Structure Formation - From a Cloud of Atoms to a Crystal -

(T11) On the medium-range order in alloys of aluminum with transition metals

H. Solbrig

1. **spd electron phases**
2. **α-AlMnSi**
3. **i-AlCuFe (1/1)**
4. **Conclusions**

1. spd electron phases

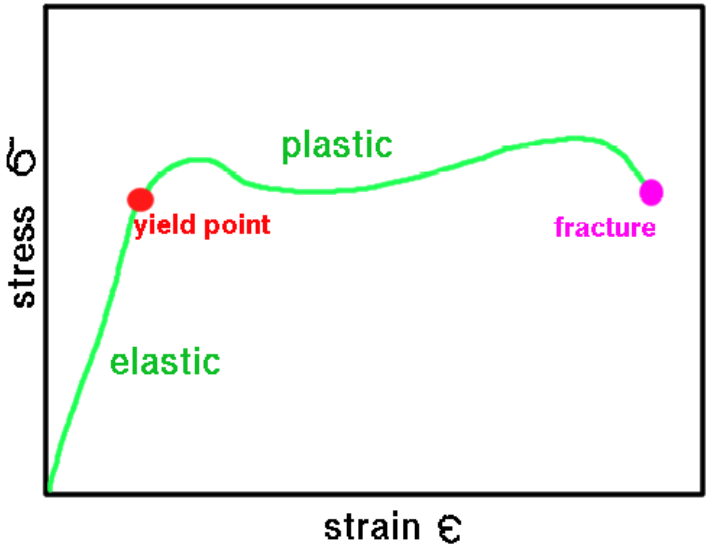
2. α**-AlMnSi**
3. i-AlCuFe (1/1)
4. Conclusions

Mechanical properties and the valence electrons

attributes

strong	concrete
hard	diamond
brittle	rock salt
soft	sodium
elastic	a spring
ductile	aluminum
plastic	polymer

applying strain



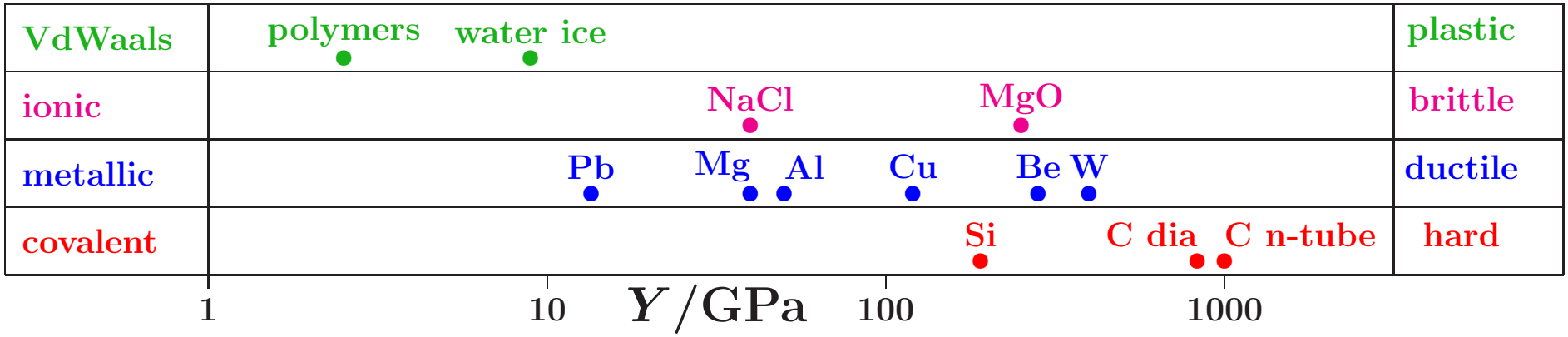
Hook's law

in the elastic range:

