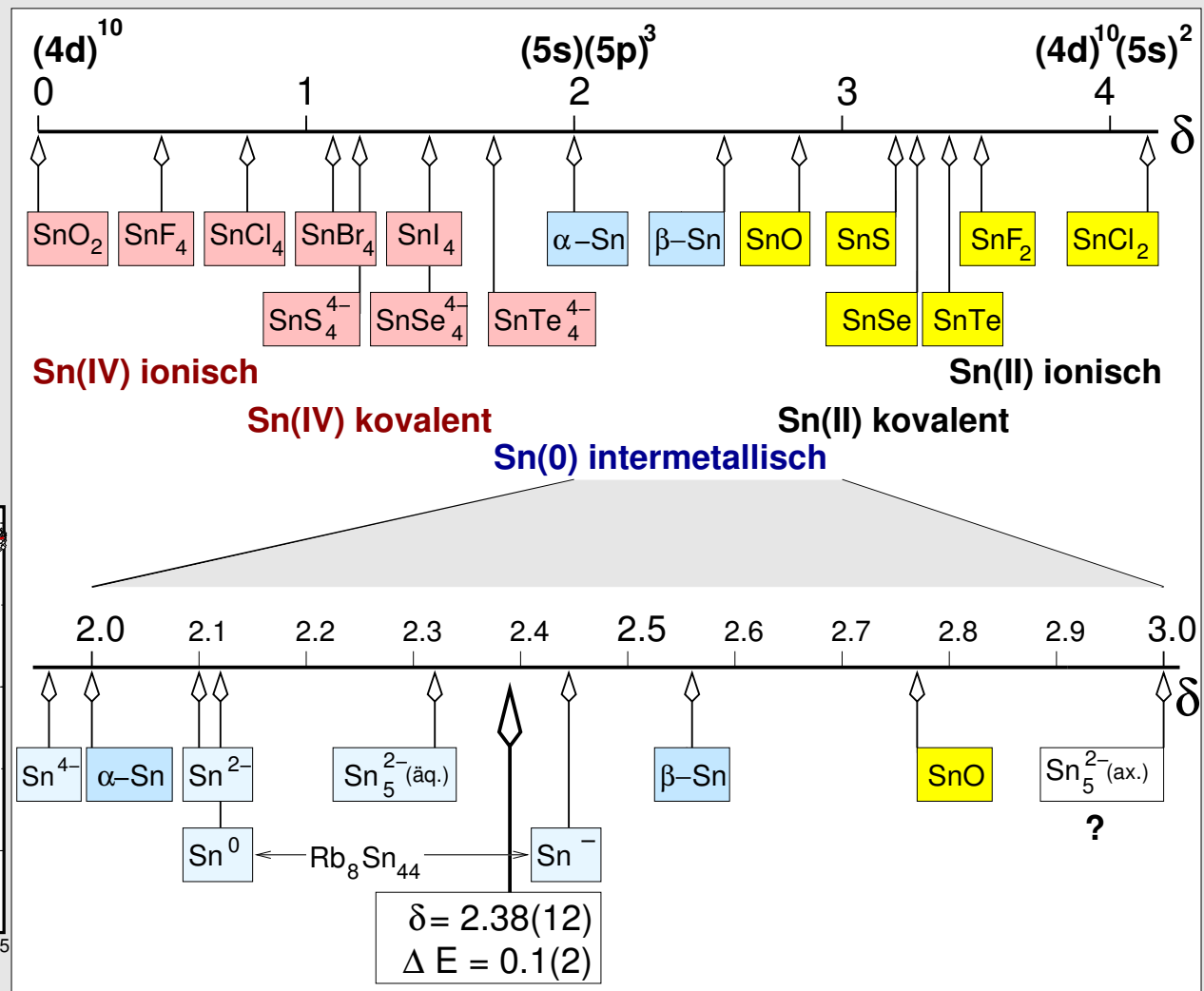
| | | |
|----------------------|-----|------------------------|
| Strukturtyp | | KGe |
| Kristallsystem | | kubisch |
| Raumgruppe | | $P\bar{4}3n$, Nr. 218 |
| Gitterkonstante [pm] | a | 1444.74 |
| Z | | 32 |
| R-Werte | R1 | 0.0395 |
| | wR2 | 0.0709 |



RbSn: ^{119}Sn -Mößbauer-Spektrum

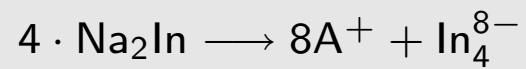


Spektrum von RbSn

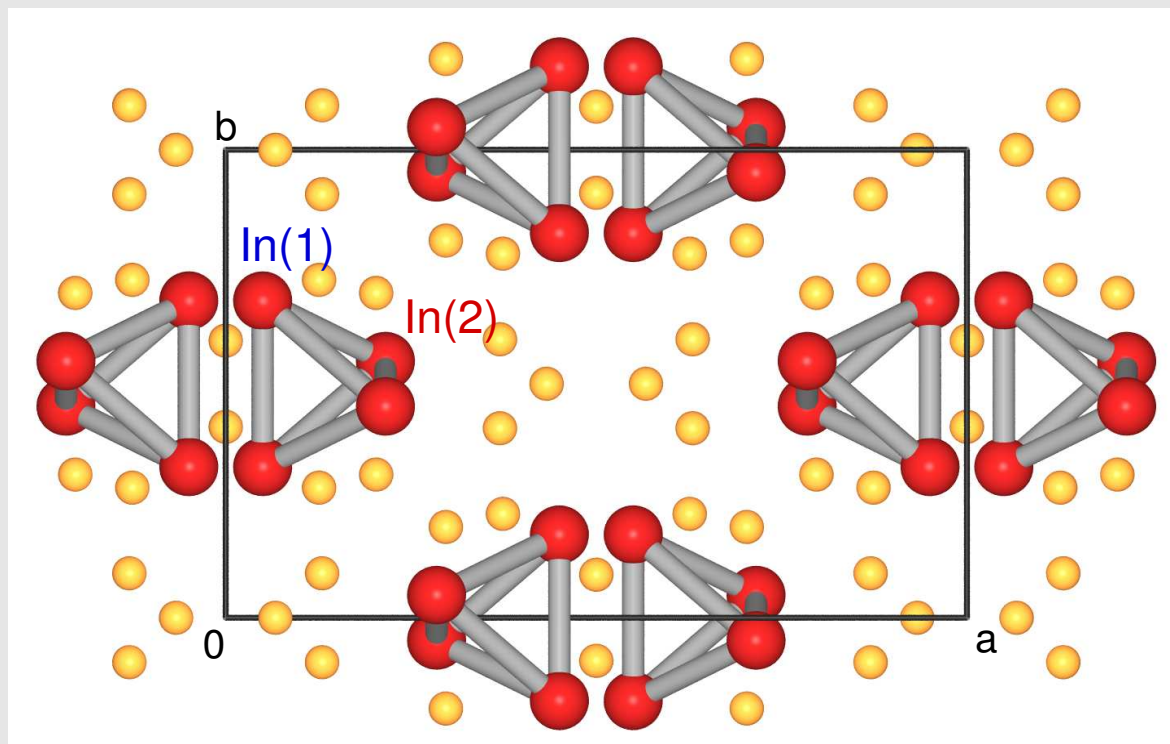


Skala der ^{119m}Sn -Isomerieverschiebungen

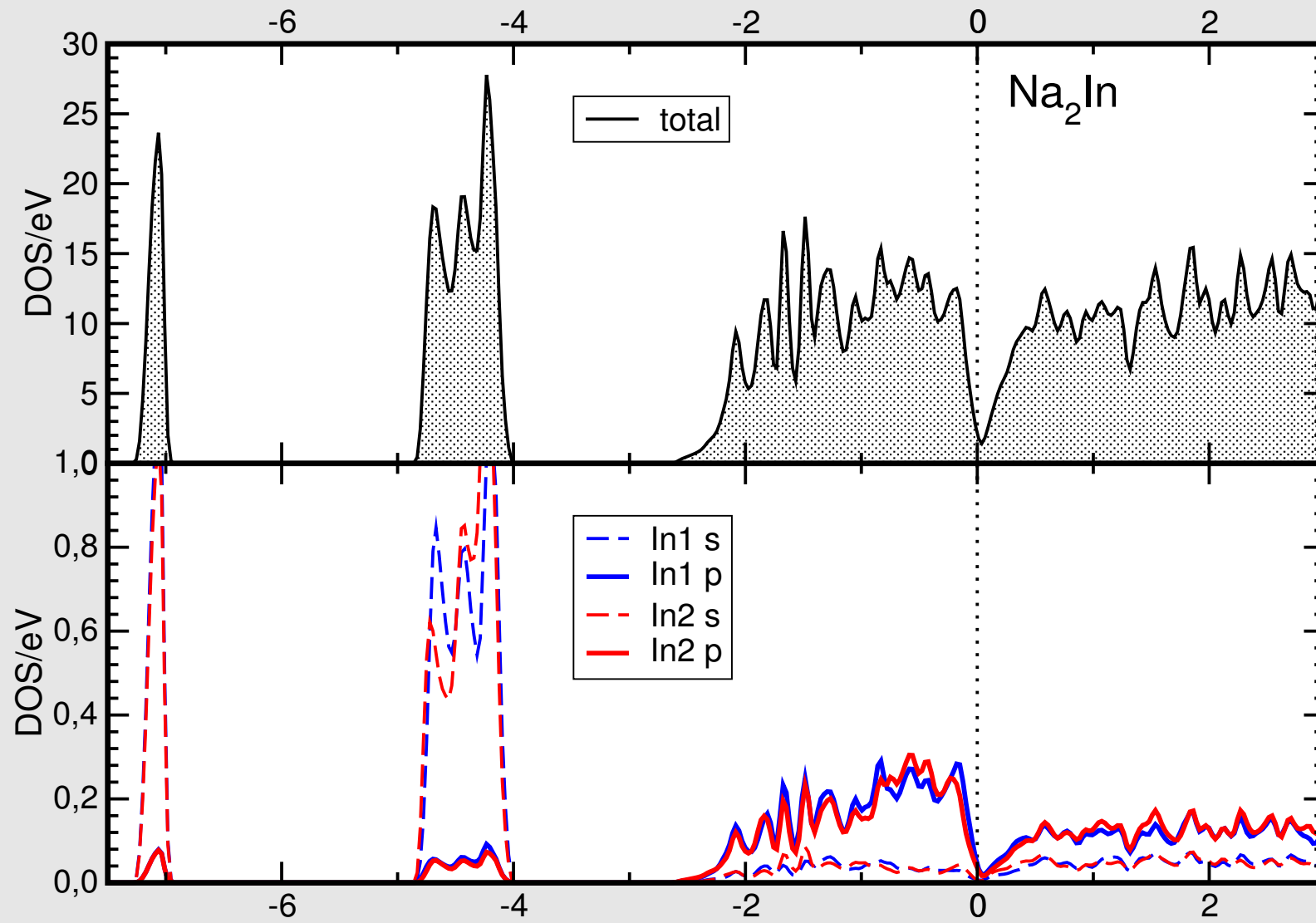
Na₂In: Struktur



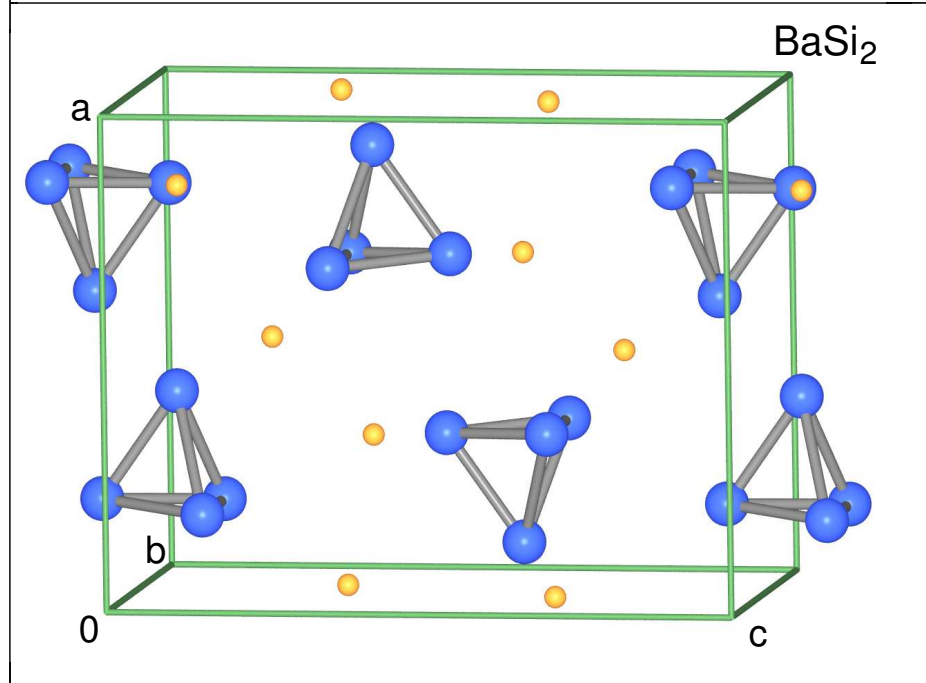
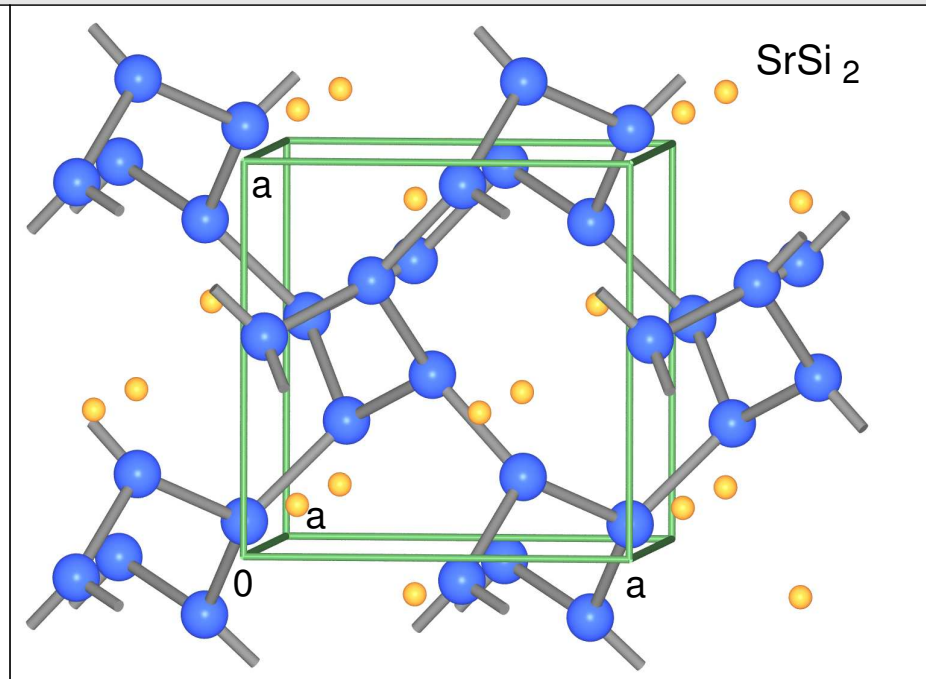
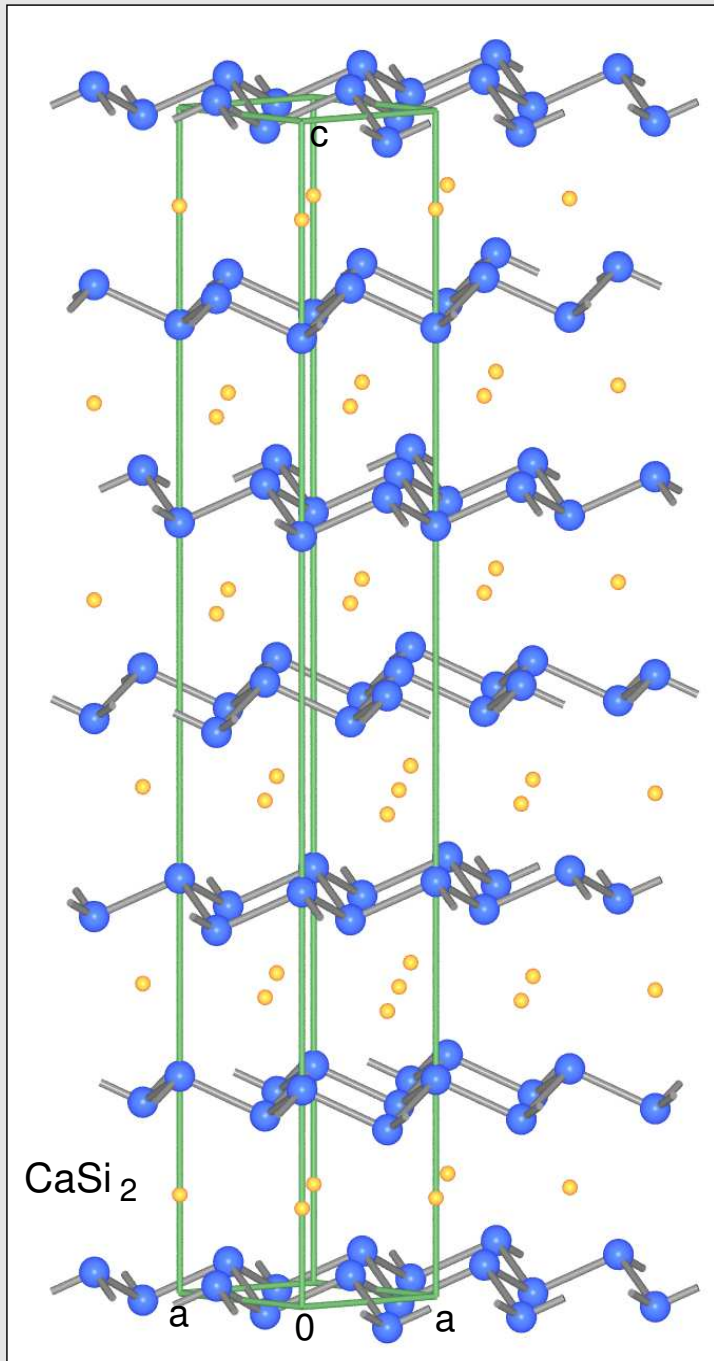
| | | |
|-------------------------|---|----------------------|
| Strukturtyp | | Na ₂ Tl |
| Kristallsystem | | orthorhombisch |
| Raumgruppe | | C 2 2 2 ₁ |
| Gitter- konstanten | a | 883.3 |
| [pm] | b | 1385.0 |
| | c | 1175.8 |
| d _{In-In} [pm] | | 307-315 |



