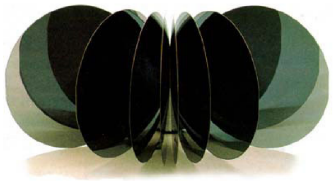
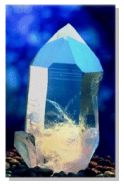
# Kristallstruktuur



## Pooljuhtmaterjalid

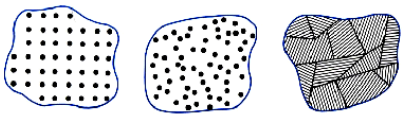
*Pooljuhid kui kristallid*



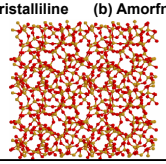


## Pooljuhid kui kristallid

- **Kristallid:** aatomid on korrastatud ning kordavad oma korrastatust perioodiliselt 3 dimensioonis.
- **3 tüüpi tahkeid aineid:**



(a) Kristalliline (b) Amorfne (c) Polükristalliline



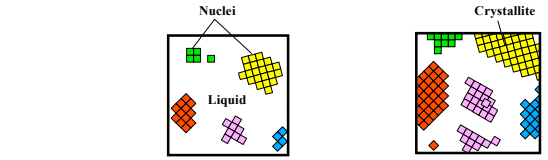
Amorfne $SiO_2$

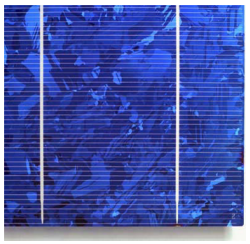
Keraamilise materjali blokid

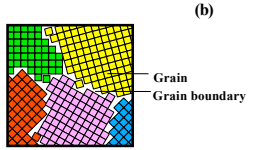


## Pooljuhid kui kristallid

- **Polükristallide moodustumine**



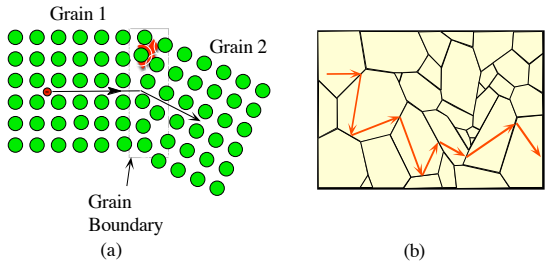






Polükristalne Si päikesepatarei

## Pooljuhid kui kristallid

- Polükristallid

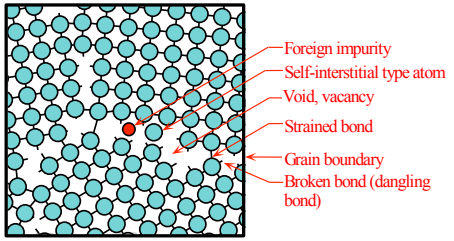



Polükristallides mängivad blokkide piirid ülitähtsat osa
ja mõjutavad otseselt elektronide liikumist