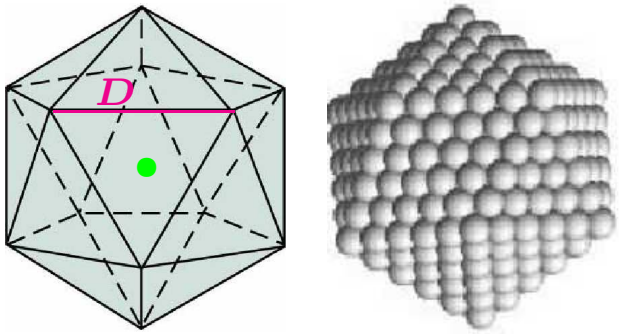
$$\sigma = Y\,\epsilon$$

Young modulus

typical ranges of the Young modulus



Icosahedral clusters in complex alloys

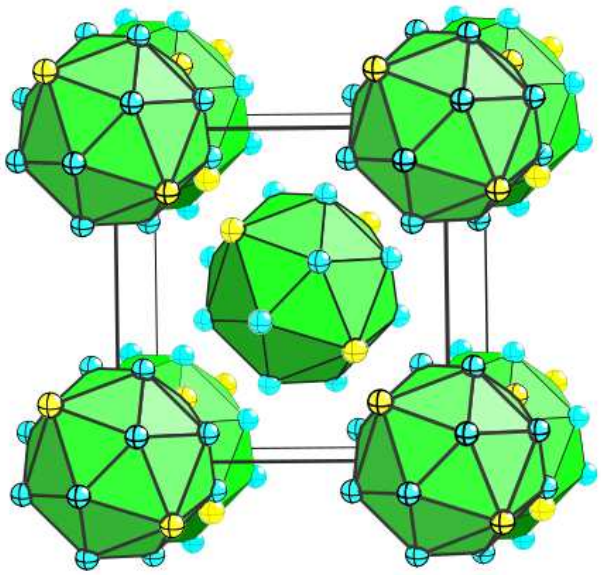


icosahedron: polyhedron(20 faces, 12 vertices, 30 edges)

- 12 vertices (spacing D)
  on a sphere (radius 0.951 D, center ●)
- **decorations** found with 12 or much more atoms
- **generated** by fast local relaxation,
  space-filling arrangement avoided by fivefold symmetry

"cluster materials": periodic arrangements of large complex clusters

e.g. bcc lattices of icosahedral clusters,
space between clusters filled with so-called "glue atoms"
(not shown)

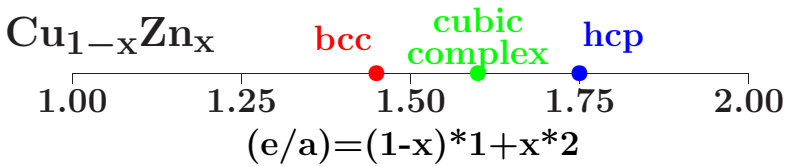


conclusion:

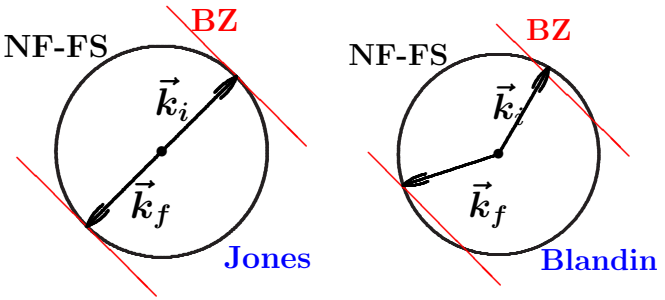
- subsystems contribute **hardness** or **ductility**

Concepts for electronic phase stabilization

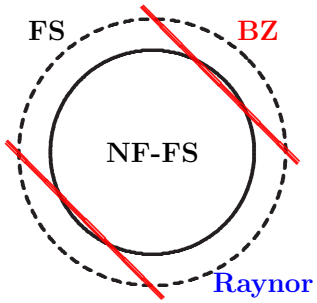
order parameter for *sp* alloys:
(e/a) controls structure (Hume-Rothery 1926)



diffraction picture:
nearly-free Fermi sphere touches/cuts a Brillouin zone
$\Longrightarrow$ a pseudogap opens at ϵ_F (Jones 1937, Blandin 1965)