Na₂In : Totale und partielle In Zustandsdichte




Strukturen der Erdalkalimetall-Disilicide $A^{II}M_2^{IV}$

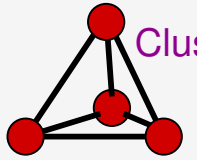
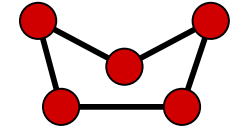


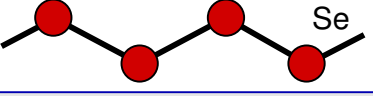
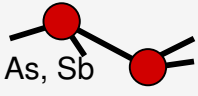
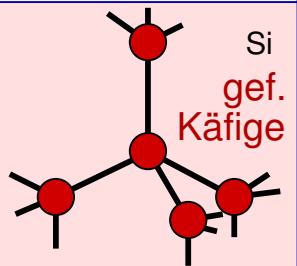


II. Polyanionen mit $N = 4$ (elektronenpräzise, Tetrel-isoster)

- 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

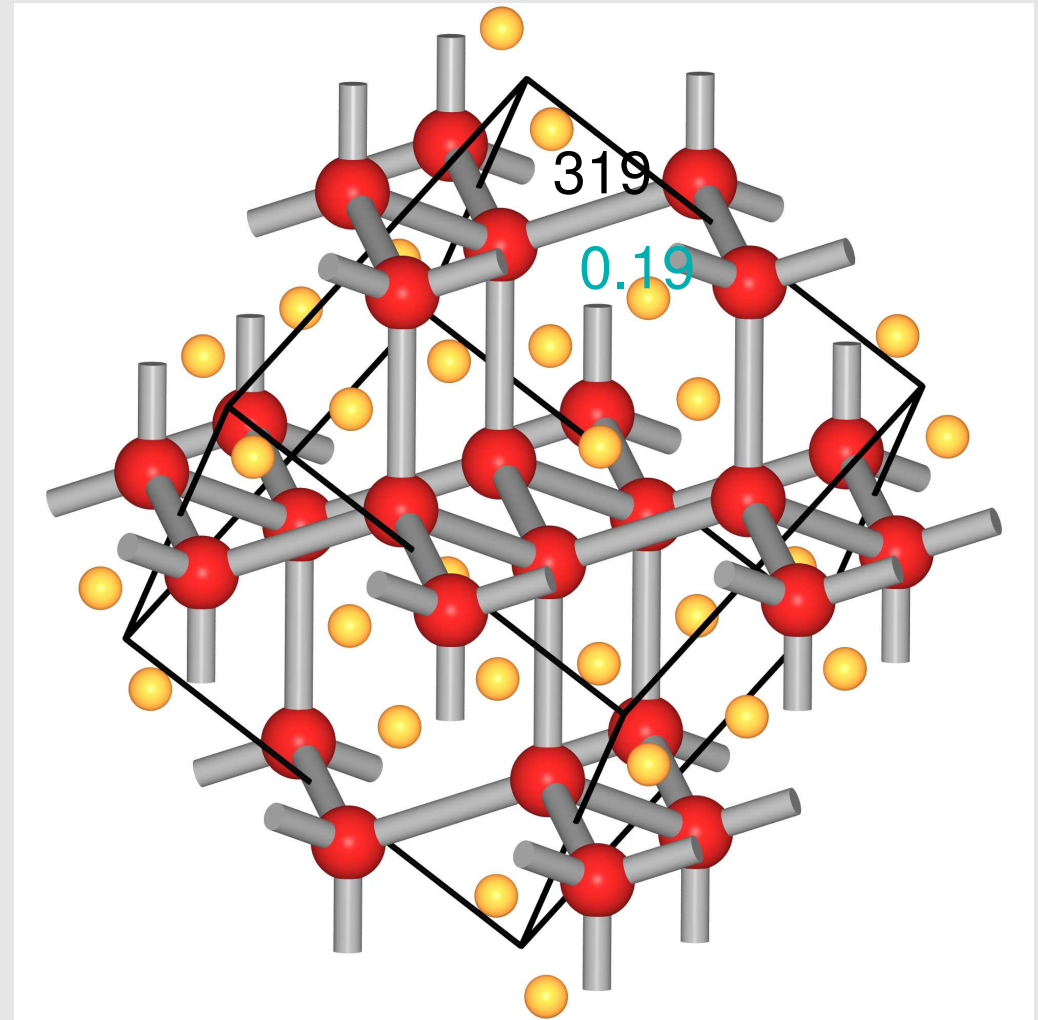


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| 3-dim. (Raumnetz) | kondensierte Cluster | |  Si gef. Käfige | SrSi ₂ -Typ ThSi ₂ -Typ | | |

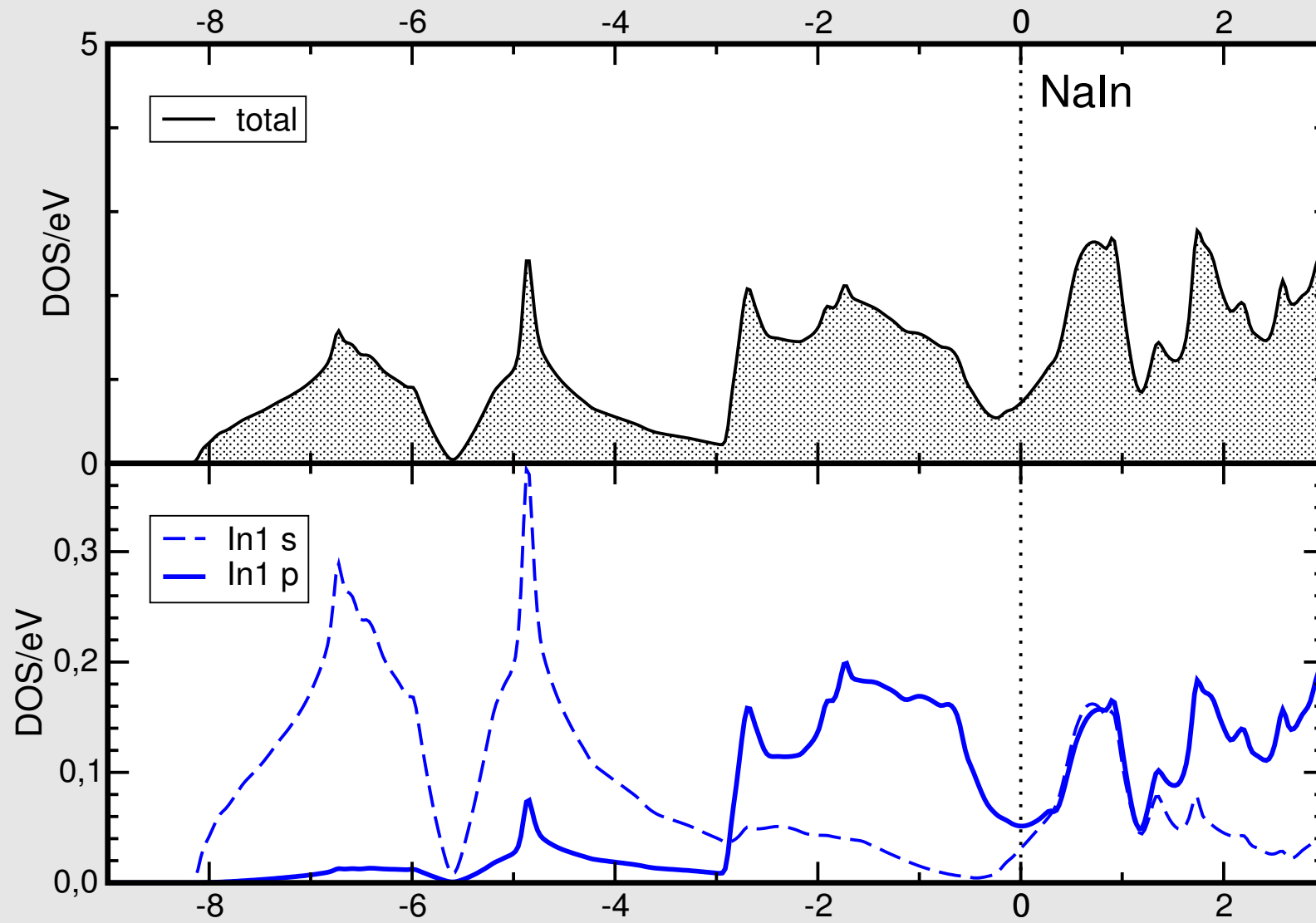
NaIn: Struktur



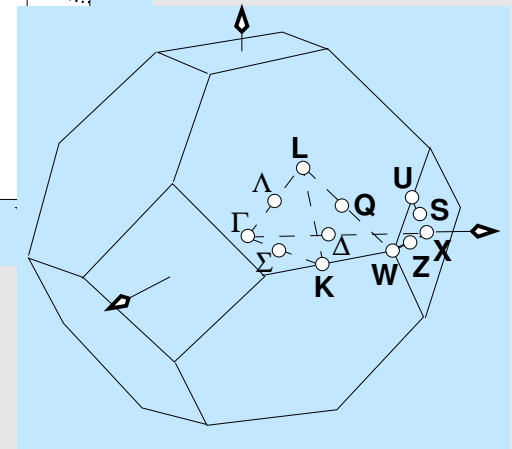
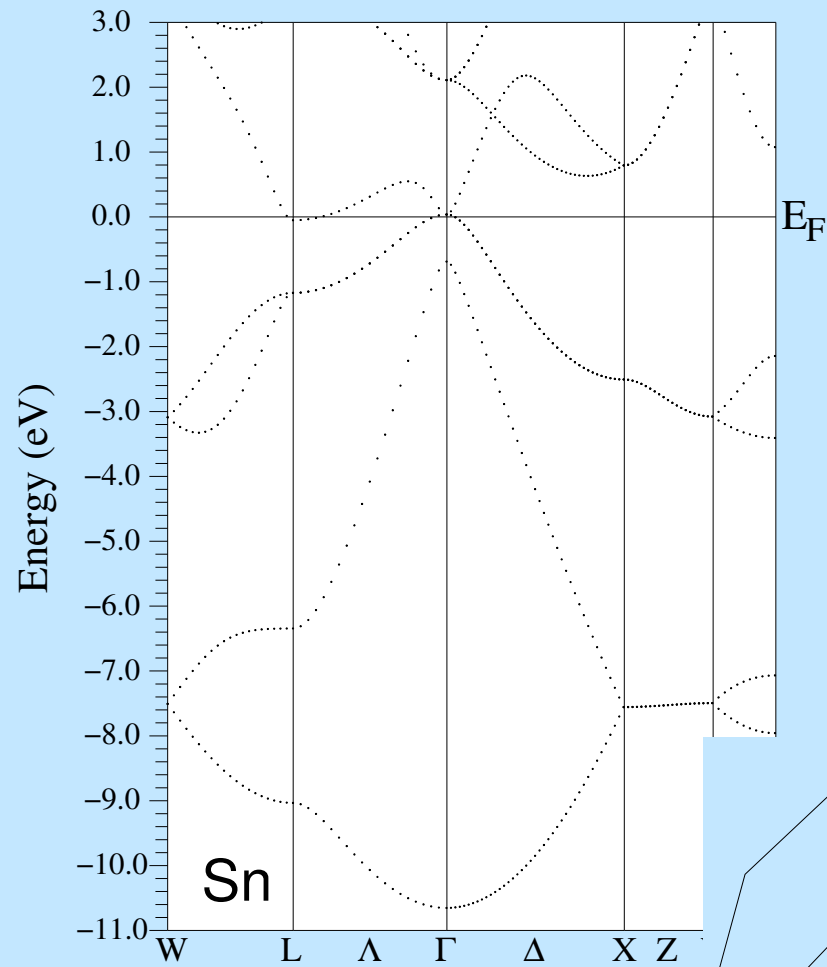
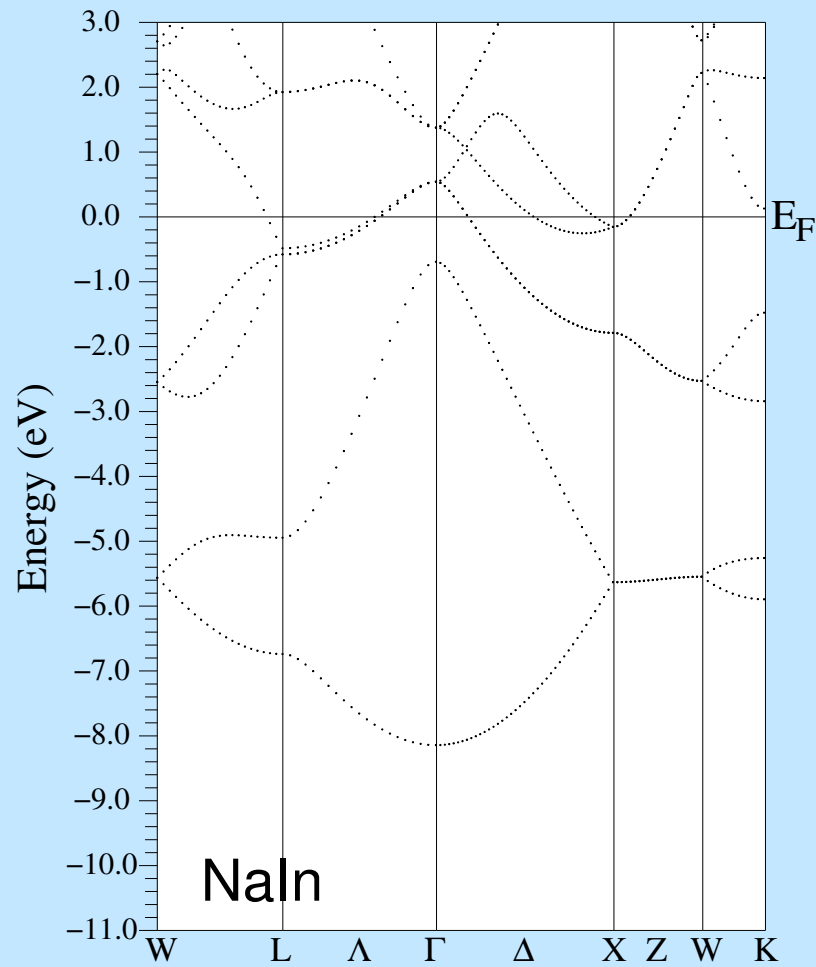
| | |
|-------------------------|-----------------|
| Strukturtyp | NaTl |
| Kristallsystem | kubisch |
| Raumgruppe | $F d \bar{3} m$ |
| $d_{\text{In-In}}$ [pm] | 319 |