## Pooljuhid kui kristallid

- Defektid polükristallides - piirpinnad kui olulised defektide esinemiskohad

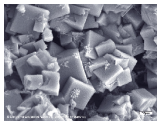


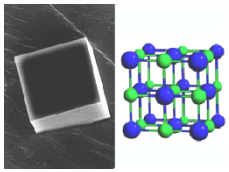


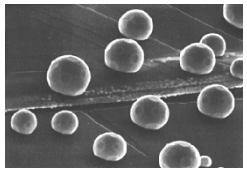

## Kristallide näited


Lumi


Kvarts


CuO

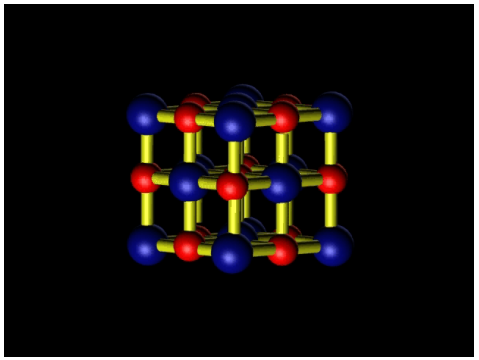

Soola (NaCl) kristall


Kulla (Au) kristallid 1000 C

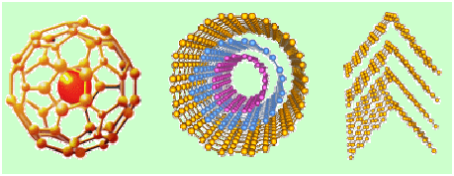


## Kristallide näited

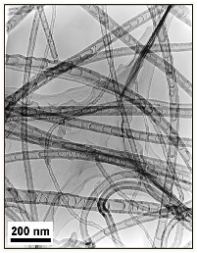
Keedusoola (NaCl) kristall



## Kristallide näited



Fullerene | Süsiniku nanotoru | Süsiniku nanofiiber




TEM foto
süsiniku nanotorudest

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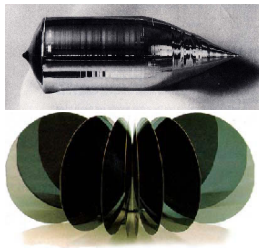
## Kristallide näited

Teemandi monokristallid.



Räni monokristallid.

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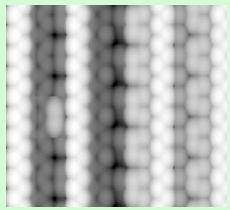
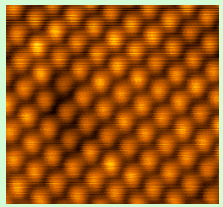
## Aatomlahutusega mikroskoobi pildid kristallide pinnast

- STM (Scanning Tunneling Microscope) pildid



Räni (Si) pind



FeSi pind

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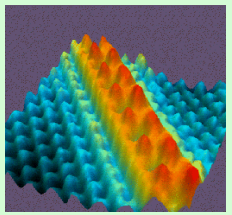
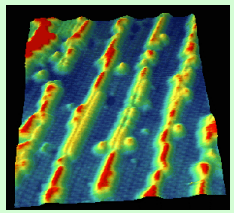
## Aatomlahutusega mikroskoobi pildid kristallide pinnast

- 3D-STM (Scanning Tunneling Microscope) pildid



Räni (Si) pind



Vesiniku ioonid
räni pinnal.

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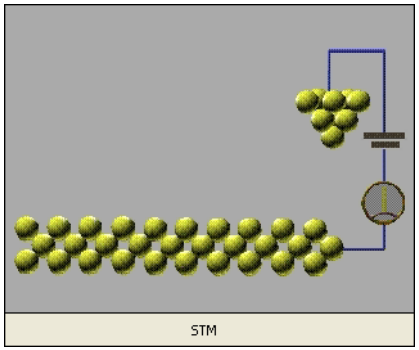
## Aatomlahutusega mikroskoobi pildid kristallide pinnast

- Scanning Tunneling Microscope

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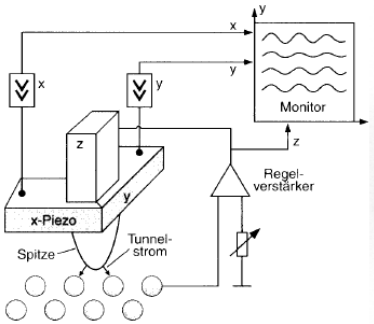
## STM tööpõhimõte

- Scanning Tunneling Microscope

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## Aatomlahutusega mikroskoobi pildid kristallide pinnast

- Scanning Tunneling Microscope

**Digital Instrument (Nano Scope Multimode)**
- Contact mode Atomic Force Microscopy (AFM)
- Non Contact AFM
- Tapping mode AFM
- Magnetic Force Microscopy (MFM)
- Electric Force Microscopy (EFM)
- Surface Potential Microscopy (SPM)
- Lateral Force Microscopy (LFM)
- Scanning Tunneling Microscopy (STM)
- Chemical Force Microscopy (CFM)

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## Aatomlahutusega mikroskoobi pildid kristallide pinnast

- TEM (Tunneling Electron Microscope) pildid

TEM pilt blokkide piirist kulla pinnal.

