Phonon Workshop Cracow 2010-12-03

工学部
材料学科
9研究室

# Electron-Phonon-coupling in $Fe_{1-x}Co_xSi$

**Experimental IR-, Raman-Data and frozen Phonon-calculations**

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http://www.angelfire.com/wi/wunder/jpleb2.html

## Progress in Solid-State-Physics is based on the effort of experimentalists and theoreticians

**Nobel-Prize-recipients**

Curie 1903

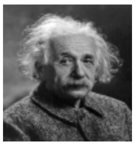
Bednorz 1987

Planck 1918

L.Boltzmann(1887)

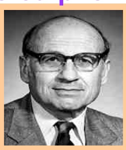
I.Tamm 1958

**discovered phonons**



Einstein 1921 Pauli 1945 Schrödinger 1933

**developed atom model**



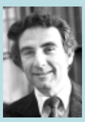
W. Kohn 1998

**discovered DFT**

Raman 1930

Muller 1987

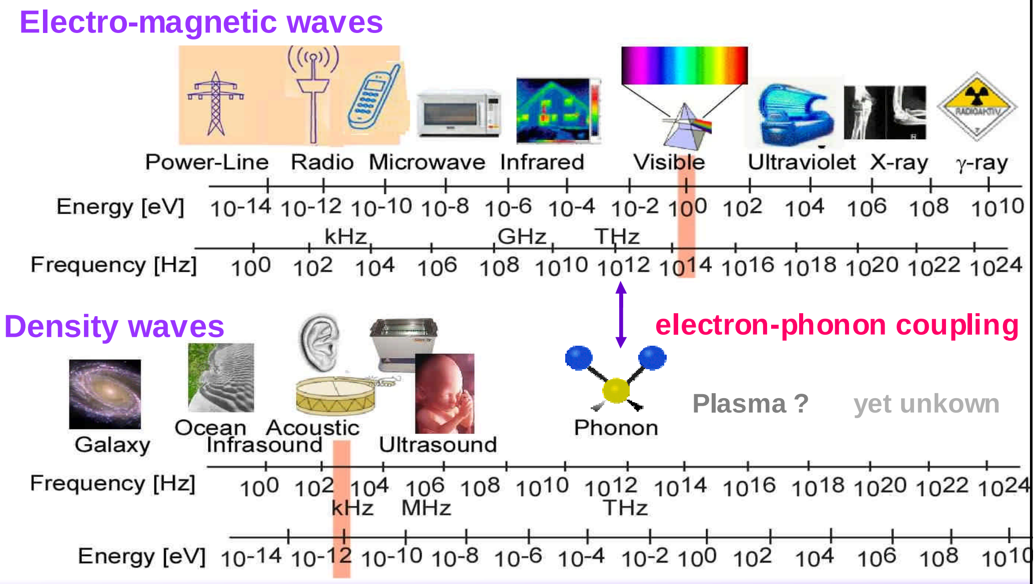
**discovered HTSC**



Bardeen Cooper Schrieffer'72

PHONON

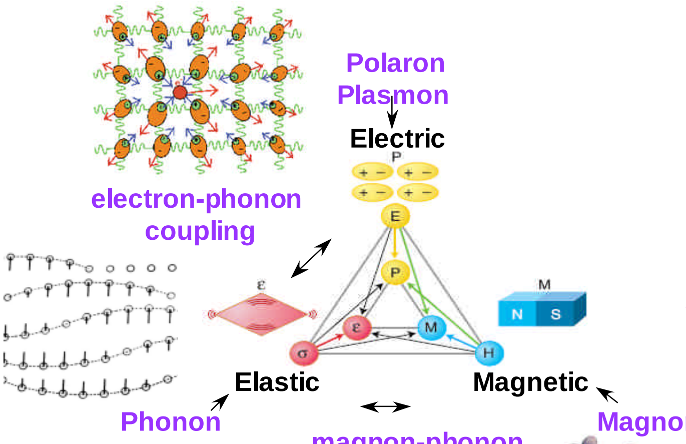
## Electron-phonon coupling on the energy scale



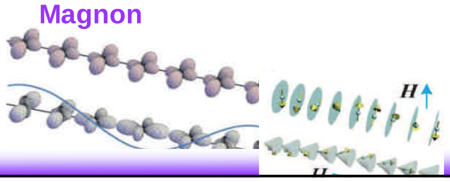

## This lecture …

- ○ Electron-phonon coupling in materials development
- ○ Why FeSi
- ○ Experimental XPS, Raman-data
- ● Frozen Phonon calculations
- ○ Thermoelectric data
- ○ Electron-phonon coupling

## Importance of electron-phonon coupling for materials development




Spaldin 2005 doi: 10.1126/science.1113357



**Properties**
- ○ Electric resistivity
- ○ Thermodynamic data
- ● Thermoelectric data
- ○ Superconductivity
- ○ Charge transport
- ○ Heat transport
- ○ Thermal expansion
- ○ Superconductivity

**Analysis**
- ○ Optical spectroscopy
- ○ Raman scattering
- ○ Electron (hole) lifetimes

## Importance of electron-phonon coupling for materials development

### Prediction of Superconductivity

Spectral function at Eliashberg theory

$$\alpha^2F(\omega)=\frac{1}{2\pi\ N_F}\sum_{\mathbf{q}j}\frac{\gamma_{\mathbf{q}j}}{\omega_{\mathbf{q}j}}\delta(\hbar\omega-\hbar\omega_{\mathbf{q}j}).$$

electron-phonon coupling mass enhancement

$$\lambda=2\int_0^{\infty}\frac{\alpha^2F(\omega)}{\omega}\,d\omega$$

McMillan formula for critical Temperature

$$T_c^{\mathrm{McM}}=\frac{\omega_{\log}}{1.2}\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right)$$

Savrasov PRB 54 16470 (1996)
Bauer et.al. PRB 57 11276 (1998)

### Specific heat

Sommerfeld coefficient of specific heat

$$\frac{c}{T}=\gamma+\beta T^2 \quad 1+\lambda_{s-h}=\frac{3\gamma}{2\pi^2k_BN(\epsilon_F)},$$

Savrasov PRB 54 16487 (1996)

Al 0.45, Au 0.17, Na 0.18. Nb 1.33
In 0.88, Pb 1.68, Ta 0.86, Cu 0.14

### Transport

$$\tau_{\epsilon}^{-1}=\frac{E^2_{\pm}\,m^3_{\pm}}{4\pi\hbar^4dT^*_{\pm}}\times\ln\left(\frac{1+\exp(-T^*_{s\pm}+\eta^*-x^2/16T^*_{s\pm}+x/2)}{1+\exp(-T^*_{s\pm}+\eta^*-x^2/16T^*_{s\pm}-x/2)}\right)$$

Vining JAP 69, 331 (1991)

$$\lambda_{\mathrm{tr}}^{\mathrm{exp}}=\frac{c_1\omega_p^2}{8\pi^2k_B},\quad \omega_p^2=\frac{8\pi N(\epsilon_F)\langle v_x^2\rangle}{\Omega_{\mathrm{cell}}}.$$ plasma frequency

Savrasov PRB 54 16487 (1996)

### Specific resistivity

Matthiesen rule $\rho = \rho_o + a\,T + \rho_i + \rho_d + .$

### Line width of Raman mode

$$\Gamma/\omega_0 = \pi N(0)\hbar\omega_0/\chi.$$

### Phonon-phonon coupling

$$\kappa_{\mathrm{latt}}T=\frac{R^{3/2}}{3\gamma^2\varepsilon^3N_0^{1/3}}\frac{T_m^{3/2}\rho^{2/3}}{A^{7/6}}$$

γ Grueneisen constant,
ε is the fractional amplitude
Tm is the melting point,
A is the mean atomic weight

R.W. Keyes, Phys. Rev. 1959, 115, 564.