NaIn: Totale und partielle In Zustandsdichte



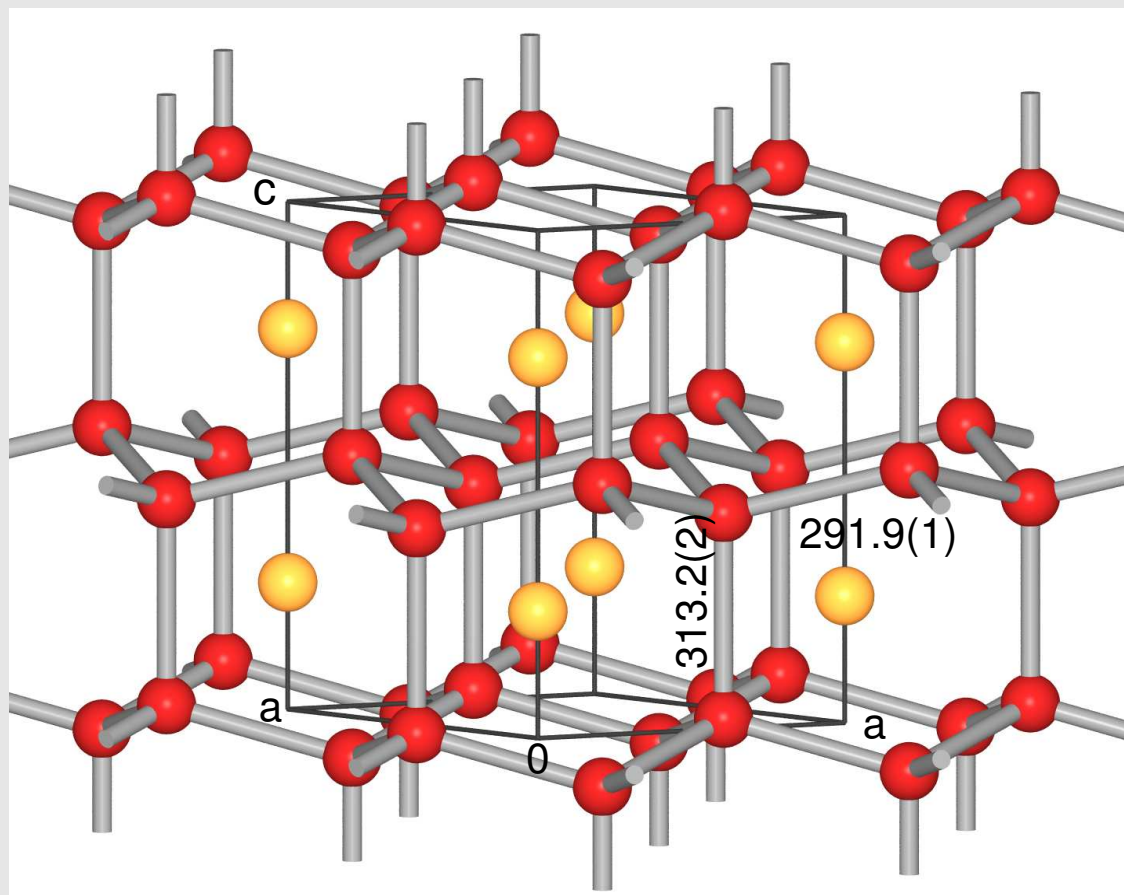
NaIn und α -Sn: Vergleich der Bandstrukturen



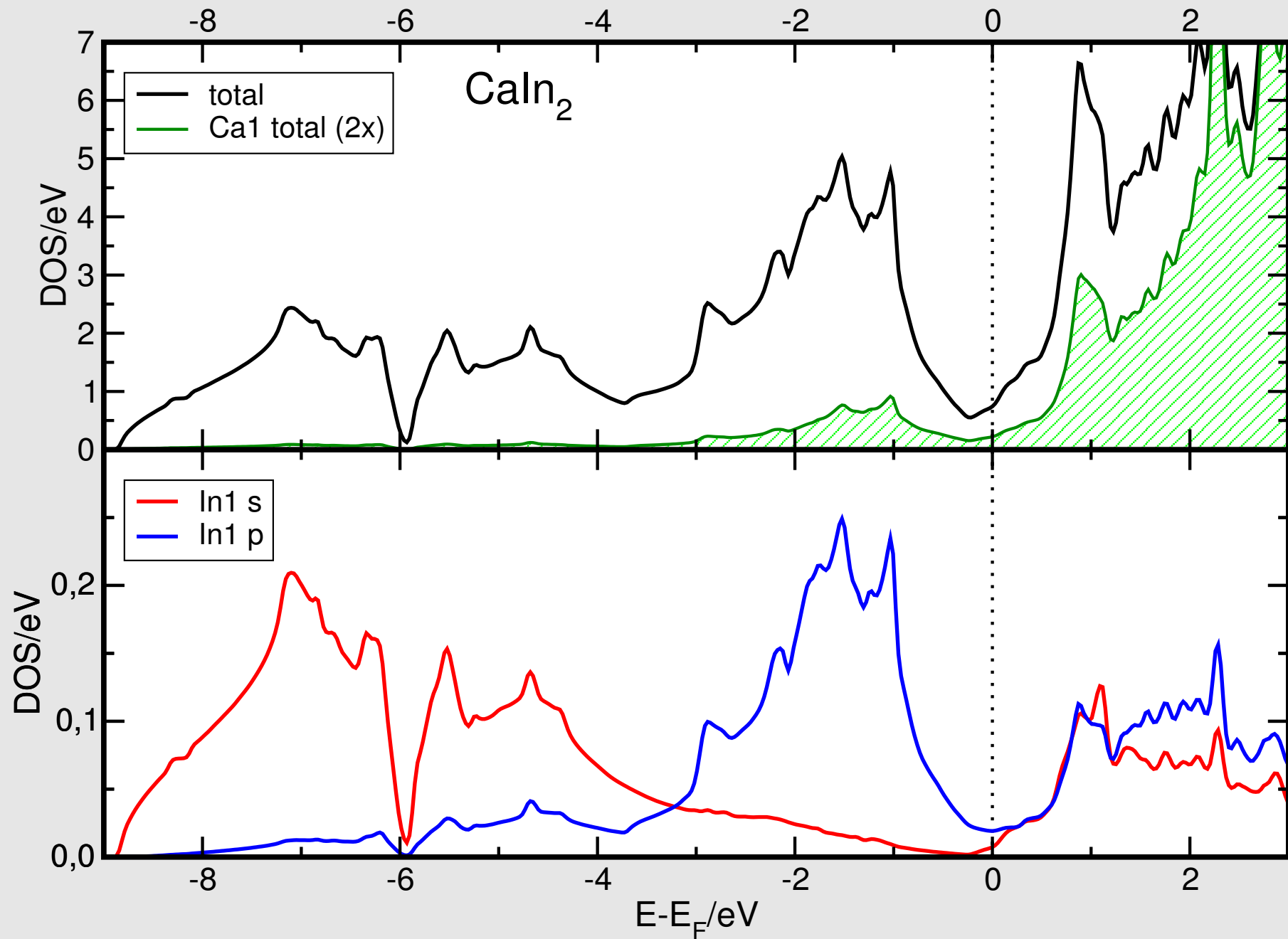
CaIn₂ : Struktur



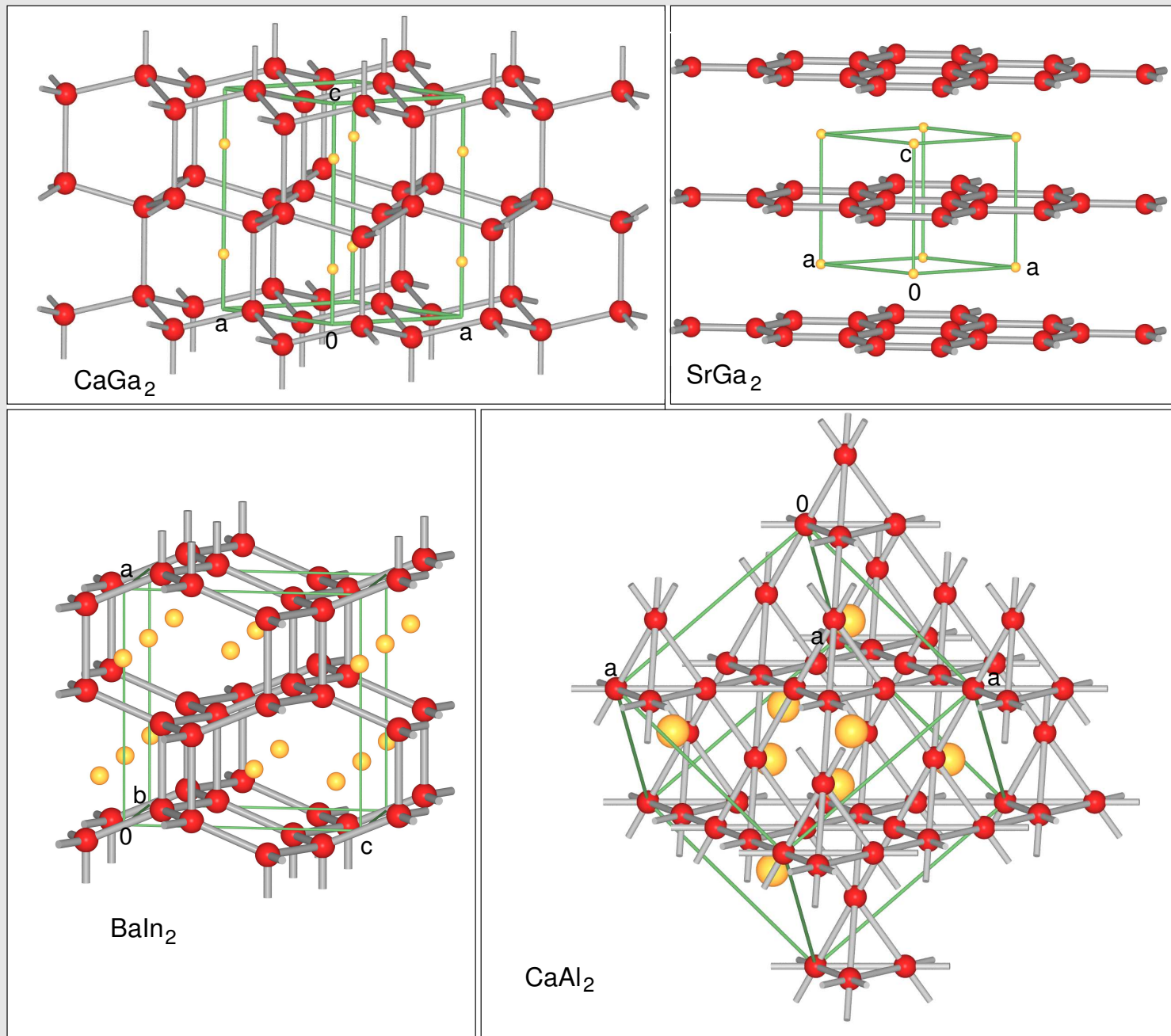
| | | CaIn ₂ | SrIn ₂ |
|----------------------------------------|----|-------------------------------|-------------------|
| Strukturtyp | | CaGa ₂ | |
| Kristallsystem | | hexagonal | |
| Raumgruppe | | P6 ₃ /mmc, Nr. 194 | |
| Gitter- | a | 489.2 | 500.9 |
| konstanten | c | 773.9 | 803.6 |
| [pm]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



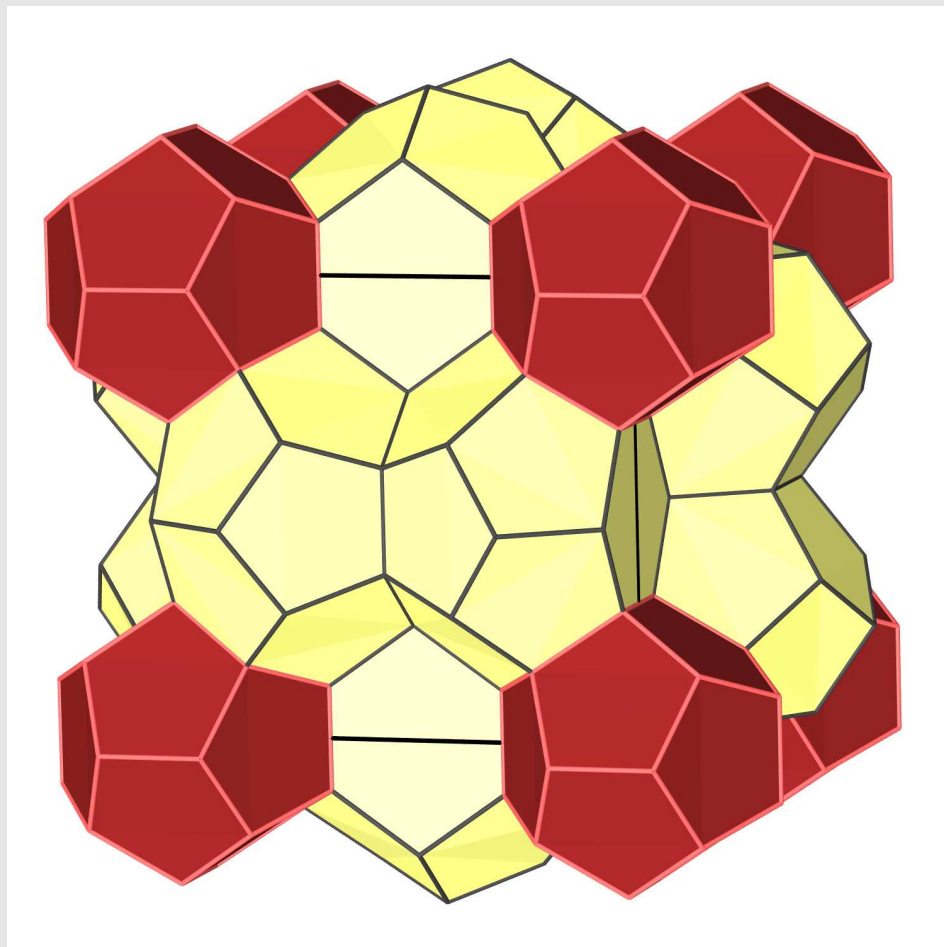
CaIn₂: Totale und partielle In Zustandsdichte