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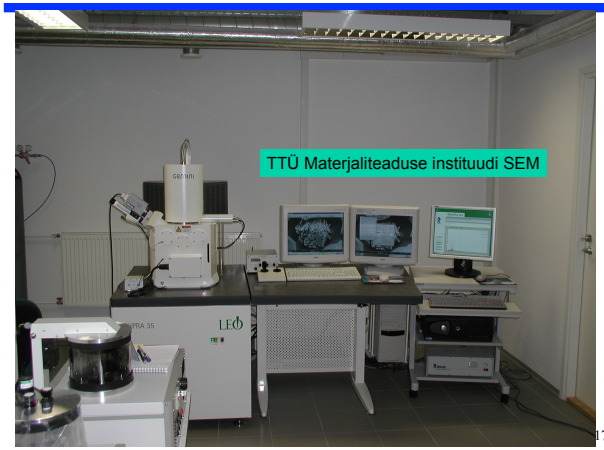
## SEM (Scanning Electron Microscope)

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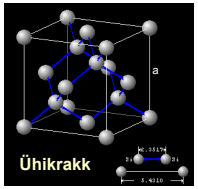
## Kristallstruktuurid

- Aatomite perioodilist paiknemist nimetatakse **kristallvõreks.**
- **Ühikrakk:**
  On kogu võre elementaarseim esindaja, mille perioodilisel kordumisel saadakse kogu võre.
- **Primitiivne rakk:**
  Väikseim ühikrakk.





Primitiivne rakk

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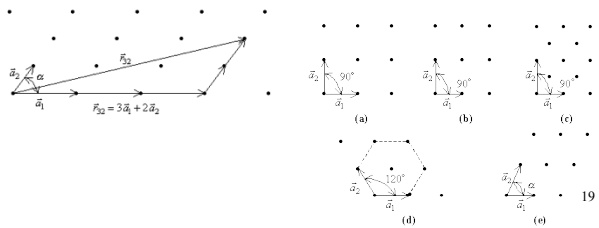
## Kristallstruktuurid

- **Koordinaadid:**
  - **x, y, z antakse kui ühikraku tahud.**

$$\vec{r}_{xyz} = x\vec{a} + y\vec{b} + z\vec{c}$$

*Näide:*

a,b,c – ühikvektorid koordinaat-telgede sihis.

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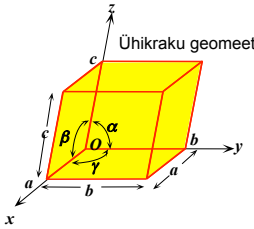
## Kristallvõrede tüübid

- **Bravais võred:**

Pikkus ja nurk




| | | | |
|---|---|---|---|
| Trikliinne | a≠b≠c | α≠β≠γ≠90° | $K_2CrO_7$ |
| Monokliinne | a≠b≠c | α=γ=90°≠β | β-S, $CaSO_4 \cdot 2H_2O$ |
| Ortorombiline | a≠b≠c | α=β=γ=90° | α-S, Ga, $Fe_3C$ |
| Tetragonaalne | a=b≠c | α=β=γ=90° | β-Sn, $TiO_2$ |
| Kuubiline | a=b=c | α=β=γ=90° | Cu, Ag, Zn, NaCl |
| Heksagonaalne | $a_1=a_2=a_3 \neq c$ | α=β=90°, γ=120° | Zn, Cd |
| Rombiline | a=b=c | α=β=γ≠90° | As, Sb, Bi |

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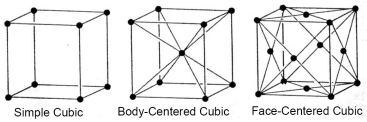
## Kristallstruktuurid

Kristallsüsteemides võib elementaarne rakk omada erinevaid variatsioone.