## Importance of electron-phonon coupling for materials development

### from specific heat

Sommerfeld coefficient of specific heat

$$\frac{c}{T} = \gamma + \beta T^2$$

$$1+\lambda_{s-h} = \frac{3\gamma}{2\pi^2 k_B N(\epsilon_F)},$$

Savrasov PRB 54 16487 (1996)

### electron-phonon coupling

$$\Gamma/\omega_0 = \pi N(0)\hbar\omega_0/\chi.$$

Line width of Raman mode

linewidth

### Phonon-phonon coupling

$$\kappa_{\rm latt} T = \frac{R^{3/2}}{3\gamma^2\varepsilon^3 N_0^{1/3}} \frac{T_m^{3/2}\rho^{2/3}}{A^{7/6}}$$

$\gamma$ Grueneisen constant,
$\varepsilon$is the fractional amplitude
Tm is the melting point,
A is the mean atomic weight
R.W. Keyes, Phys. Rev. 1959, 115, 564.

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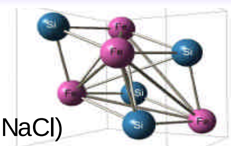
## Motivation: Why FeSi?

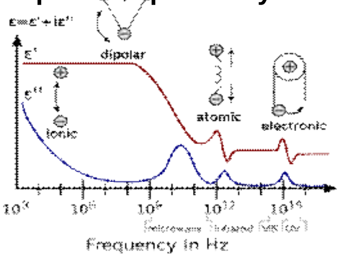


### To study electronic correlation

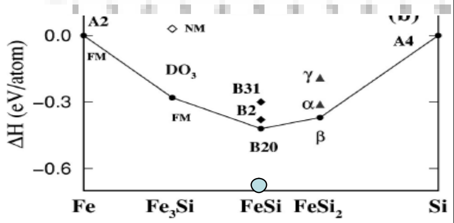
**Low bandgap**
**Dia-magnet at low temperatures then Paramagnet**

- **Single crystal**

- **Many Spectroscopic data available:**
  **Photoemission (PES)**
  **Raman**
  **Optical Ellipsometry**




cubic B20-Strukture
(along [111] Distorted NaCl)
SG P2$_1$3 a=0.4470nm



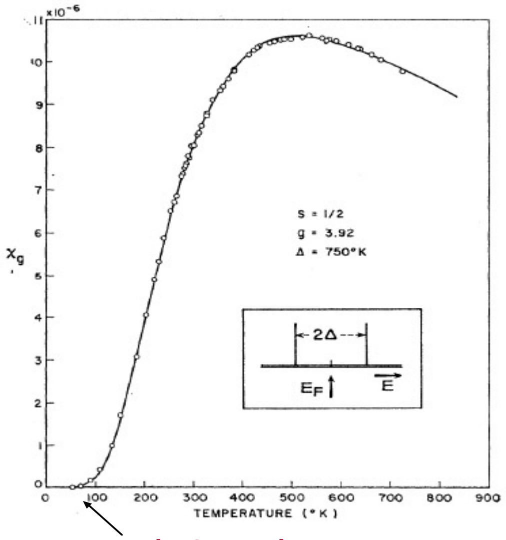

Moroni, Wolf, Hafner, Podlucky PRB 59 12860 (1999)

## Motivation: Why FeSi?

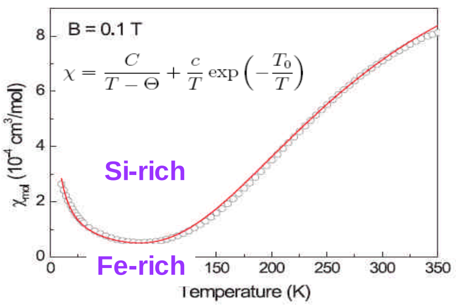
- Asymmetric phonon shape;
  high-frequency phonon does not follow the usual temperature behavior;
  softening below the gap energy
  → Electron-phonon coupling
- In-gap spectral weight comes from energies much higher than the optical band gap ( $\hbar\omega > 2.5$ eV )
- Photoemission spectra show full band gap ($E_{gap}$ = 30 meV)
- Experimental density of states matches self-energy-corrected single-particle band structure calculation
  → no Kondo physics
- Raman spectroscopy: Linewidth analysis within a classical semiconductor model gives a gap of 30 meV

More arguments against a strongly correlated Kondo system.

## Magnetic properties of FeSi

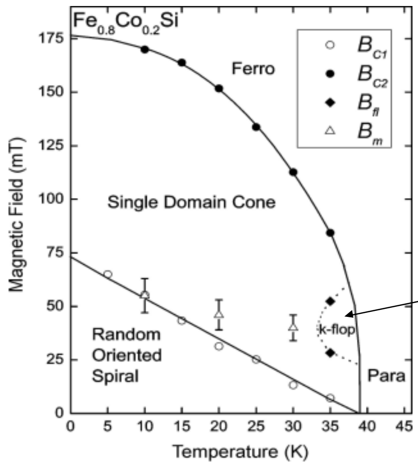


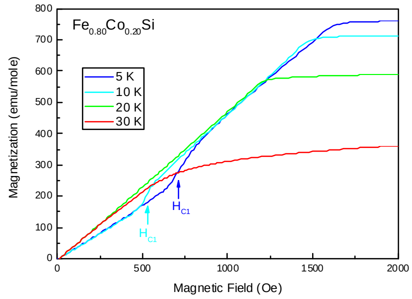

Kondo-Screening =
Un-magnetic ground state




Low bandgap
Dia-magnet at low temperatures
then Paramagnet

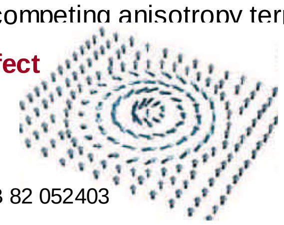
# $Fe_{1-x}Co_xSi$ – Small Angle Neutron Scattering (SANS)




A-Phase: ***k***-vector is points perpendicular to the applied magnetic field (2 competing anisotropy terms)