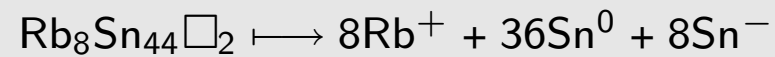
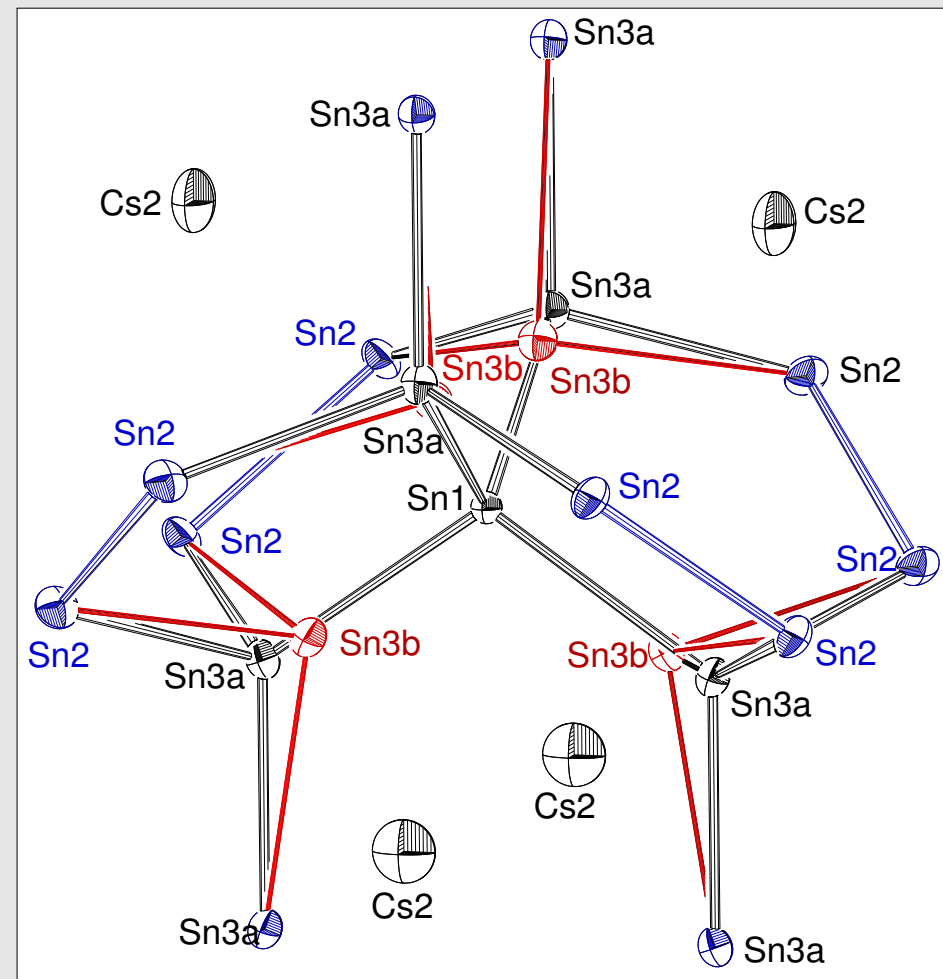
Strukturen der Erdalkalimetall-Ditriehalide $A^{II}M_2^{III}$



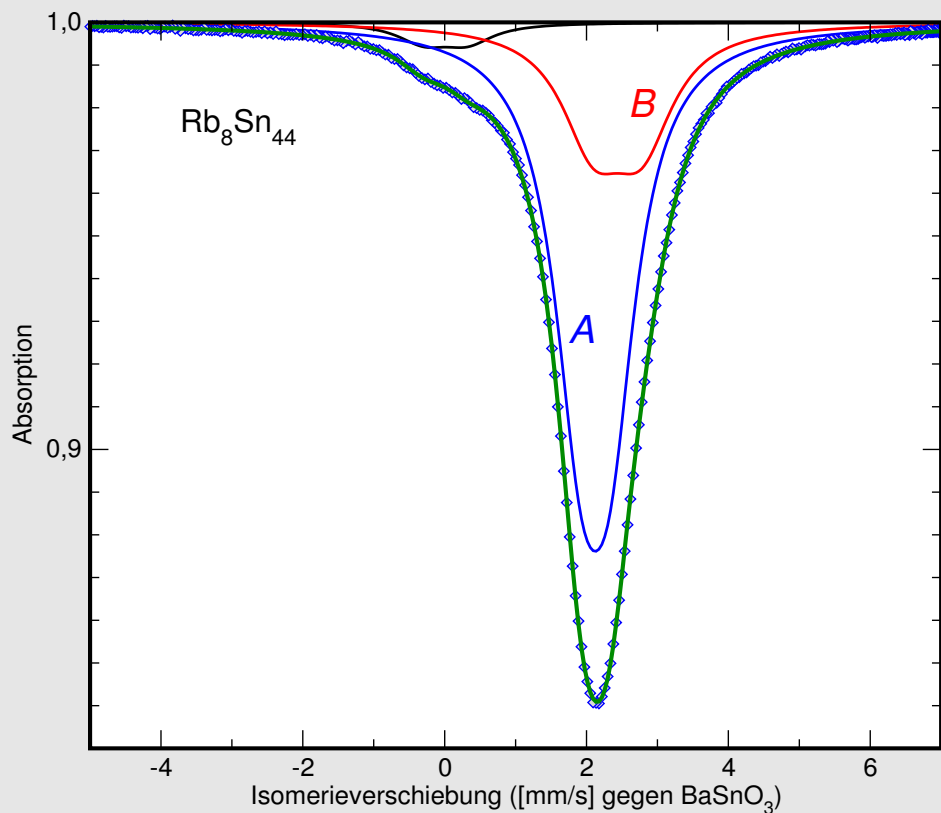
Strukturen von $A_8Sn_{44}\square_2$ (A=Rb, Cs)



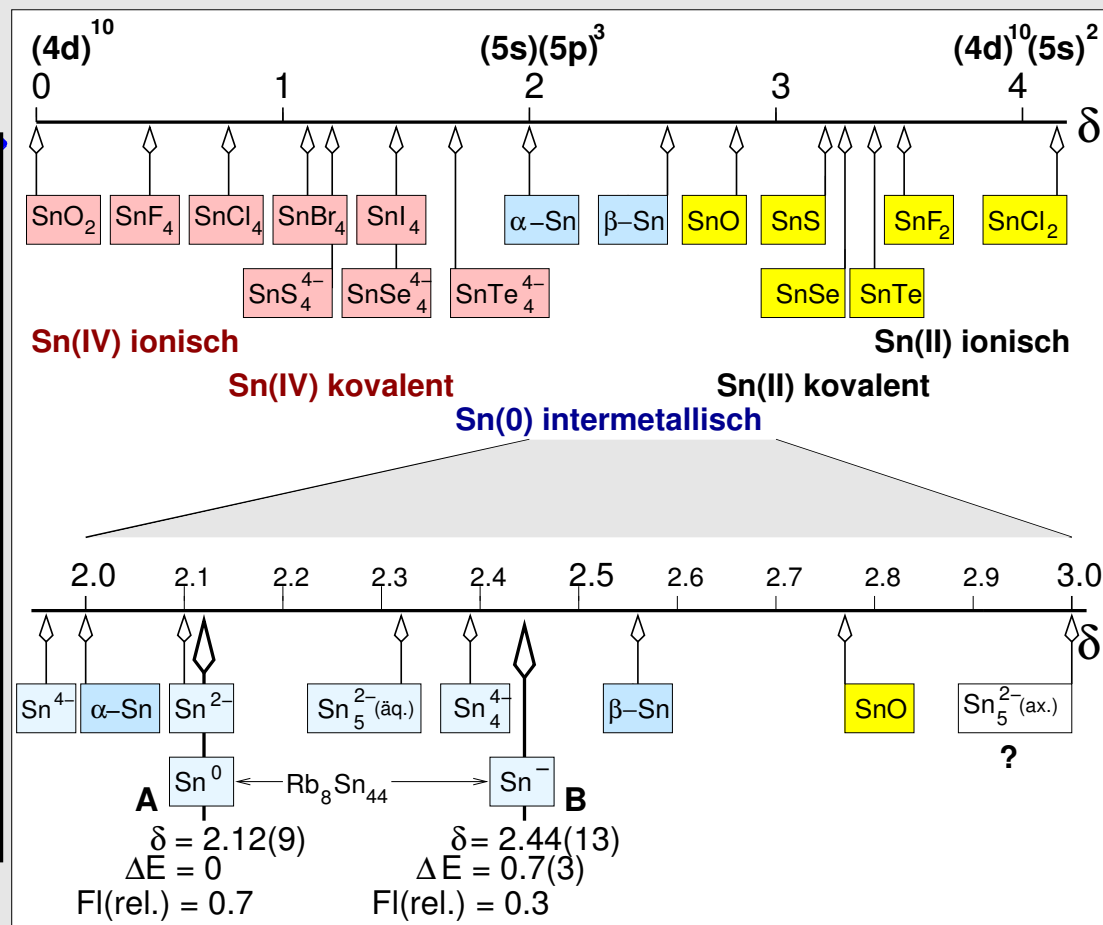
Clathrat-I-Struktur



Rb₈Sn₄₄: ¹¹⁹Sn-Mößbauer-Spektrum



Spektrum von Rb₈Sn₄₄




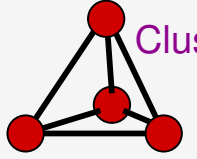
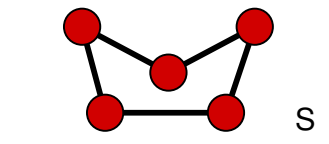
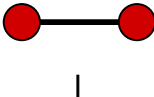

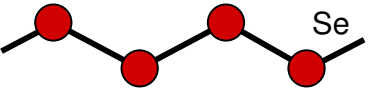
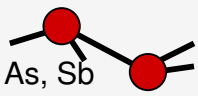
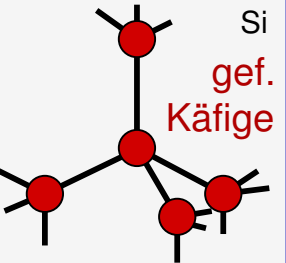
Skala der ^{119m}Sn-Isomerieverschiebungen

III. Polyanionen mit $N < 4$

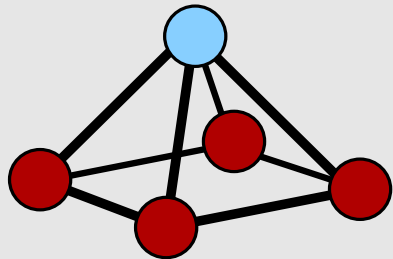
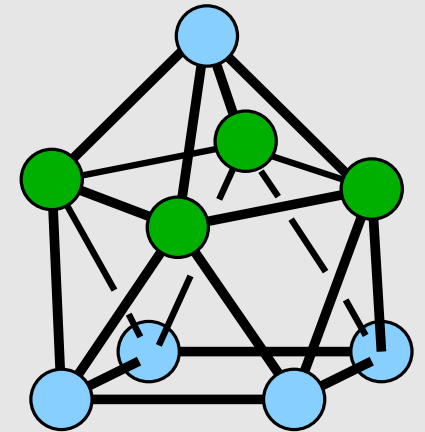
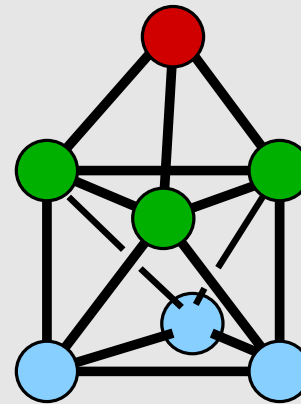
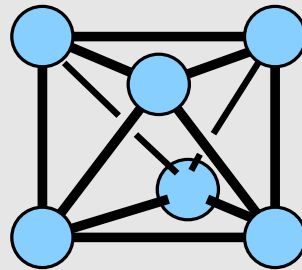
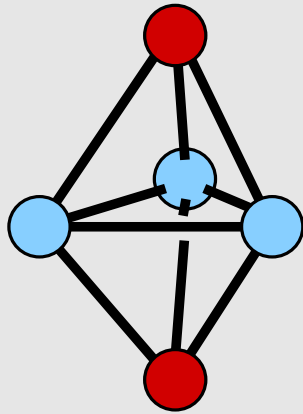
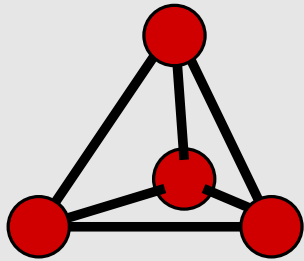
- Elektronenmangelverbindungen (vgl. Borane)
- 3-Zentren-2-Elektronen-Bindung
- Wade-Mingos-Regeln für Clusterstabilitäten
 - ◇ $N+1$ e^- -Paare: Closo-Cluster
 - ◇ $N+2$ e^- -Paare: Nido-Cluster
 - ◇ $N+3$ e^- -Paare: Arachno-Cluster

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

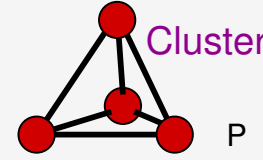
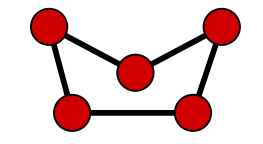
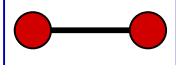

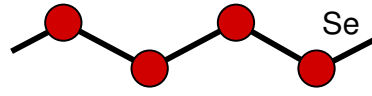
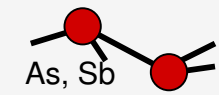
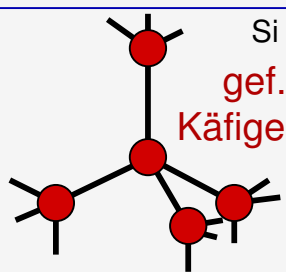


1. Isolierte Cluster

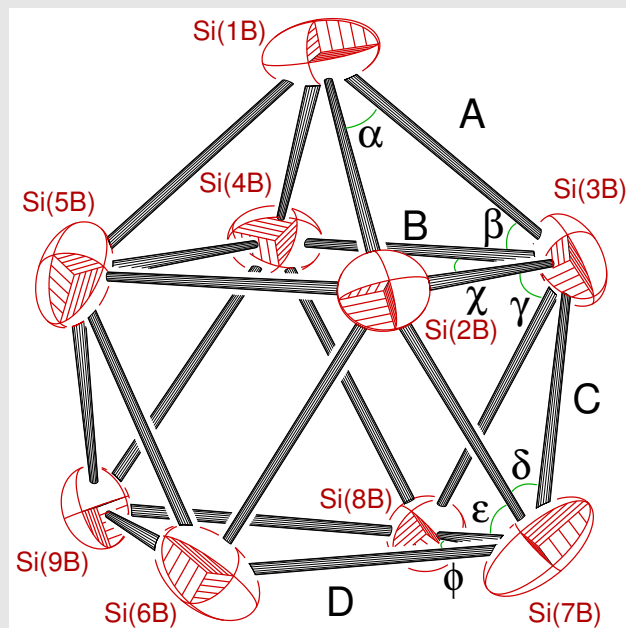
- Alkalimetall-Tetrelide $A_4^I M_9^{IV}$, $A_{12}^I M_{17}^{IV}$ und $A_{52}^I M_{82}^{IV}$ (Bsp: $M^{IV} = \text{Sn}$)