Bravais näitas, et kõik ruumvõred on kirjeldatavad 14 standardse elementaarrakuga.

Nende hulgas on nelja põhisüsteemi elementaar-rakke:

1. lihtsad elementaarrakud
2. ruumtsentreeritud elementaarrakud
3. tahktsentreeritud elementaarrakud
4. alustsentreeritud elementaarrakud



Simple Cubic | Body-Centered Cubic | Face-Centered Cubic

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## Kristallvõrede tüübid: Grupp (I)

| | | |
|---|---|---|
| Triclinic<br>$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$ | Monoclinic<br>$a \neq b \neq c$, $\alpha = \gamma = 90°$ $\beta \neq 90°$ | Monoclinic<br>$a \neq b \neq c$, $\alpha = \gamma = 90°$ $\beta \neq 90°$ |
| Orthorhombic<br>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$ | Orthorhombic<br>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$ | Orthorhombic<br>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$ |

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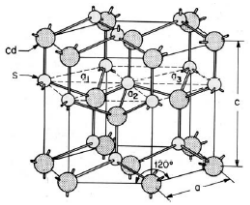
## Kristallvõrede tüübid: Grupp (II)

| | | |
|---|---|---|
| Orthorhombic<br>$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$ | Hexagonal<br>$a_1 = a_2 = a_3 \neq c$, $\alpha = \beta = 90°$ $\gamma = 120°$ | Rhombohedral<br>$a = b = c$, $\alpha = \beta = \gamma \neq 90°$ |




CdS võre

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## Kristallvõrede tüübid: Grupp (III)

| | | |
|---|---|---|
| Tetragonal<br>$a = b \neq c$, $\alpha = \beta = \gamma = 90°$ | Tetragonal<br>$a = b \neq c$, $\alpha = \beta = \gamma = 90°$ | Cubic<br>$a = b = c$, $\alpha = \beta = \gamma = 90°$ |
| Cubic<br>$a = b = c$, $\alpha = \beta = \gamma = 90°$ | Cubic<br>$a = b = c$, $\alpha = \beta = \gamma = 90°$ | |

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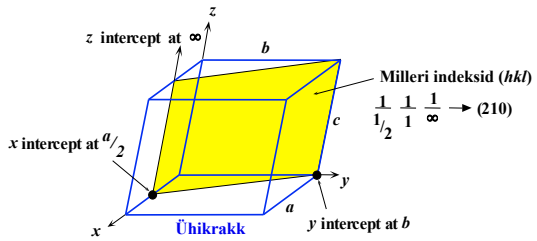
## Milleri tähistused

| *Tähistus* | *Tähendus* |
|---|---|
| (hkl) | Kristalli tasand |
| {hkl} | Ekvivalentsed tasandid |
| [hkl] | Kristalli suund |
| <hkl> | Ekvivalentsed suunad |



## Kristalli tasand

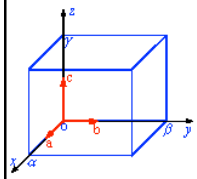
❑ Kristalli tasandi identifitseerimine:






## Kristalli tasandid

❑ Milleri indeksite leidmine:




Step 1 : Identify the intercepts on the x- , y- and z- axes.
Intercept on the *x*-, *y*-, and *z*-axis is at $x = \alpha$, $y=\beta$, and $z=\gamma$, respectively. If the surface is parallel to an axis, there would be no intercept on the axis. We shall consider the intercept to be at infinity ($\infty$) for the special case where the plane is parallel to an axis.
Intercepts : $\alpha, \beta, \gamma$