**Skyrmion-effect**



S. V. Grigoriev, D. Menzel, et.al.PRB **76**, 224424 (2007)
Ishimoto et.al. J.MagMagMat 90 163 (1990)

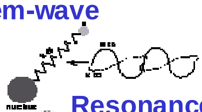
Butenko PRB 82 052403

# Optical conductivity is related to Lorentz oscillators

## Dynamic of Electrons under em-wave

$$J_\alpha(\omega) = \sum_{\beta=1}^{d} \sigma_{\alpha\beta}(\omega)\, E_\beta(\omega)$$

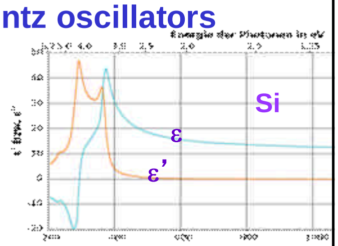
$$m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + m\beta\frac{\mathrm{d}x}{\mathrm{d}t} + m\omega_0^2 x = -e E^0_{\mathrm{lokal}} e^{-i\omega t}$$




**Resonance**


## Solutions

$$x(t) = -\frac{e}{m}\frac{1}{\omega_0^2 - \omega^2 - i\beta\omega} E^0_{\mathrm{lokal}} e^{-i\omega t}$$



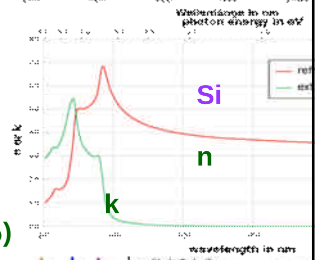

## Frequency depended dielectric function ε(ω)

$$\varepsilon = 1 + \frac{N_v}{\varepsilon_0/\alpha(\omega) - N_v/3} = 1 + \frac{N_v}{\frac{\varepsilon_0 E^0_{\mathrm{lokal}} e^{-i\omega t}}{e x(t)} - N_v/3}$$

**Kramers-Kroning**

$$\varepsilon(\omega) \equiv \varepsilon'(\omega) + i\varepsilon''(\omega)$$

$$\varepsilon'(\omega) = 1 + \frac{N_v e^2}{\varepsilon_0 m}\frac{\omega_1^2 - \omega^2}{(\omega_1^2 - \omega^2)^2 + \beta^2\omega^2} \qquad \varepsilon''(\omega) = \frac{N_v e^2}{\varepsilon_0 m}\frac{\beta\omega}{(\omega_1^2 - \omega^2)^2 + \beta^2\omega^2}$$




## Relation of dielectric ε(ω) to optical properties n(ω), k(ω)

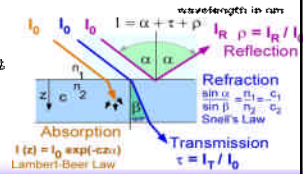
$$n = \sqrt{\frac{\sqrt{\varepsilon'^2 + \varepsilon''^2} + \varepsilon'}{2}} \qquad k = \sqrt{\frac{\sqrt{\varepsilon'^2 + \varepsilon''^2} - \varepsilon'}{2}}$$

$$\hat{N} = n + ik \qquad \hat{N} = \sqrt{\varepsilon\mu} \qquad v_{\mathrm{medium}} = c/n$$

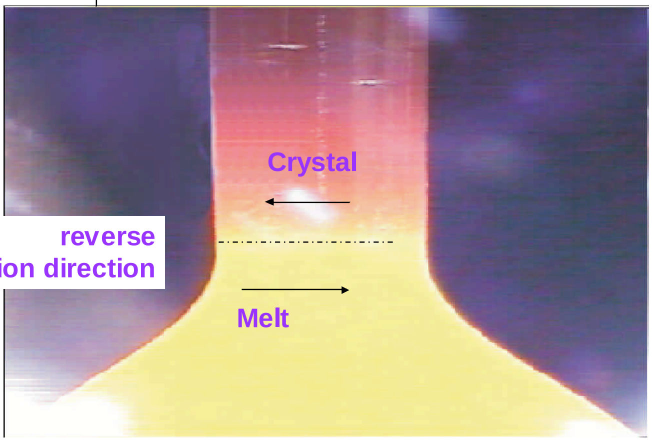
$$I = I_0\, e^{-2k\frac{\omega}{c_0}z} = I_0\, e^{-\alpha z}$$

$$\alpha = 2k\frac{\omega}{c_0}$$

**Refractive index n(ω)**
**Extinction index k(ω)**
**Absorption coefficient α(ω)**



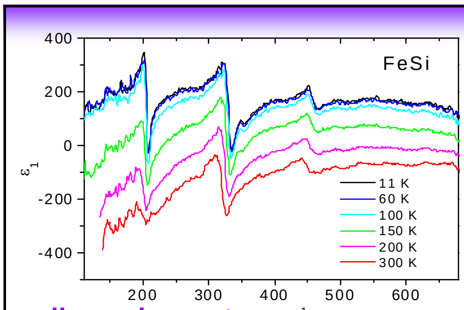
## Single Crystal growth using Triarc-Czochralski-Method




5 ~ 10 cm length
5 mm thickness

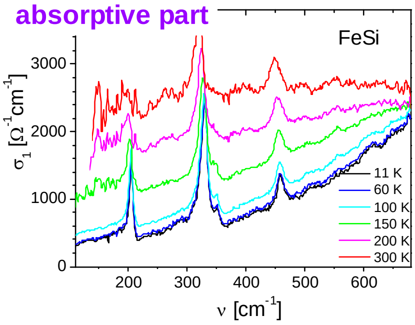


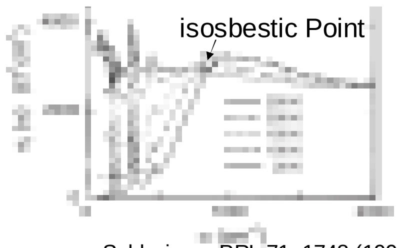
## IR-Spectroscopy on FeSi



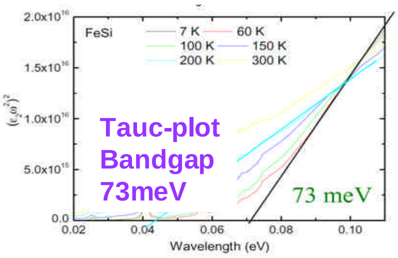

**dispersive part**

**absorptive part**



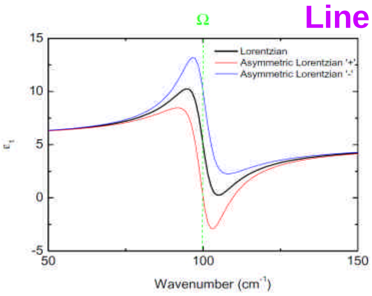

Schlesinger PRL 71, 1748 (1993)