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 | |  |  |  |  |
| 1-dim. (Kette) | | | |  | | |
| 2-dim. (Schicht) | | |  | | | |
| 3-dim. (Raumnetz) | kondensierte Cluster | |  | <p>SrSi₂-Typ ThSi₂-Typ</p> | | |

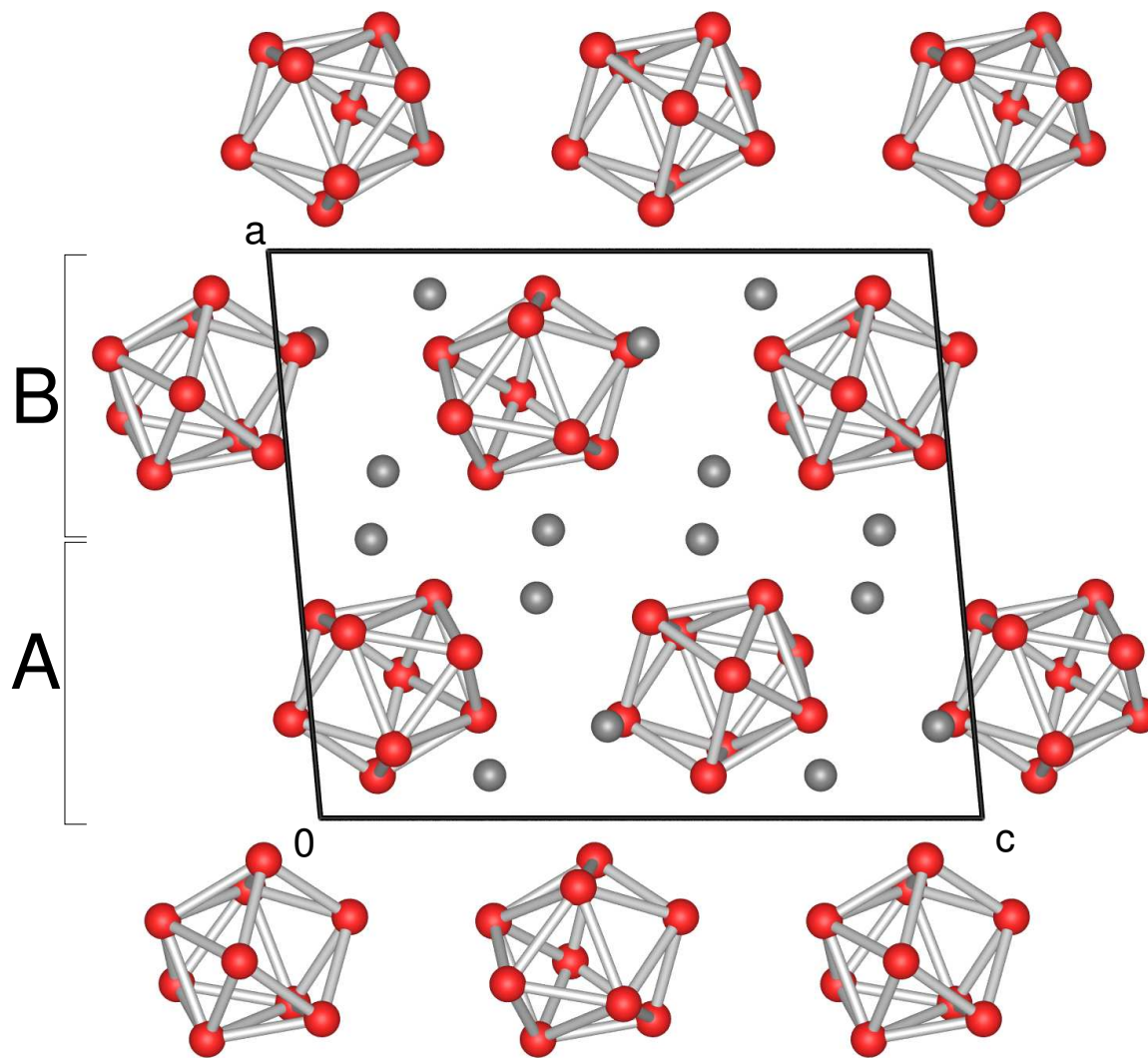
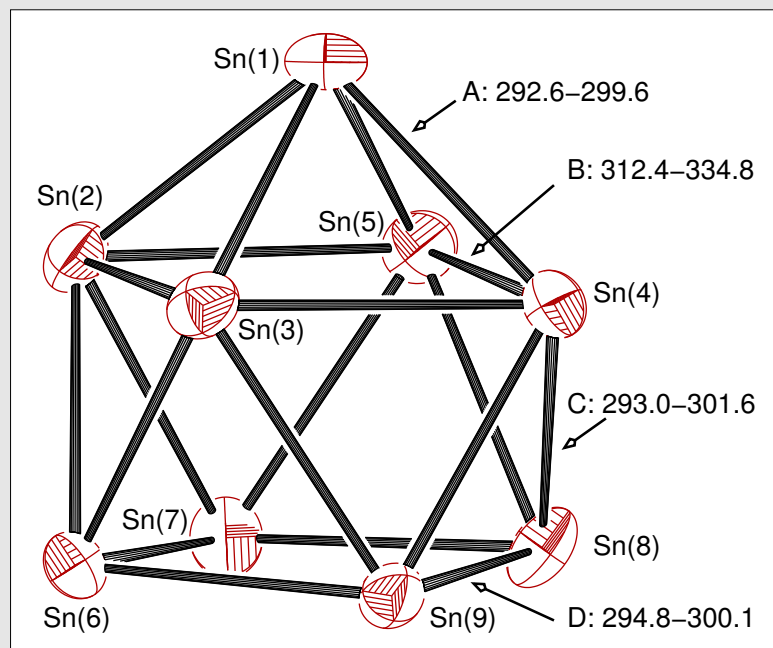
Wade-Cluster M_9



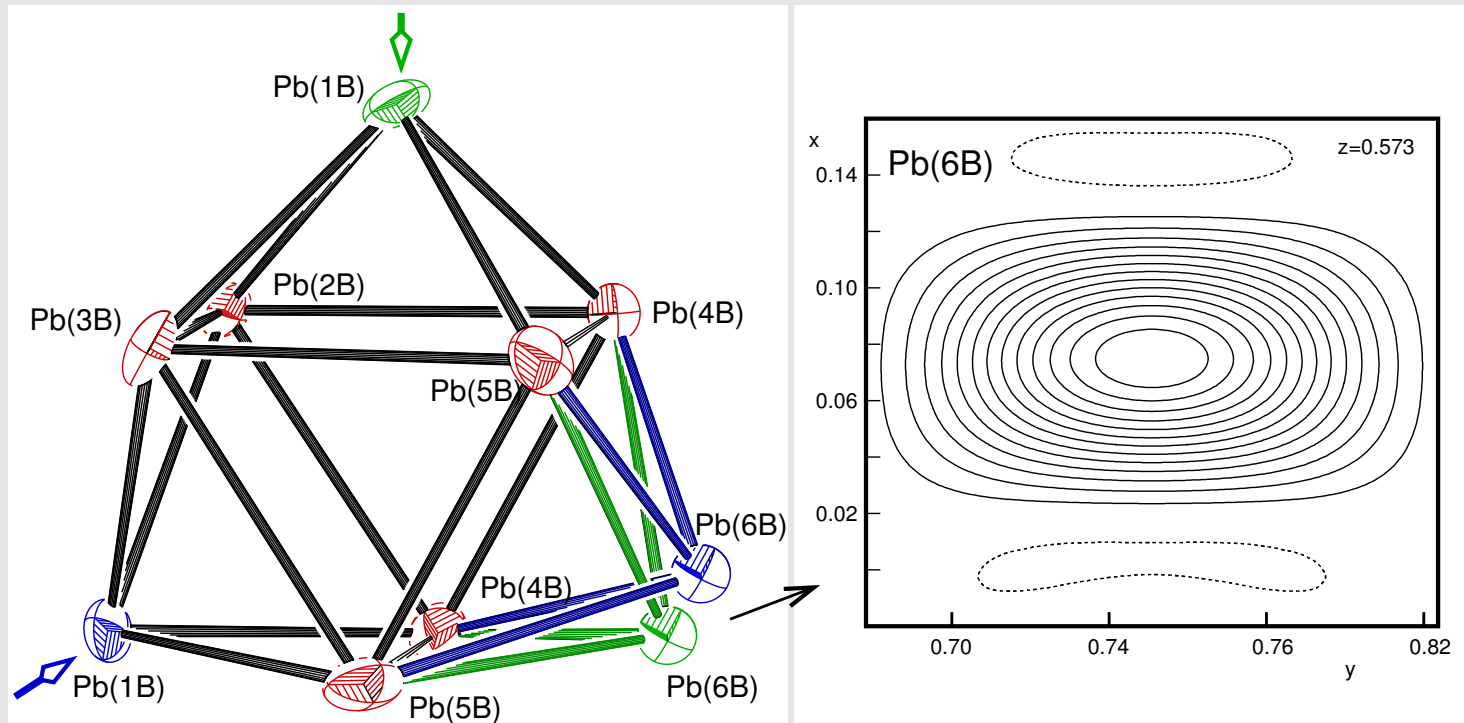
| N | Cluster | Gesamtzahl an | | Exo- e^- - Paare | Gerüst- e^- -Paare | Wade- Cluster |
|---|---------------|------------------------|---------------|-----------------------|-------------------------|------------------|
| | | Elektronen | e^- -Paaren | | | |
| 9 | $[Sn_9]^{4-}$ | $(4 \cdot 9) + 4 = 40$ | 20 | 9 | $11 = N + 2$ | nido |
| 9 | $[Bi_9]^{5+}$ | $(5 \cdot 9) - 5 = 40$ | 20 | 9 | $11 = N + 2$ | nido |
| 9 | $[Sn_9]^{2-}$ | $(4 \cdot 9) + 2 = 38$ | 19 | 9 | $10 = N + 1$ | closo |
| 8 | $[Bi_8]^{2+}$ | $(5 \cdot 8) - 2 = 38$ | 19 | 8 | $11 = N + 3$ | arachno |



| | | |
|------------------|----------------------------|-----------|
| 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 |



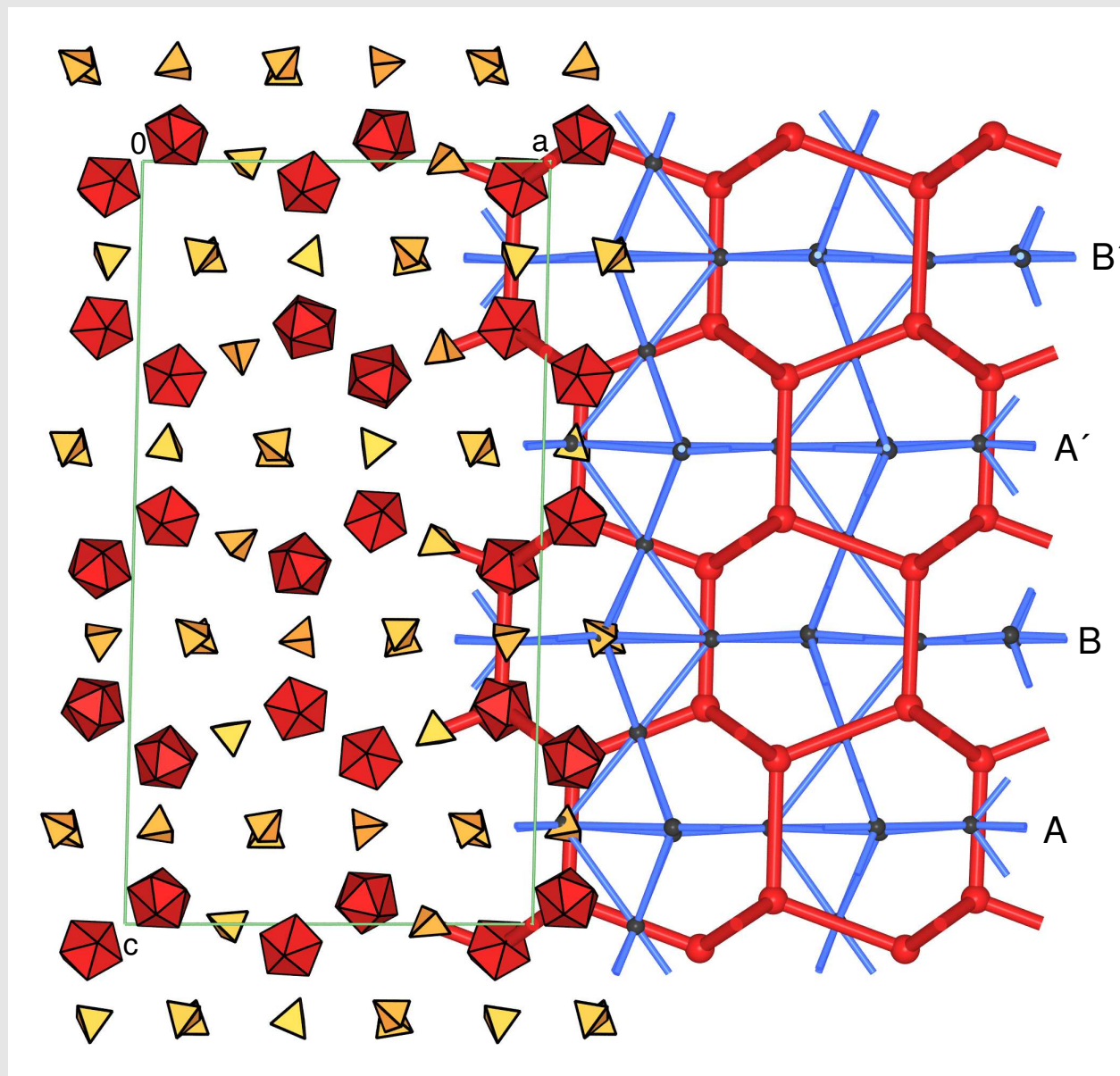
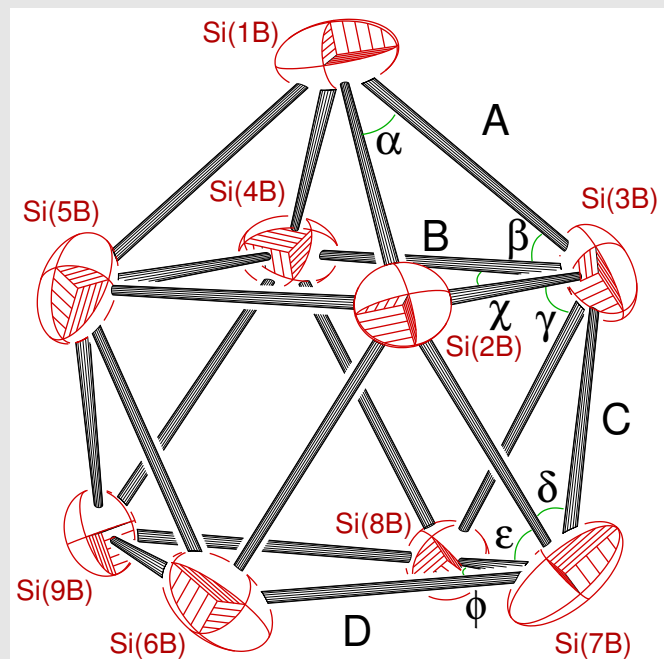
A_4Pb_9 (A=K, Rb): Fehlordnung der Cluster B