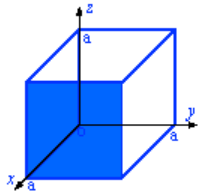
Step 2 : Specify the intercepts in fractional co-ordinates.
Coordinates are converted to fractional coordinates by dividing by the respective cell dimension. For example, a point $(x, y, z)$ in a unit cell of dimensions $a \times b \times c$ has fractional coordinates of $(x/a, y/b, z/c)$. In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant, a.
Fractional Intercepts : $\alpha/a, \beta/b, \gamma/c$

Step 3 : Take the reciprocals of the fractional intercepts.
This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (....) when one is specifying a unique surface such as that being considered here.
The reciprocals of 1 and $\infty$ are 1 and 0, respectively.
Miller Indices : (*hkl*)



## Milleri indeksite leidmine

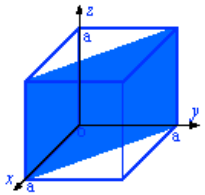
❑ Näited:




Step 1 : Identify the intercepts on the x- , y- and z- axes.
Intercepts : a, ∞, ∞

Step 2 : Specify the intercepts in fractional co-ordinates.
Fractional Intercepts : a/a, ∞/a, ∞/a *i.e.* 1, ∞, ∞

Step 3 : Take the reciprocals of the fractional intercepts.
Miller Indices : (100)



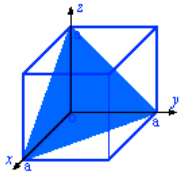

Step 1 : Identify the intercepts on the x- , y- and z- axes.
Intercepts : a, a, ∞

Step 2 : Specify the intercepts in fractional co-ordinates.
Fractional Intercepts : a/a, a/a, ∞/a *i.e.* 1, 1, ∞

Step 3 : Take the reciprocals of the fractional intercepts.
Miller Indices : (110)

## Milleri indeksite leidmine

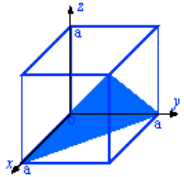
❑ **Näited:**




Step 1 : Identify the intercepts on the x- , y- and z- axes.
Intercepts : a, a, a

Step 2 : Specify the intercepts in fractional co-ordinates.
Fractional Intercepts : a/a, a/a, a/a *i.e.* 1, 1, 1

Step 3 : Take the reciprocals of the fractional intercepts.
Miller Indices : (111)



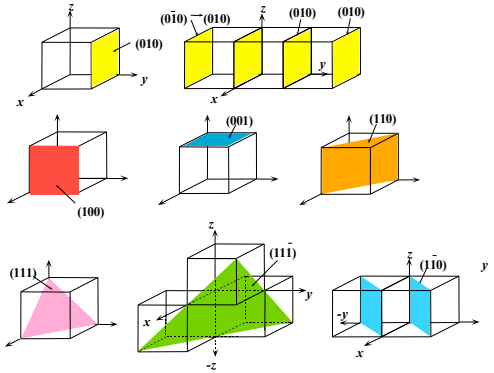

Step 1 : Identify the intercepts on the x- , y- and z- axes.
Intercepts : a, a, -a

Step 2 : Specify the intercepts in fractional co-ordinates.
Fractional Intercepts : a/a, a/a, -a/a *i.e.* 1, 1, -1

Step 3 : Take the reciprocals of the fractional intercepts.
Miller Indices : $(11\bar{1})$



## Kristallitasandid kuubilises võres






## Kristallitasandid

❑ **Tasandite vaheline kaugus (XRD-s just neid leitaksegi)**

❖ **Kuubiline :** $d = \dfrac{a^2}{\sqrt{h^2+k^2+l^2}}$

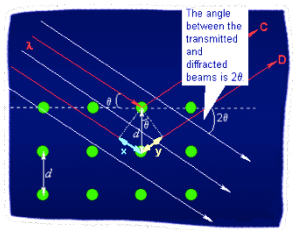
❖ **Tetragonaalne :** $\dfrac{1}{d^2} = \dfrac{h^2+k^2}{a^2} + \dfrac{l^2}{c^2}$