Menzel et.al. PRB 79 165111

**IR-active phonon-modes: 232, 314, 370, 401, 507 cm$^{-1}$**

# Line shape analysis



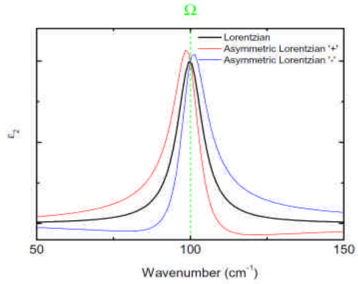

Classical Lorentzian oscillator:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \sum_{j=1}^{N} S_j \frac{\Omega_j^2}{\Omega_j^2 - \omega^2 - i\omega\Gamma_j}$$

$S_j$ : oscillator strength

$\Omega_j$ : resonant frequency

$\Gamma_j$ : damping




Asymmetric Lorentzian oscillator:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \sum_{j=1}^{N} S_j \frac{\Omega_j^2 - i\omega\sigma_j}{\Omega_j^2 - \omega^2 - i\omega\Gamma_j}$$

$$\sum_{j=1}^{N} \sigma_j = 0$$

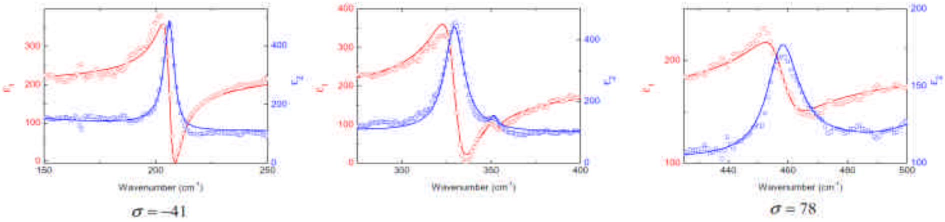
$\sigma_j$ : response with coupled modes

J. Humlíček, R. Henn, and M. Cardona, Phys. Rev. B **61**, 14554 (2000)

Menzel et.al. PRB 79 165111

Line shape analysis

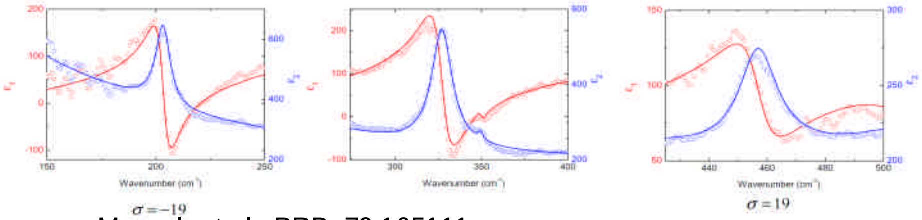
FeSi, T= 7 K




asymmetric symmetric asymmetric

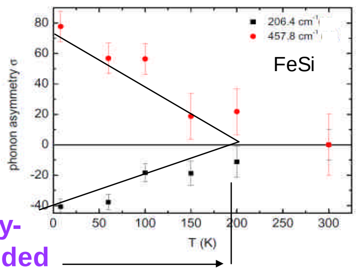
**Asymmetry -> Electron-Phonon coupling**

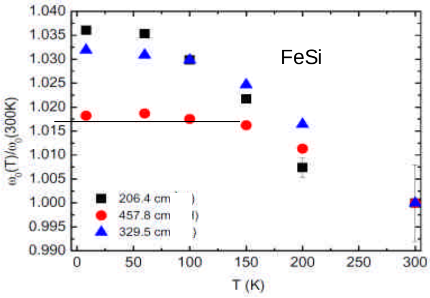
FeSi, T= 150 K



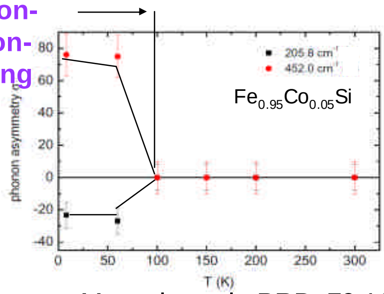

Menzel et.al. PRB 79 165111

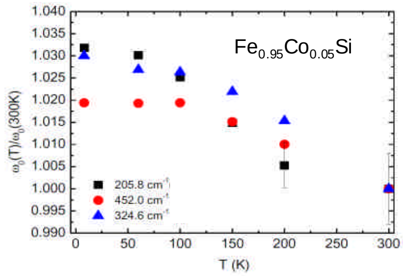
## Phonon asymmetry and resonant frequency




**Energy-depended Electron-Phonon-coupling**

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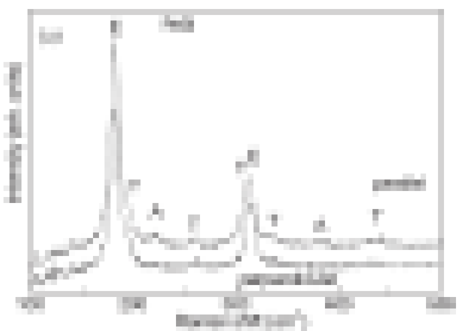
Menzel et.al. PRB 79 165111

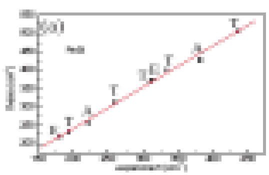
## Raman Spectroscopy on FeSi



**Racu, Menzel et.al. PRB 76 115103**

**Raman-active phonon modes at 181, 194, 218, 257, 314, 370, 401, 507cm⁻¹.**

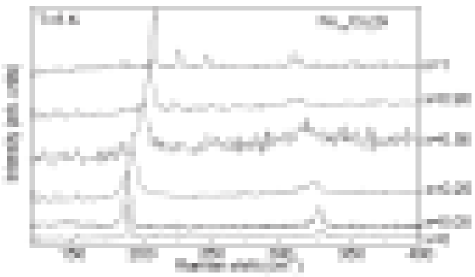
Nyhus, et.al.PRB 51 15626 (1995)

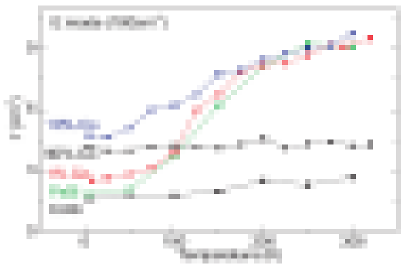


Factor group analysis FGA

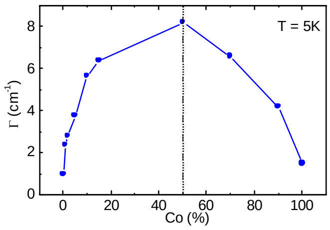
Racu, Menzel, Schoenes, PRB 76, 115103 (2007)

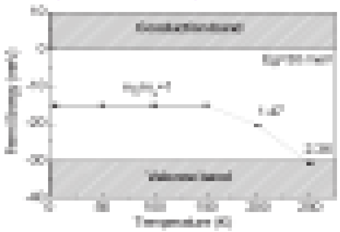
## Line width-analysis of Raman 180cm$^{-1}$ mode





Temperature dependence of the linewidth

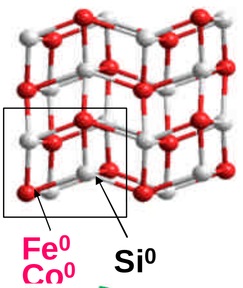


**Temperature-dependent chemical potential**

Racu, Menzel,et.al. PRB 76 115103 (2007)

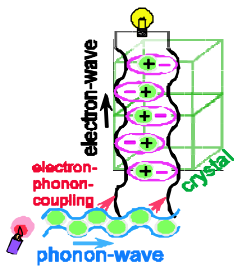
## Can we learn something about electron-phonon coupling from ab-initio frozen-phonon calculations?