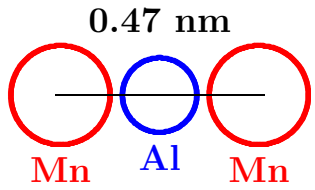


negative valence of transition metals (TM):
TM atoms fill empty *d* orbitals, carry negative charges
$\Longrightarrow$ smaller nearly-free Fermi sphere (Raynor 1947)



amorphous Hume-Rothery phases:
main diffraction peak K_p close to $2k_F$
$\Longrightarrow$ a pseudogap opens at ϵ_F (Nagel 1975, Häußler 1983)

virtual bound states model:
TM impurity atom in a *sp* matrix (e.g. Al)
$\Longrightarrow$ TM *d*-DOS has Lorentz profile, TM not charged
(Friedel 1956, Anderson 1961)



generalized to complex TM alloys with *d* resonances at ϵ_F
$\Longrightarrow$ *sp* neighbors of TM atoms increase their *sp*-DOS below ϵ_F
(Trambly de Laissardiére 1995)

sp-*d* hybridization

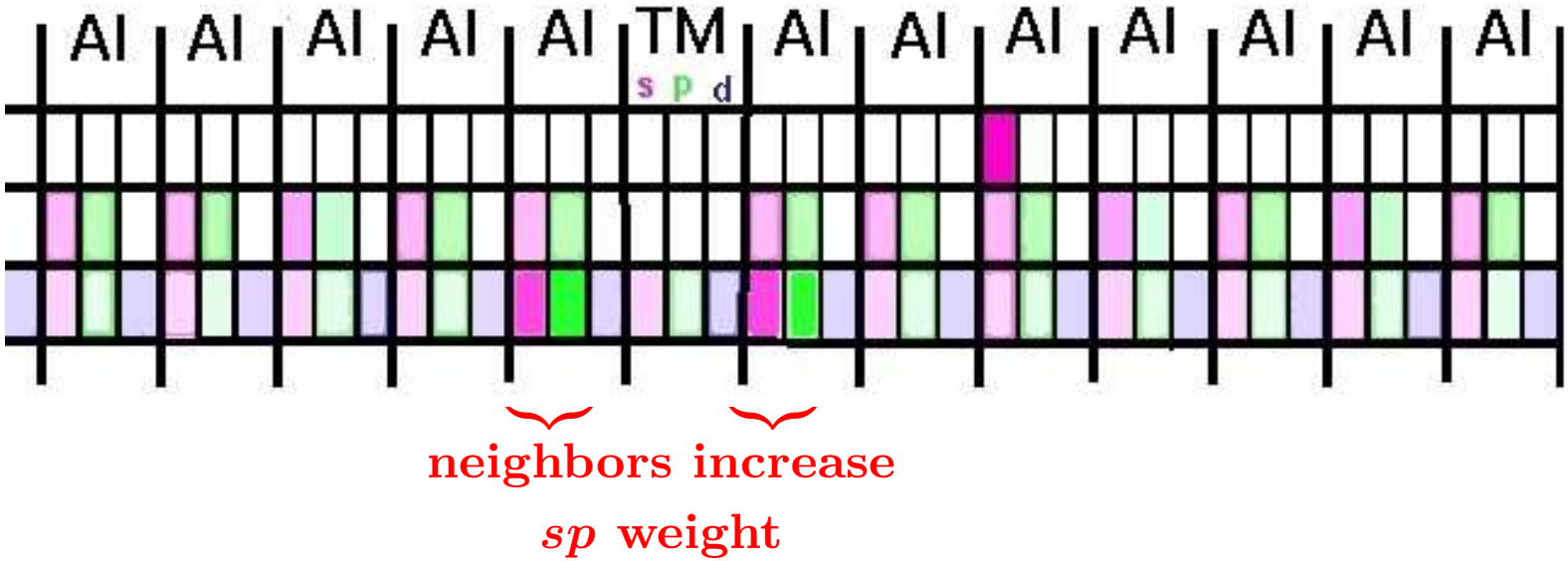
electronic band states are hybridized

$$|\nu\vec{k}\rangle = \sum_{sL}^{cell} \psi_{sL}(\nu\vec{k})|sL\rangle, \qquad \sum_{sL}^{cell} |\psi_{sL}(\nu\vec{k})|^2 = 1$$

s-Al electron

unrealistic

realistic



conclusions:

- Band states with considerable *sp*-Al/*d*-TM hybridization are pinned at TM atoms, are less diffusive, do not belong to the nearly-free Fermi sphere.
- The negative TM valence corresponds to the total increase of *sp* weight at neighboring Al atoms.