❖ **Heksagonaalne :** $\dfrac{1}{d^2} = \dfrac{4}{3}\left(\dfrac{h^2+hk+k^2}{a^2}\right) + \dfrac{l^2}{c^2}$



## Kristallitasandid

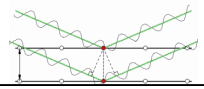
❑ **X-Ray difraktsioon**




➢ **Iga tasandite kooslus omab kindlat tasanditevahelist kaugust, mis röntgenikiirte difraktsioonis annab kindla piigi.**
➢ **Braggi valem seob röntgenkiirguse lainepikkuse, tasanditevahelise kauguse ja difraktsiooninurga.**

***Bragg'i valem***

$$2d \cdot \sin\theta = n\lambda$$



## XRD

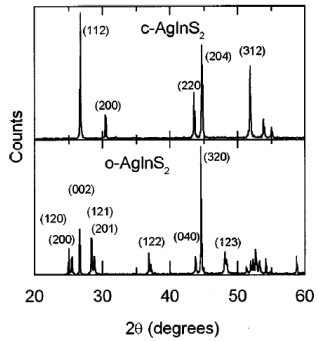
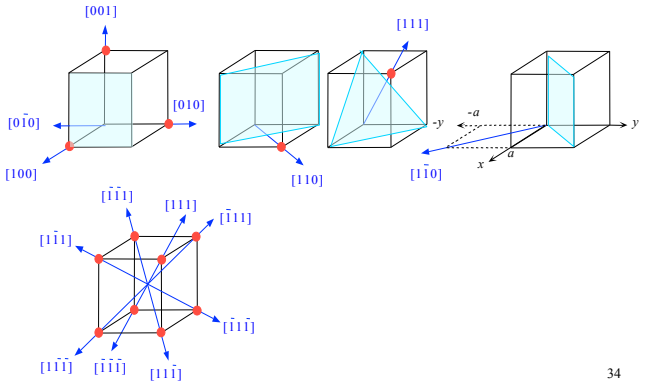



FIG. 1. X-ray diffraction patterns of our polycrystalline chalcopyrite and orthorhombic $AgInS_2$ samples.



## Kristalli suunad

- Kristalli suunad kuubilises kristallis:

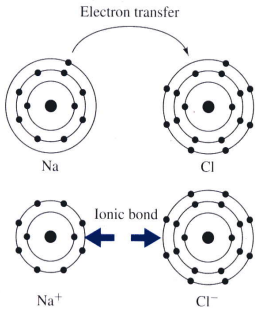





## Kuidas kristallid moodustuvad?

- Looniline side + ja - ioonide vahel.
- Vajalik elektroni ümberpaigutumine.
- Vajalik suur elektronegatiivsuste erinevus