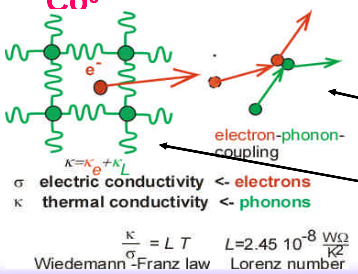



cubic B20 structure
(FeSi structure)

Space group: P2$_1$3

Lattice parameter:
a = 0.4493 nm

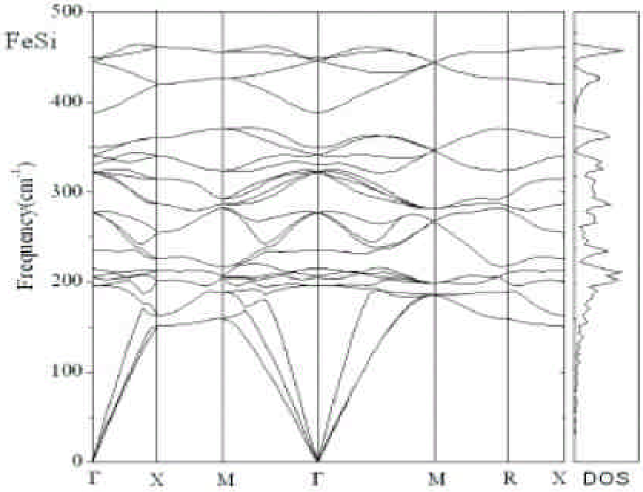



**Frozen-phonon Calculation in order to study the influence of phonons on bandstructure**

**Opposite: Influence of excited electrons on Phonon properties is more difficult**

## Phonon-Band-structure FeSi




Y.H. Zhao et al., EPL 85 47005 (6pp) doi:10.1209/0295-5075/85/47005

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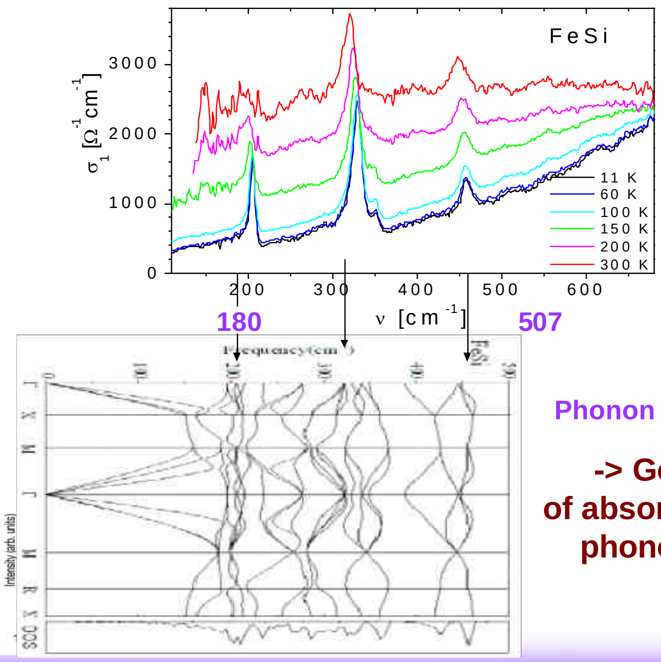


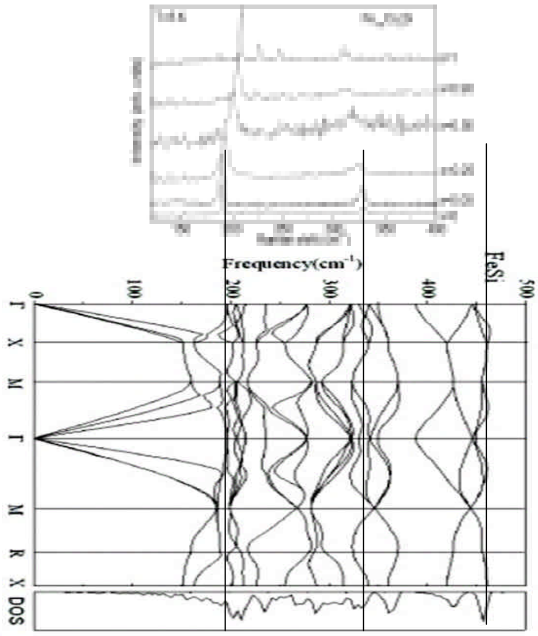

## Dielectric Function

Dispersive part $\varepsilon_1$

1eV = 8067 cm-1

Phonon spectrum

**-> Good matching of absorption peaks with phonon distribution at q=0**



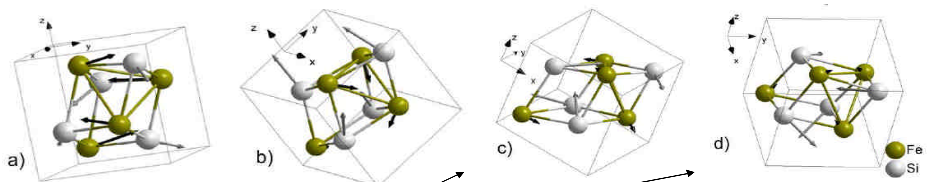

## Raman spectrum and Phonon-Band-structure $Fe_{1-x}Co_x$ Si

Y.H. Zhao et al., EPL 85 47005 (6pp)
doi:10.1209/0295-5075/85/47005

## T-Phonon modes in FeSi

(2A + 2E + 5T)

$$(u, u, u),\ (\tfrac{1}{2}+u, \tfrac{1}{2}-u, -u),\ (-u, \tfrac{1}{2}+u, \tfrac{1}{2}-u) \text{ und } (\tfrac{1}{2}-u, -u, \tfrac{1}{2}+u).$$



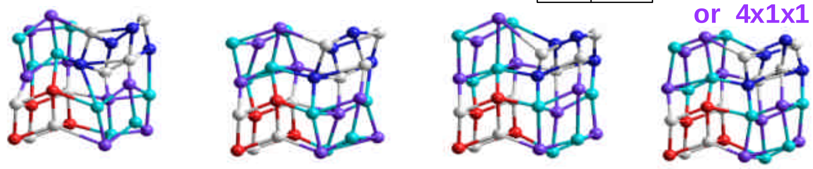

Racu, Menzel, et,al. PRB 76, 115103 (2007)

| Wellenzahl (cm$^{-1}$) | 232 | 314 | 370 | 401 | 507 |
|---|---|---|---|---|---|
| Intensität (Skt.) | 2110.80 | 5.60 | 6361.42 | 1635.03 | 2088.54 |