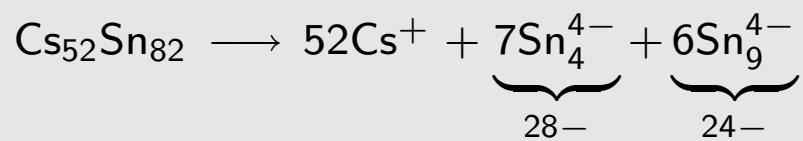


| Abstand | Cluster A | | Cluster B | |
|---------|---------------|-----------------|---------------|-----------------|
| | Bereich [pm] | Mittelwert [pm] | Bereich [pm] | Mittelwert [pm] |
| A | 307.1 - 312.5 | 310.0 | 307.6 - 318.1 | 312.9 |
| B | 335.4 - 370.3 | 346.9 | 321.8 - 390.4 | 333.0 |
| C | 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 |

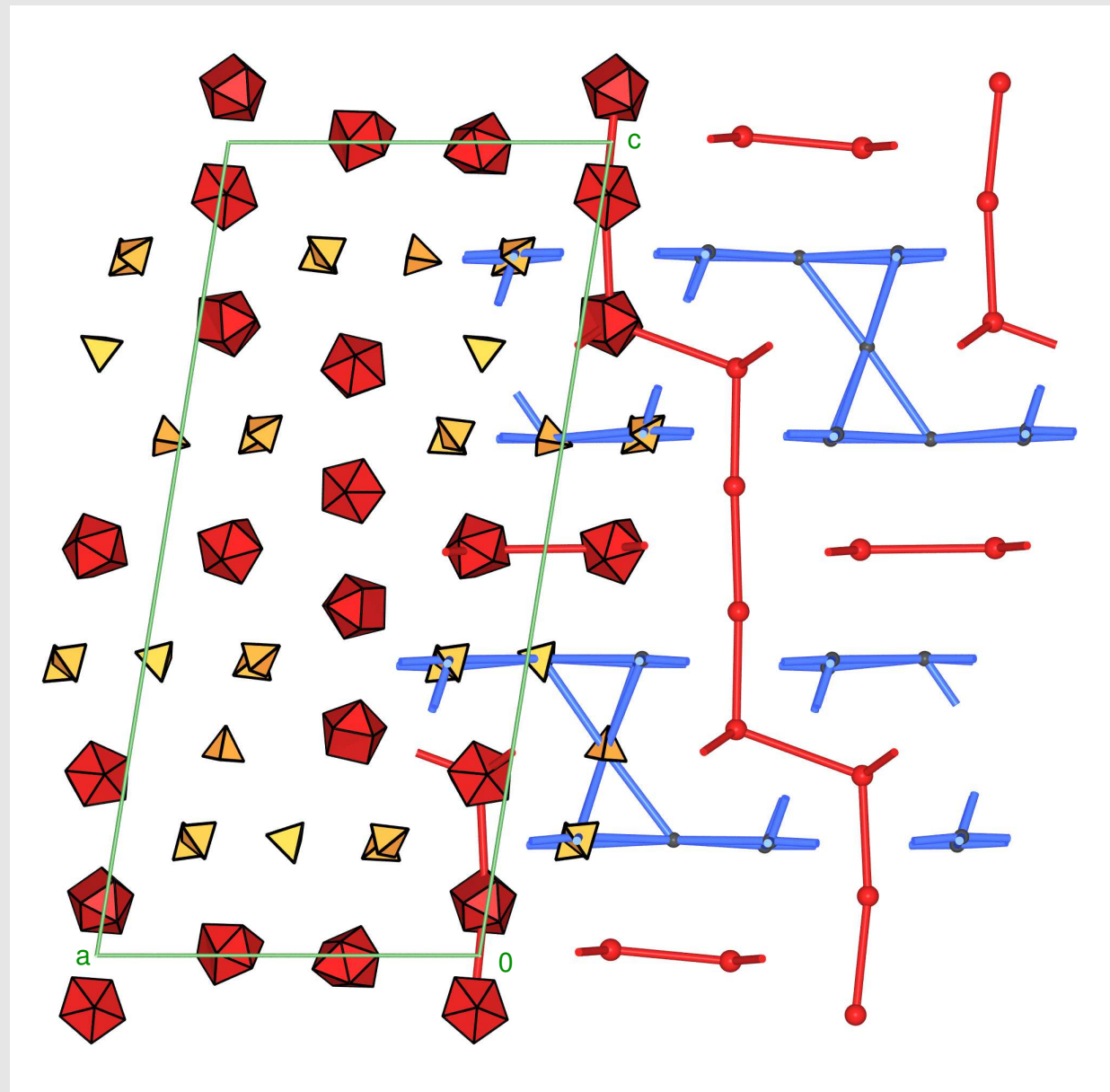


| | | |
|------------------|----|----------------------------|
| Kristallsystem | | monoklin |
| Raumgruppe | | P2 ₁ /c, Nr. 14 |
| Gitterkonstanten | a | 2413.1 |
| | b | 1371.4 |
| | c | 4500.1 |
| [pm, °] | β | 91.69 |
| Z | | 4 |
| R-Wert | R1 | 0.089 |






| | | |
|------------------|----|----------------------------------------|
| Kristallsystem | | monoklin |
| Raumgruppe | | P ₂ ₁ /c, Nr. 14 |
| Gitterkonstanten | a | 2730.4 |
| | b | 1556.5 |
| | c | 5905.0 |
| [pm, °] | β | 99.193 |
| Z | | 4 |
| R-Wert | R1 | 0.138 |

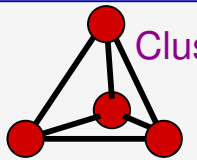
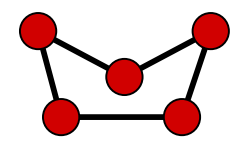


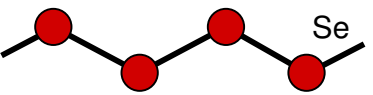
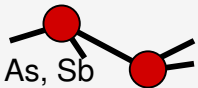
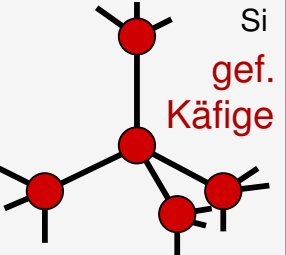


2. Kondensierte Cluster

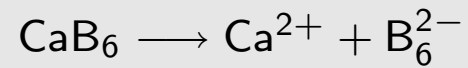
- Boride (Bsp.: CaB_6)
- Indide (Bsp.: $\text{A}^{\text{I}}\text{In}_3$, $\text{A}_2^{\text{I}}\text{In}_3$)
- Übergang zu echten Metallen (Bsp.: BaIn_4)

Zintl-Grenze



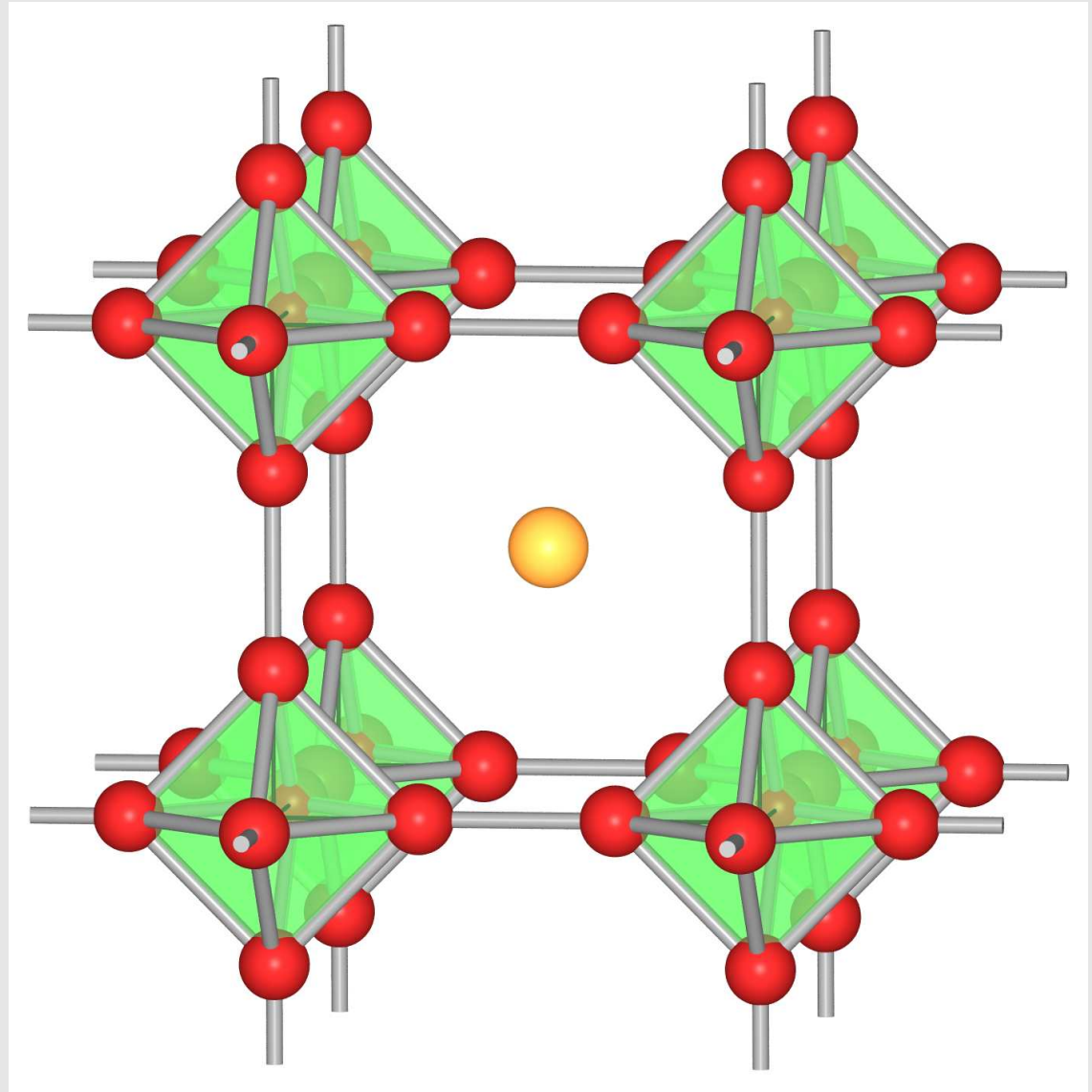
| | N=3 | N=4 | N=5 | N=6 | N=7 | N=8 |
|----------------------|----------------------|------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| | ? | (4-bindig) | (3-bindig) | (2-bindig) | (1-bindig) | (0-bindig) |
| 0-dim. (Molekül) | isolierte Cluster | |  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

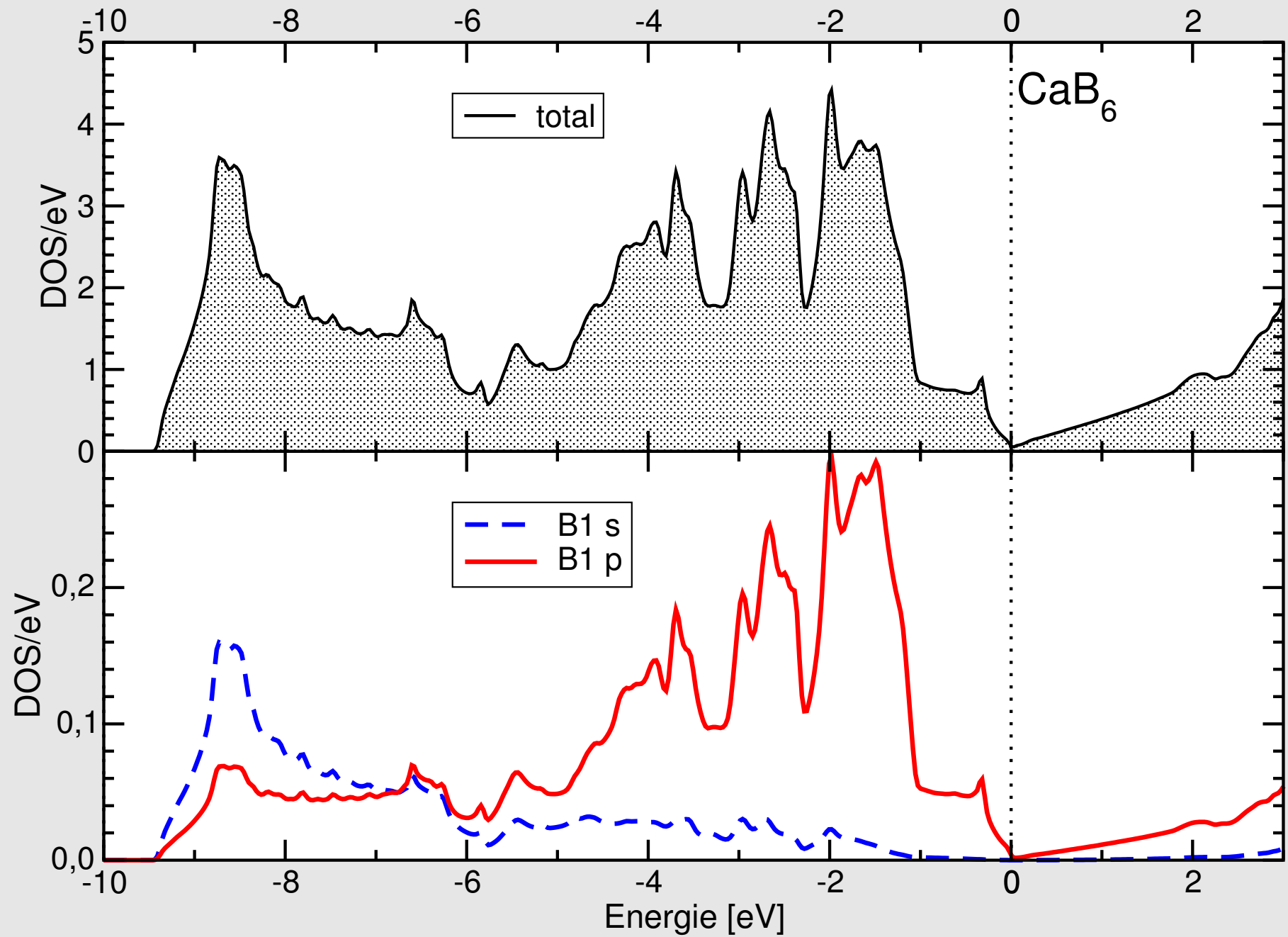


Cluster-Elektronen:

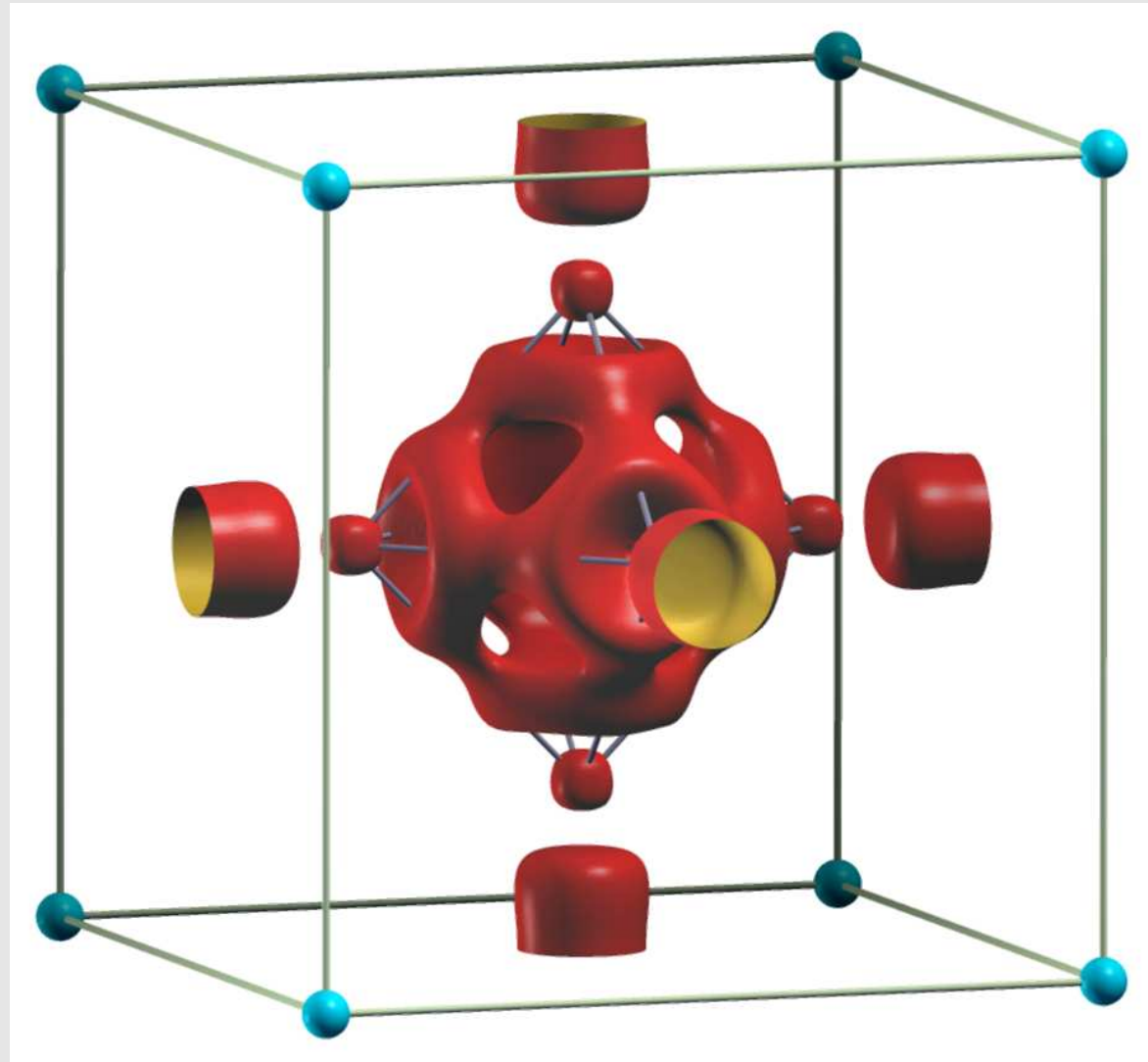
$$\underbrace{6 \cdot 3}_{\text{von B}} + \underbrace{2}_{\text{Ladung}} - \underbrace{6}_{\text{exo-b}} = 14 = 2N+2$$



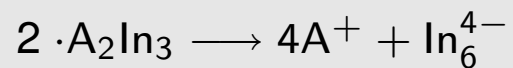
CaB₆ : Totale und partielle B-Zustandsdichte



CaB₆ : berechnete Elektronendichte



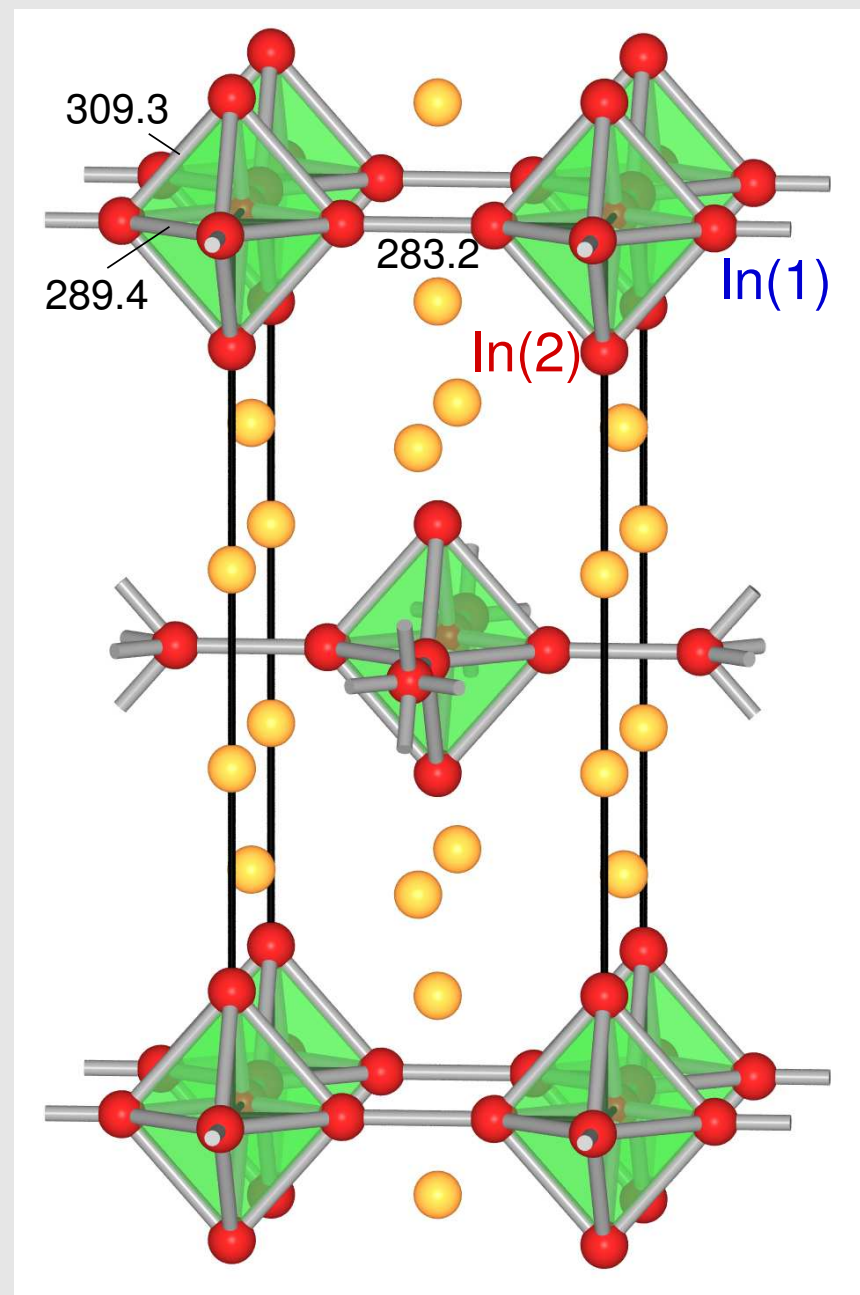
Cs₂In₃



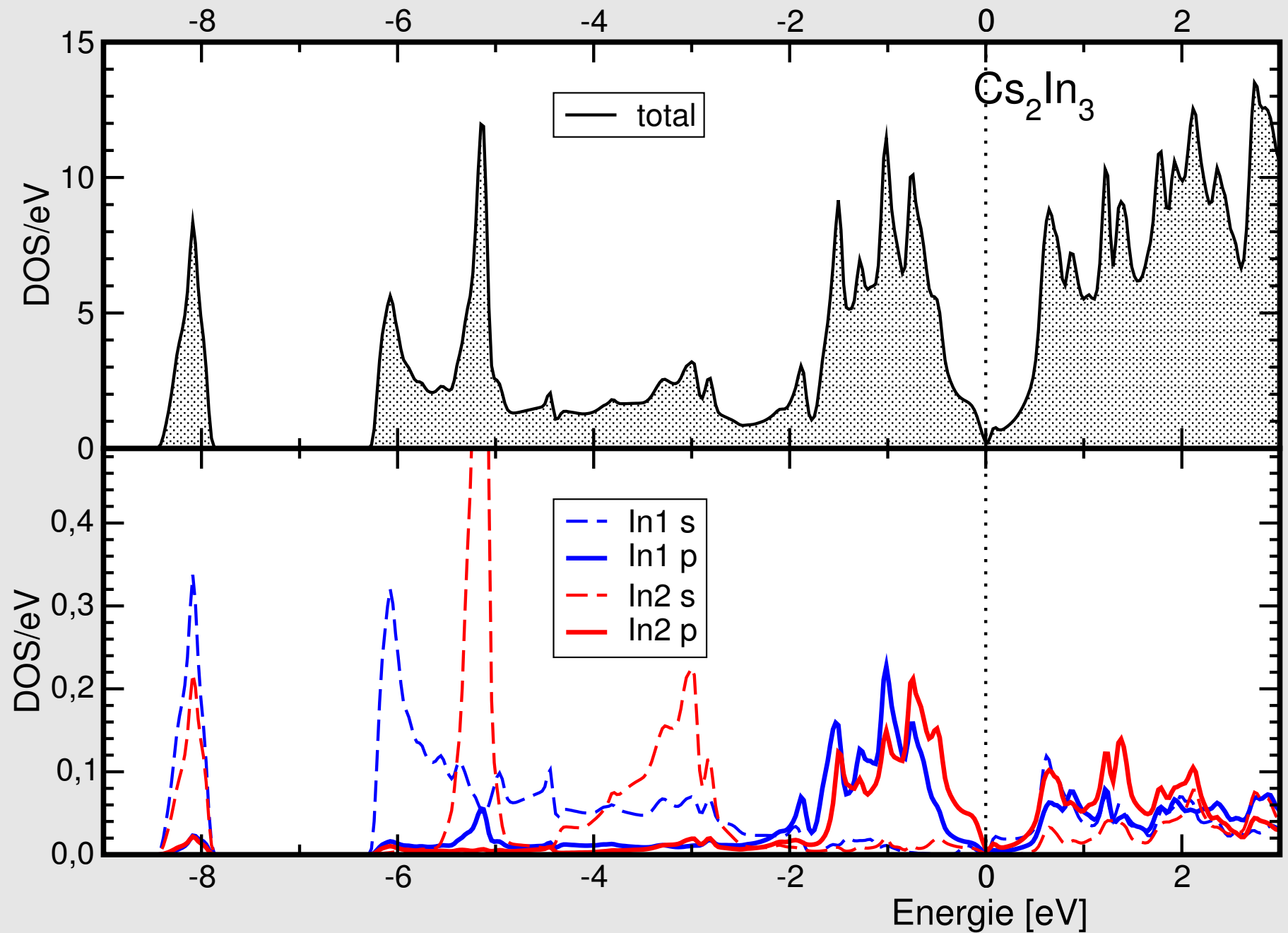
Cluster-Elektronen:

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

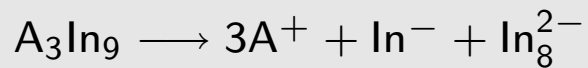
| | | |
|----------------------------------------|------|-----------------|
| Kristallsystem | | tetragonal |
| Raumgruppe | | I4/mmm, Nr. 139 |
| Gitterkonstanten | a | 692.5(1) |
| | c | 1663.2(5) |
| | [pm] | |
| VEZ [10 ⁶ pm ³] | | 932.3 |
| Z | | 4 |
| R-Wert | R1 | 0.142 |



Cs_2In_3 : Totale und partielle In Zustandsdichte



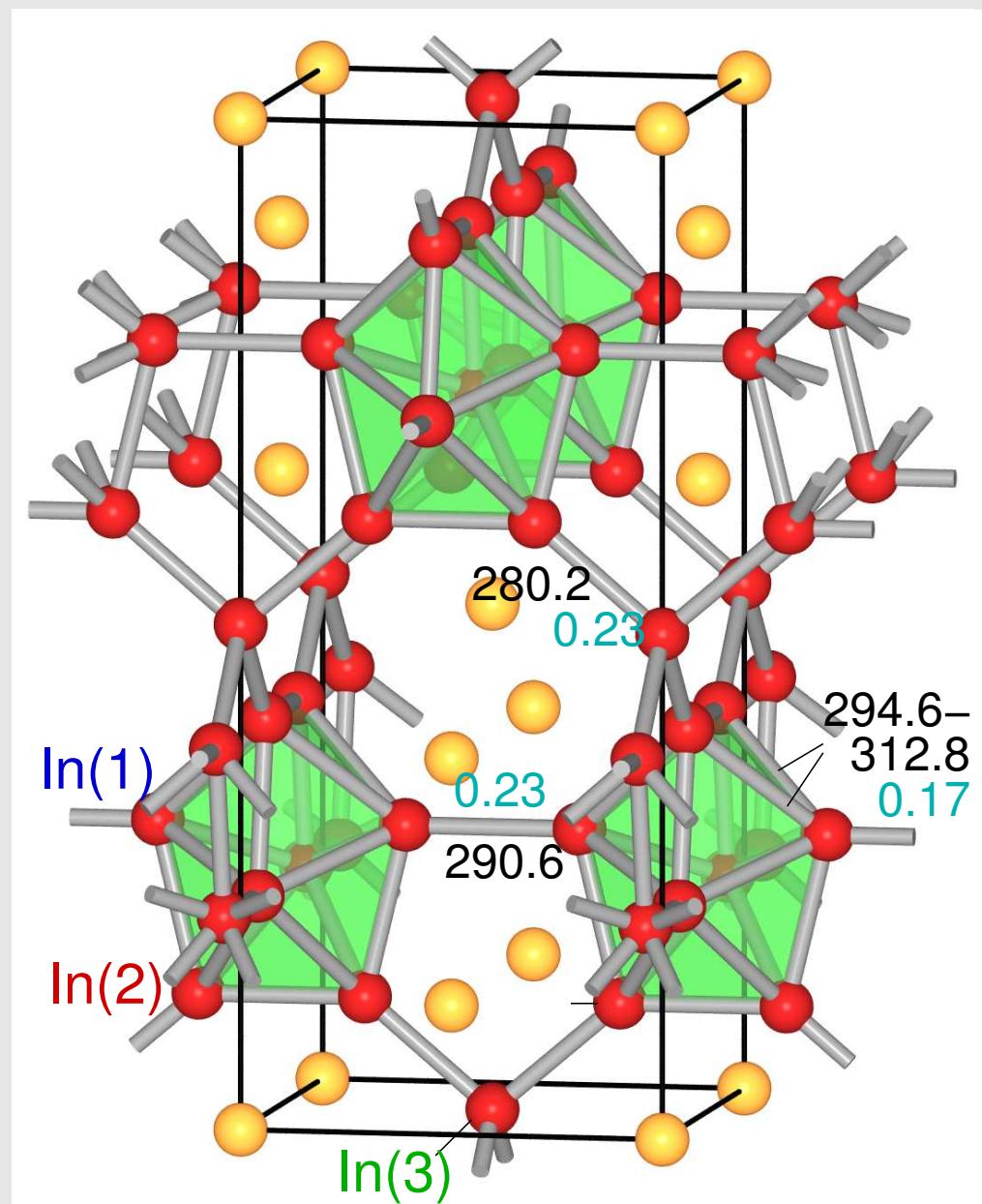
CsIn₃: Struktur



Cluster-Elektronen:

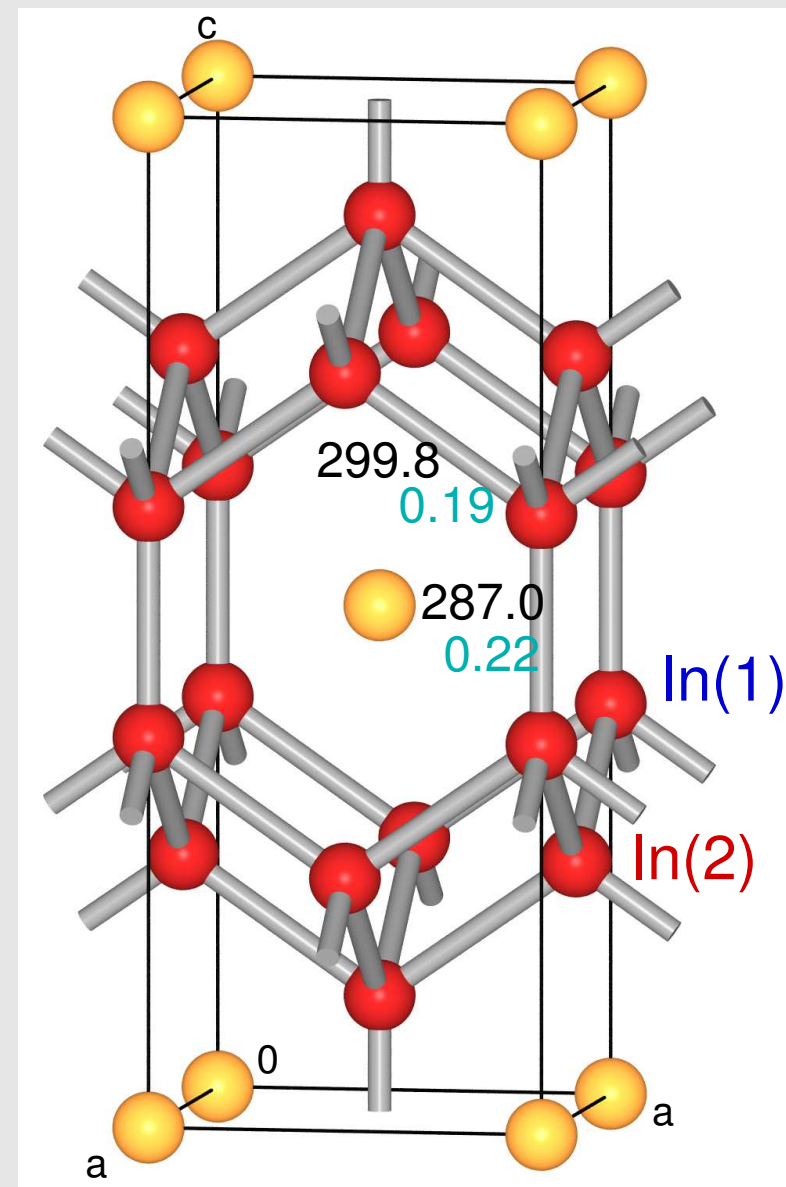
$$8 \cdot 3 + 2_{\text{Ladung}} - 8_{\text{exo-b}} = 18 = 2N + 2$$

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

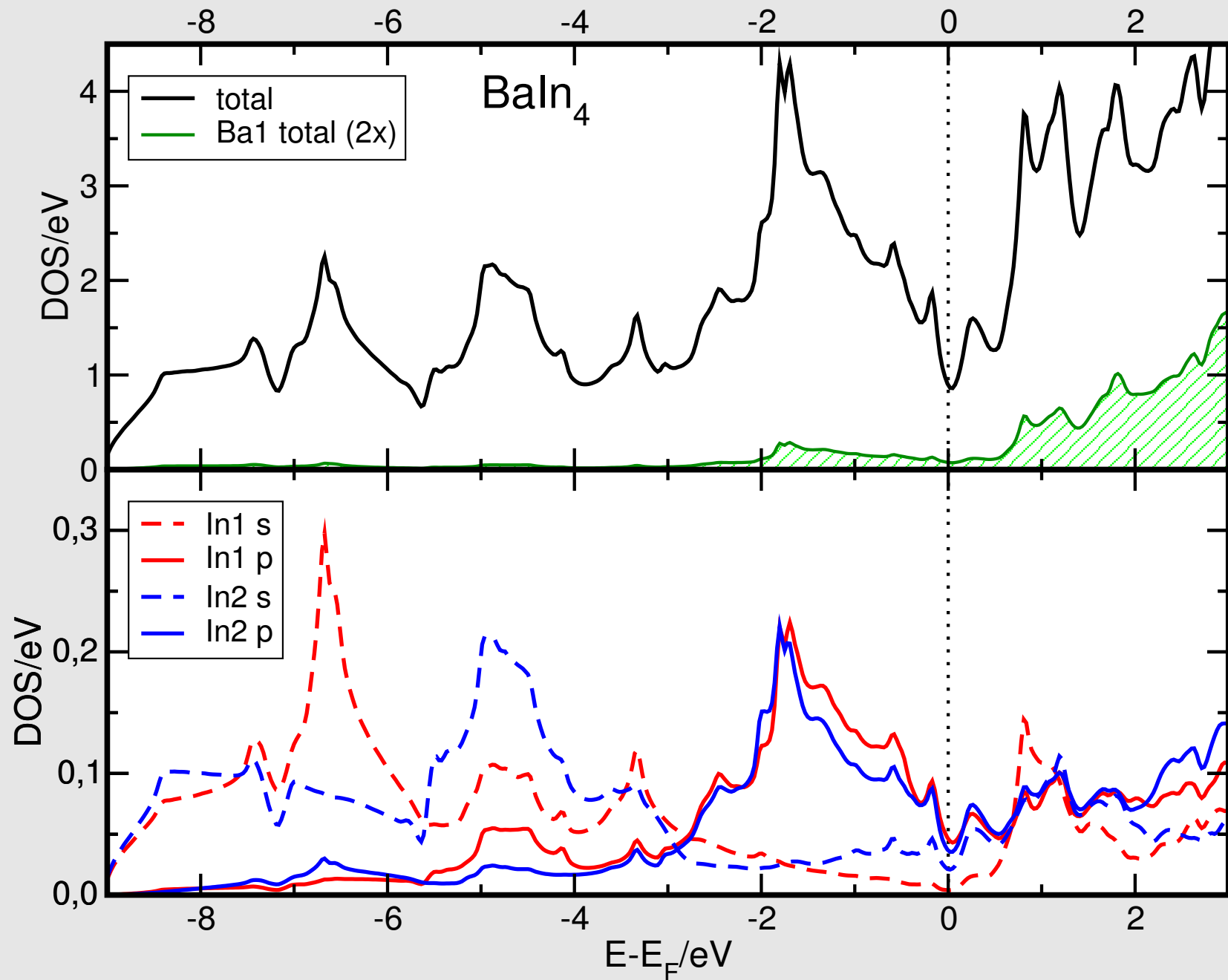


Aln₄

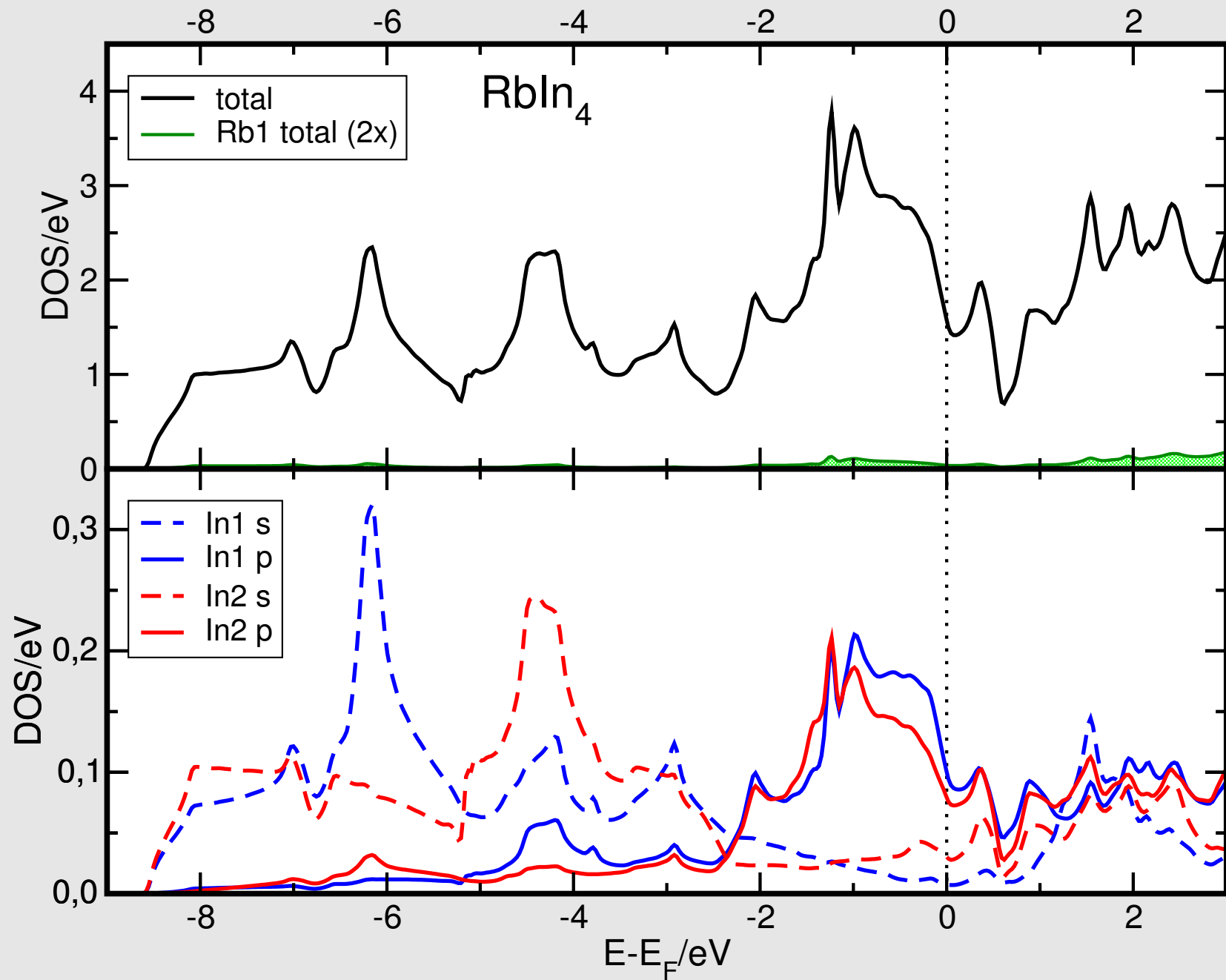
| | A | K | Rb | Ba |
|----------------------------------------|---|-----------------------|-------------------|-----------|
| Strukturtyp | | | BaAl ₄ | |
| Kristallsystem | | | tetragonal | |
| Raumgruppe | | | I4/mmm, Nr. 139 | |
| Gitterkonstanten | a | 483.97(4) | 492.8(3) | 497.0(2) |
| [pm] | 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 |



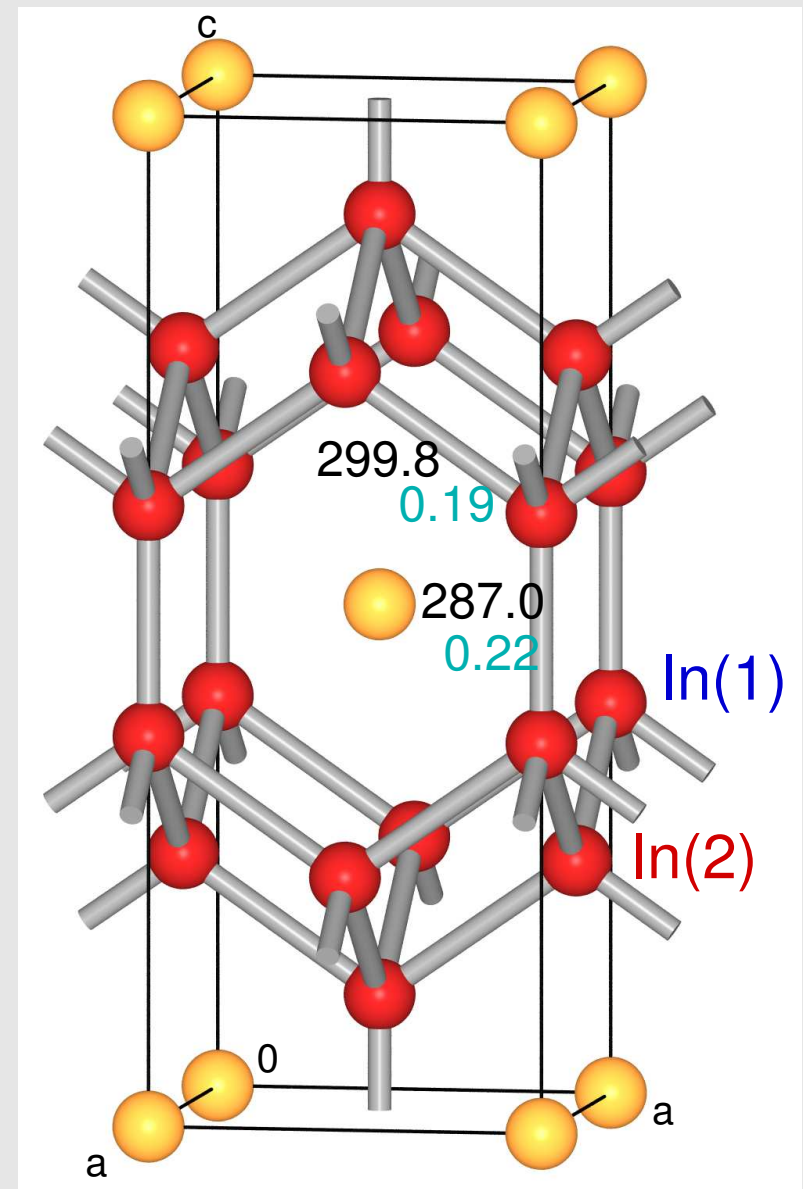
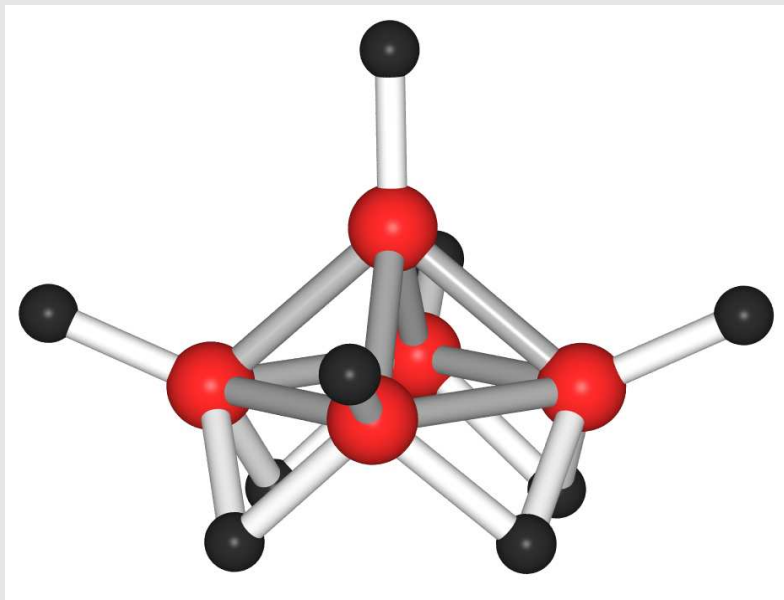
BaIn₄ : Totale und partielle In Zustandsdichte



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) !!