Näide: NaCl




Katioon

Anioon



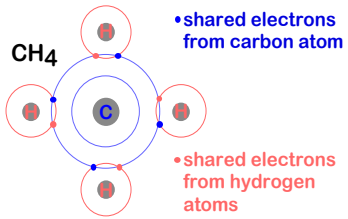
## Kovalentne side

- Vajalikud ühised elektronid
- Näide: $CH_4$

  C: 4 valents e, vajab veel 4

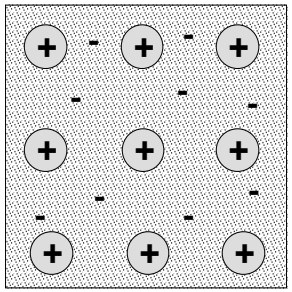
  H: 1 valents e, vajab veel 1

  Elektronegatiivsused on võrreldavad



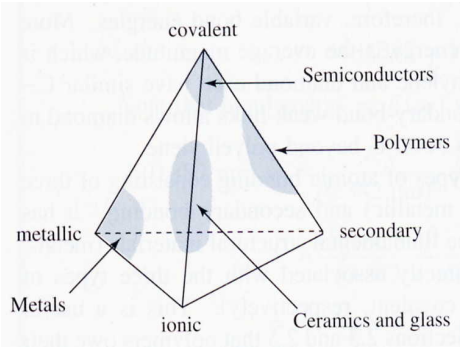
# Metalliline side

- Põhiline side metallides ja nende sulamites
- Pooljuhtides ei esine





# Keemilised sidemed - kokkuvõte






## Pooljuhtide sidemed

**Enamus pooljuhte omavad ioonilise ja kovalentse sideme segu:**

| | | Fractional ionic character |
|---|---|---|
| IV-IV | Si | 0.00 |
| | SiC | 0.18 |
| | Ge | 0.00 |

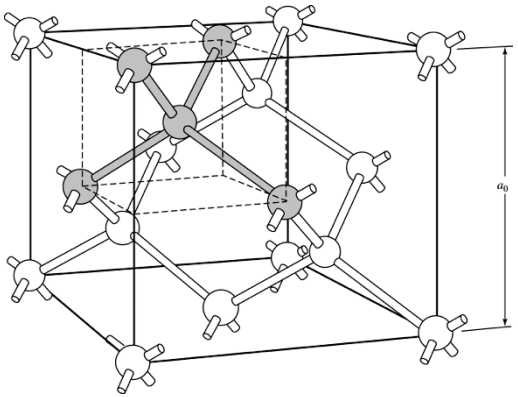
| | | Fractional ionic character |
|---|---|---|
| III-V | InP | 0.42 |
| | InAs | 0.36 |
| | InSb | 0.32 |
| | GaAs | 0.31 |
| | GaSb | 0.26 |

| | | Fractional ionic character |
|---|---|---|
| II-VI | ZnO | 0.62 |
| | ZnS | 0.62 |
| | ZnSe | 0.63 |
| | ZnTe | 0.61 |
| | CdO | 0.79 |
| | CdS | 0.69 |
| | CdSe | 0.70 |
| | CdTe | 0.67 |



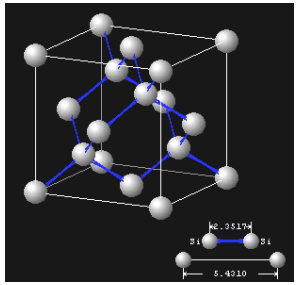
## Pooljuhtide kristallstruktuur

- **Teemandi võre (Si, Ge)**

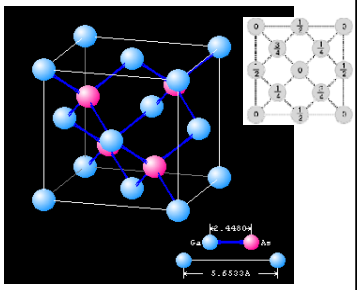


## Pooljuhtide kristallstruktuur

❑ Teemandi ja Zincblende võred



Teemandi võre
Si, Ge



Zincblende võre
GaAs, InP, ZnSe

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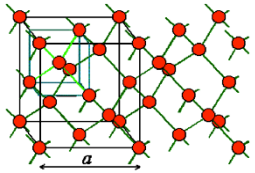
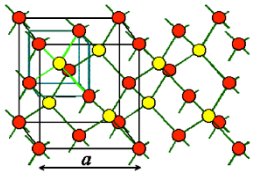
## Pooljuhtide kristallstruktuur

❑ Teemandi ja Zincblende võred:




Teemandi võre
Si, Ge




Zincblende võre
GaAs, InP, ZnSe

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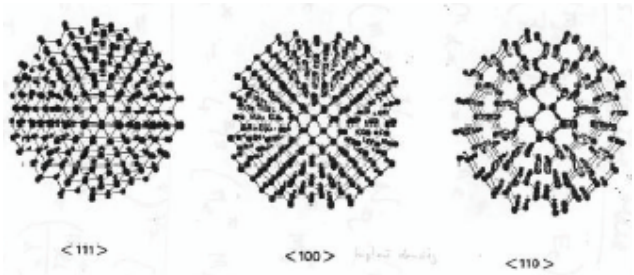
## Pooljuhtide kristallstruktuur