Too weak for exp verification ->

| | |
|---|---|
| - | + |
| 0 | - |

Modelling in 2x2x1 supercell or 4x1x1



Using VASP software Version 4.5

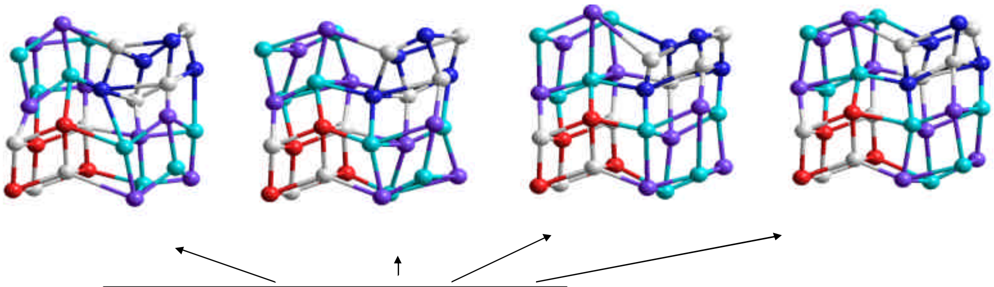
## T-Phonon modes in FeSi

$(u, u, u)$, $(\frac{1}{2}+u, \frac{1}{2}-u, -u)$, $(-u, \frac{1}{2}+u, \frac{1}{2}-u)$ und $(\frac{1}{2}-u, -u, \frac{1}{2}+u)$.

(2A + 2E + 5T)

| | |
|---|---|
| - | + |
| 0 | - |

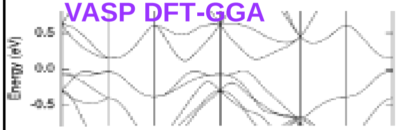
**2x2x1 supercell**



| Wellenzahl ($cm^{-1}$) | 232 | 314 | 370 | 401 | 507 |
|---|---|---|---|---|---|
| Intensität (Skt.) | 2110.80 | 5.60 | 6361.42 | 1635.03 | 2088.54 |

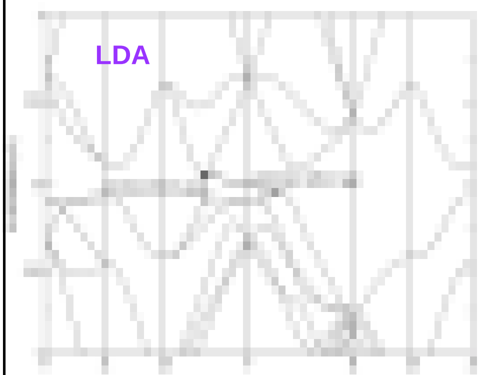
## Results: Bandstructure FeSi

VASP DFT-GGA



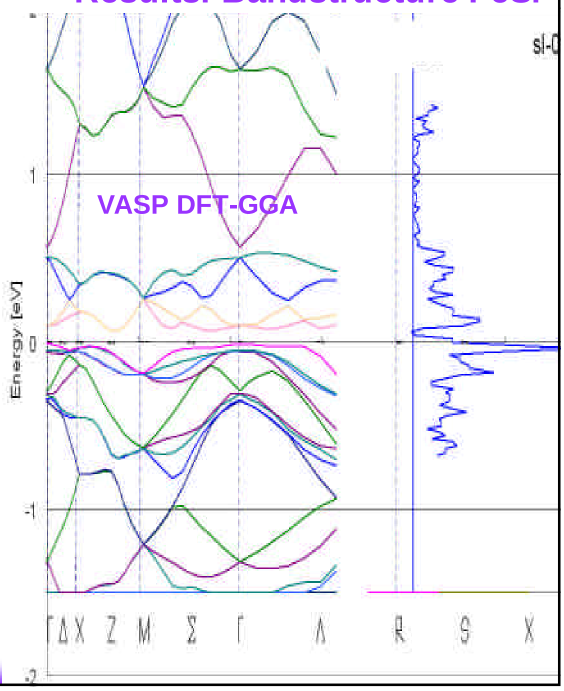

Moroni, Hafner et.al. PRB 59 12866 (1999)