❑ Teemandi võre vaadatuna erinevatest suundadest:

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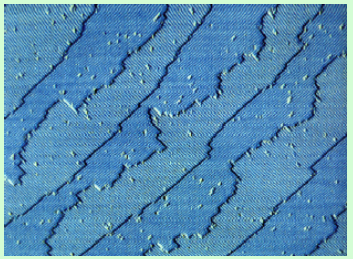
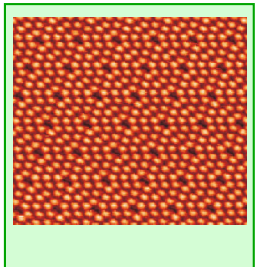
## Reaalne kristalli pind vaadatuna läbi STM-i.



Räni (100) pind



Räni (111) pind

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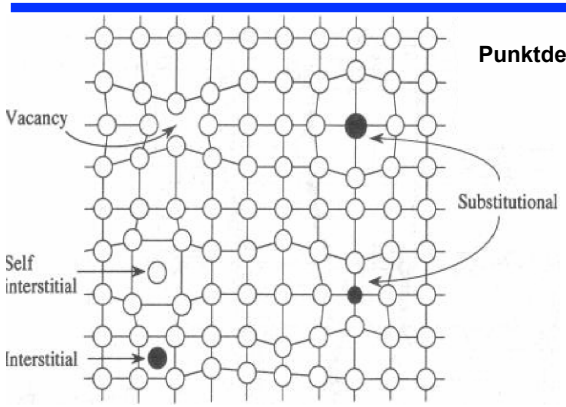
## Defektid kristallides




**Punktdefektid**

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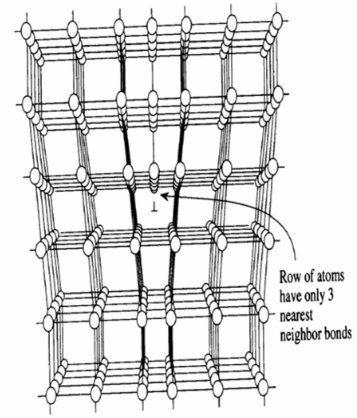
## Defektid kristallides




**Dislokatsioonid**

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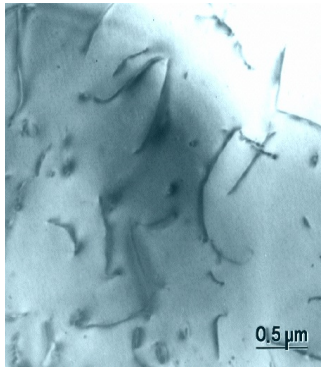
## Defektid kristallides




**Dislokatsioonid vaadatuna SEM-iga**

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## Vegardi reegel

**Mitmikühendite tahkete lahuste võreparameetrid alluvad tihtipeale Vegardi reeglile:**

Ternary alloy (ex: $In_xGa_{1-x}As$)

$$a_{A_xB_{(1-x)}C} = xa_{AC} + (1-x)a_{BC}$$

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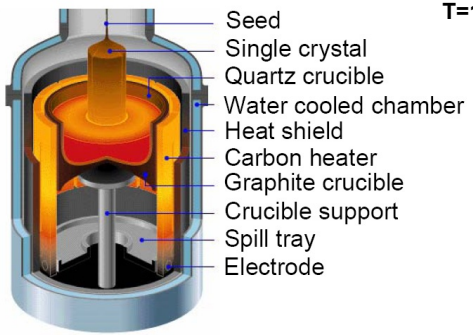
## Kristallide kasvatamine

**Czochralski meetod (Si monokristallide kasvatamine)**

**T=1412°C**

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