LDA

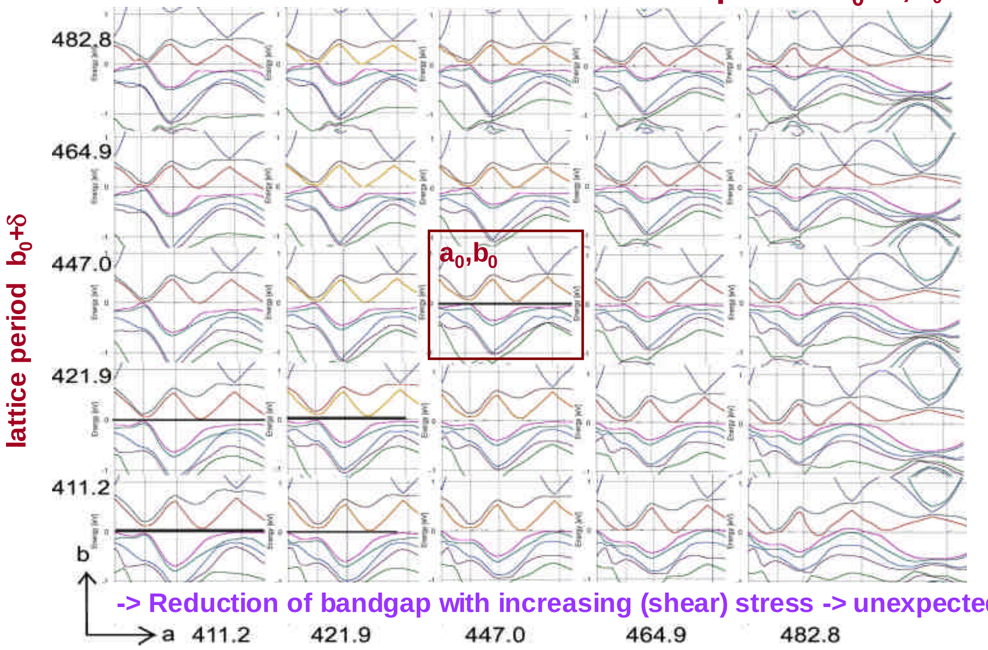


D.Menzel, et.al. PRB 79 (2009) 165111

VASP DFT-GGA



## Bandstructure FeSi with modified lattice period $a_0+\delta, b_0+\delta$



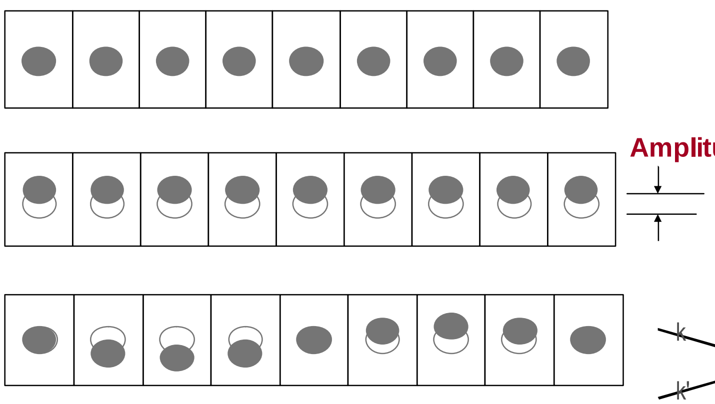

-> Reduction of bandgap with increasing (shear) stress -> unexpected

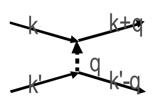
## q-dependent phonons

Equilibrium

(Frozen) Phonons q = 0

Migrating Phonons $q \neq 0$ $\lambda = \frac{h}{p}$



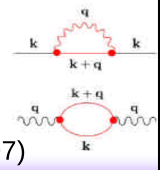




Computationally very demanding

Other method: Linear-response-theory, displacement as perturbation

Pulay-like terms, Wannier-method

(Claudia Ambrosch-Draxl)



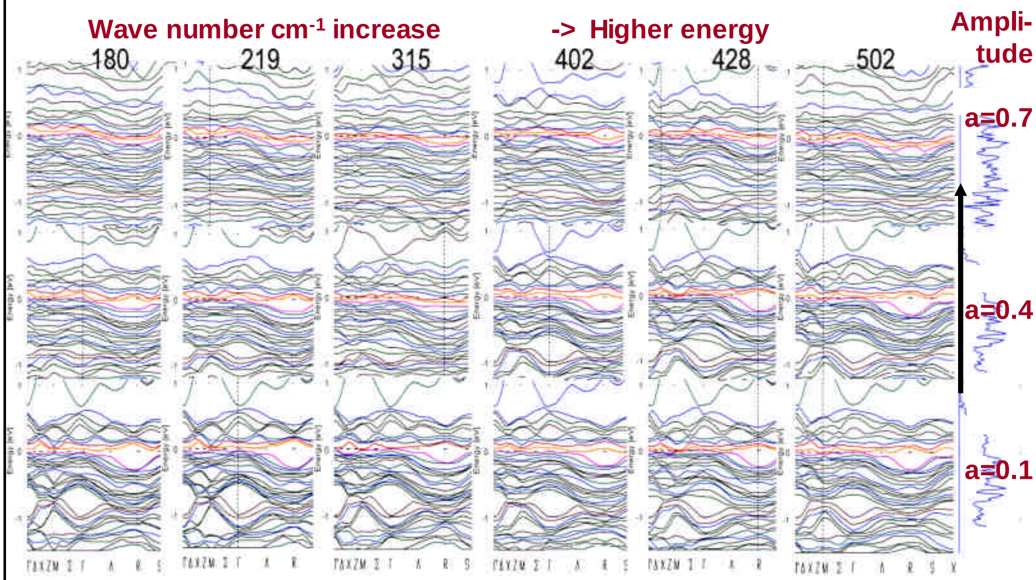

Savrasov PRB 54, 16487 (1996)

Giustino PRB 76 165108 (2007)

Sjakste, Appl. Phys. A 86 301 (2007)

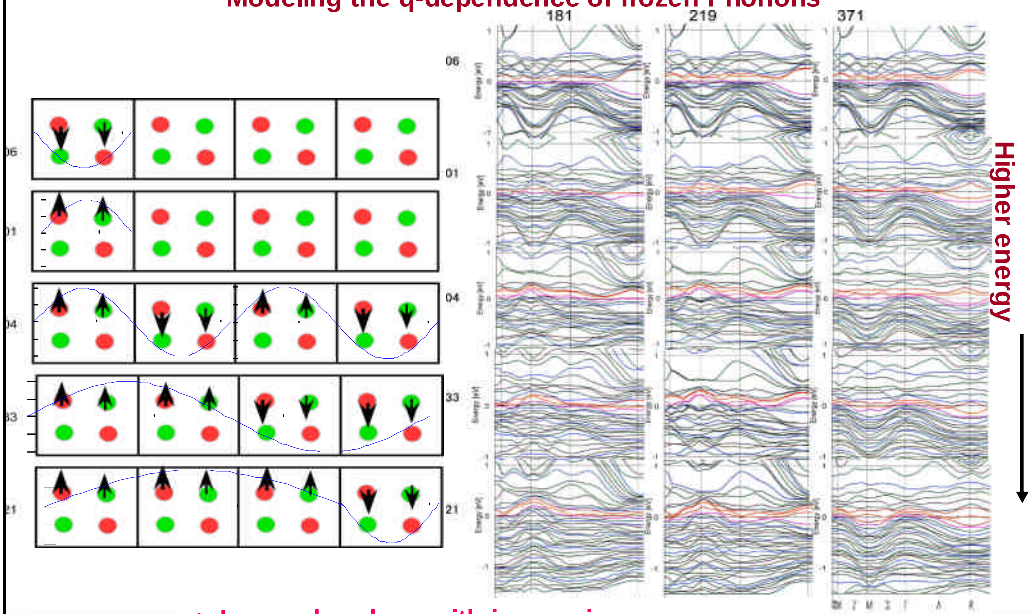
160022-

## Band-structure with phonon amplitude and wave-number dependence



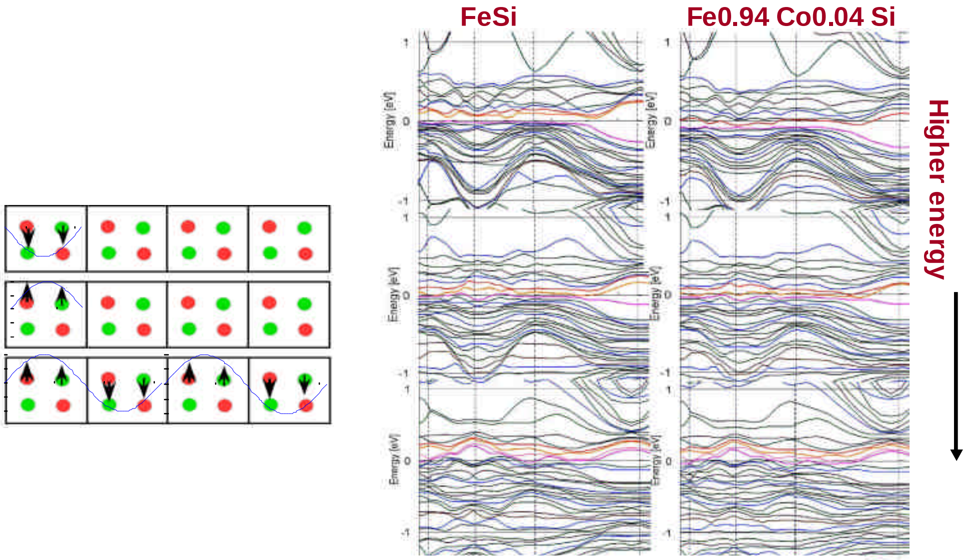

-> Destruction of bands with increasing amplitude, but decreasing energy

## Modeling the q-dependence of frozen Phonons



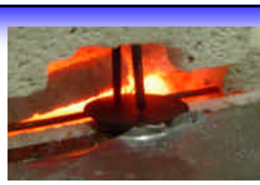

-> Lower bandgap with increasing energy

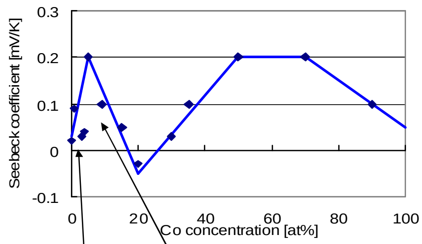
## Frozen Phonons showing the addition of Co to FeSi

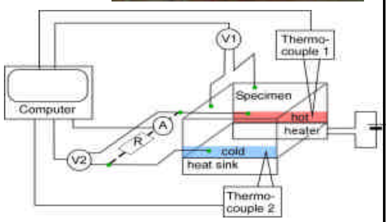



-> Band destruction with increasing "mixing entropy"

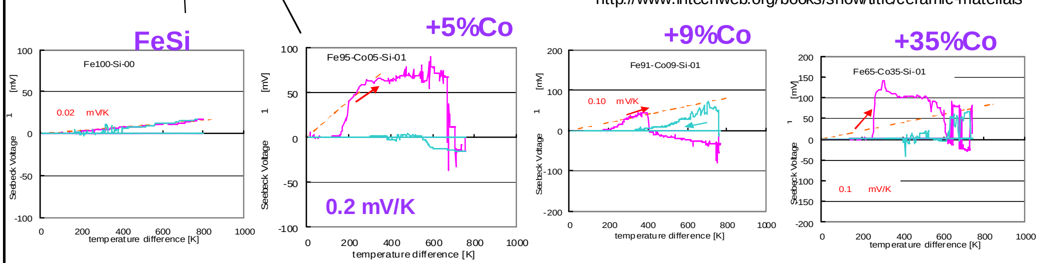
## Thermoelectric measurements



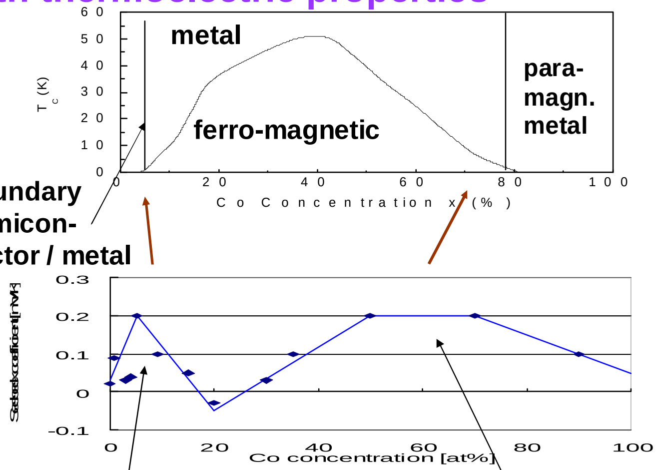



http://www.intechweb.org/books/show/title/ceramic-materials



## Comparison of Phasediagram FeSi with thermoelectric properties




FeSi | $Fe_{0.95}Co_{0.05}Si$ | $Fe_{0.9}Co_{0.1}Si$ | CoSi

**Electron-phonon-coupling / Electron-Magnon-Coupling**

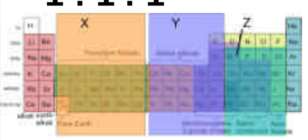
18/24

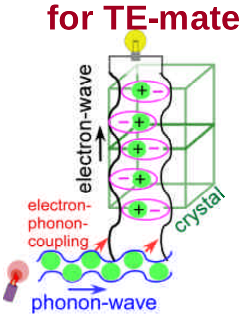
## Future: Use the Electron-phonon coupling for TE-material search

Proper crystal structure, e.g. Half-Heusler

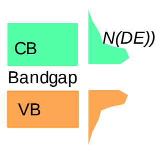
X Y Z

1 : 1 : 1

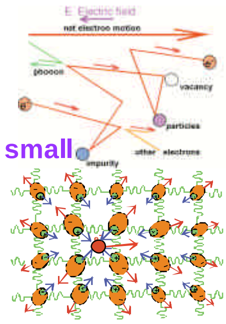



Strong Electron-phonon-coupling




Large Density-of-States at $E_F$




Large Electron mass

Figure of merit $Z=S^2\sigma/\kappa$

Seebeck coefficient $S$

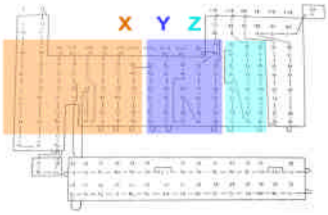
Electric conductivity $\sigma$

Thermal conductivity $\kappa$

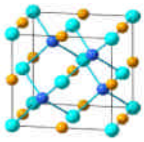
W. Wunderlich, K. Koumoto, Int. Jour. Mat. Research 97 (2006) 5 657-662

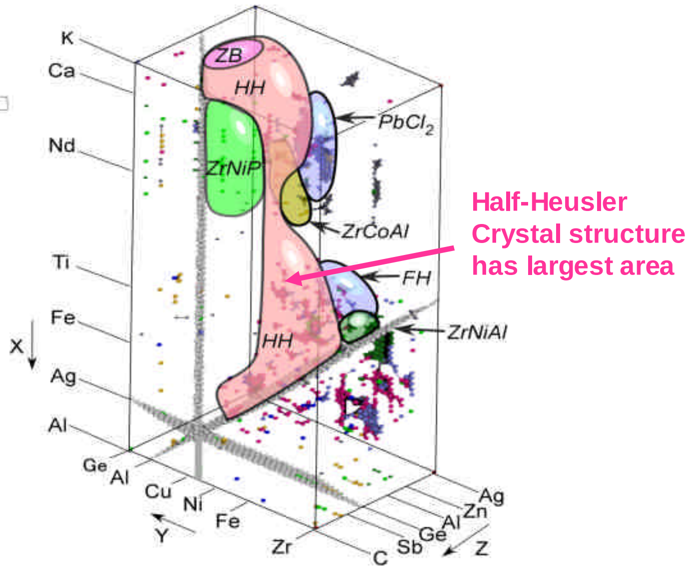
## Areas of crystal structures in 3-dim. XYZ-Pettifor map

Ordering according to Mendeleev - number




S.Ranganathan, A. Inoue, *Acta Mat.* **54** 3647 (2006)






W.Wunderlich MRS Symp. Proc. (2009) Doi:10.1557/PROC-1128-U01-10

## Conclusion

- **Spectroscopic IR- and Raman-data of FeSi can be explained by phonon modes**
- **Band-structure of frozen phonons show energy-dependence as expected**
- **Still no predictive power for thermoelectric properties.**

20/24