1. spd electron phases

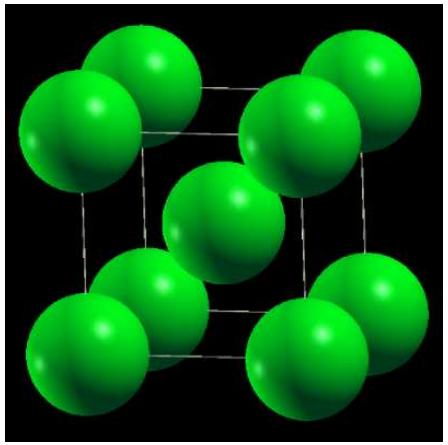
2. α-AlMnSi

3. i-AlCuFe (1/1)
4. Conclusions

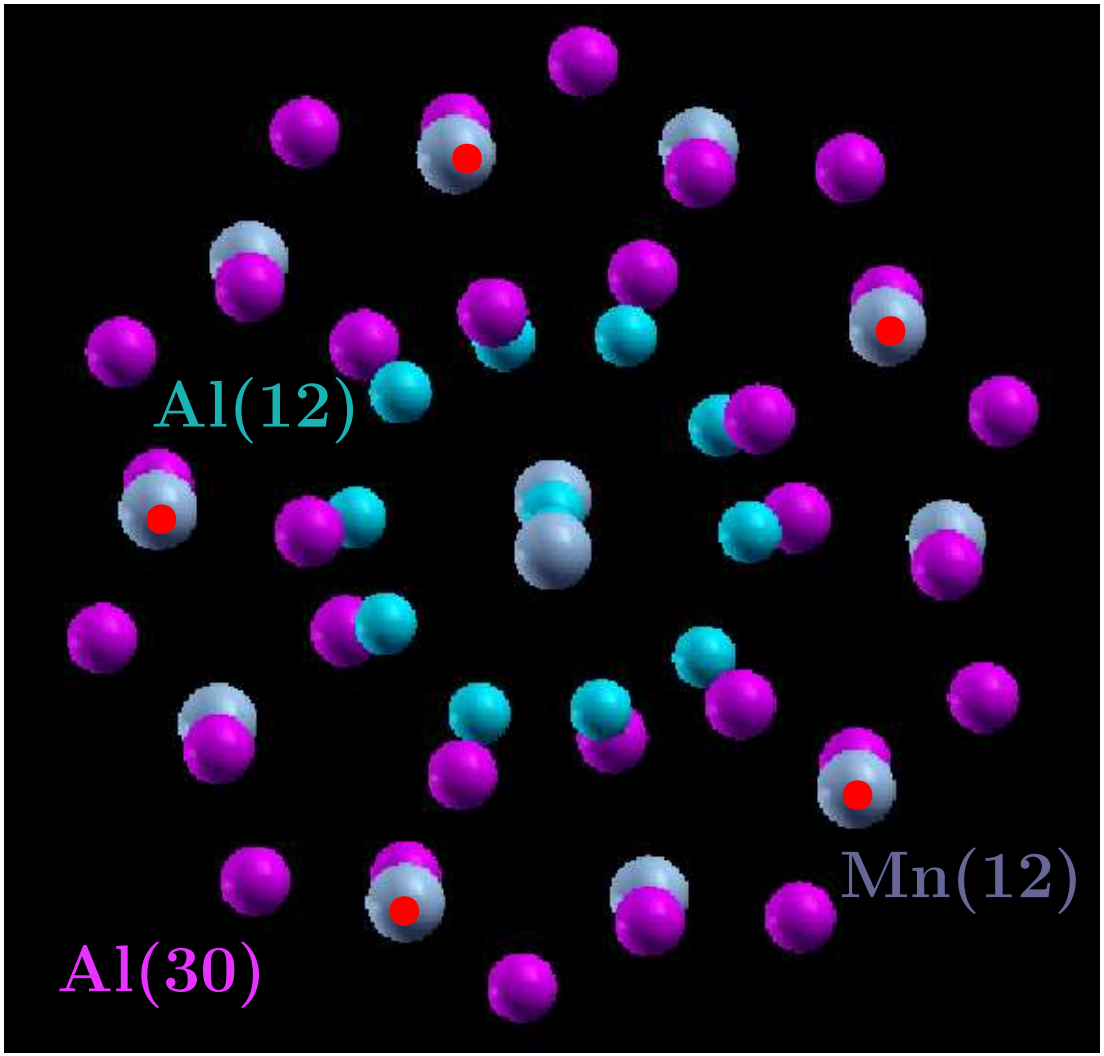
α-AlMn(Si): Mackay icosahedra

Elser-Henley model (1985)

bcc lattice of MI
and 30 Al glue atoms
(114 Al, 24 Mn)/cell



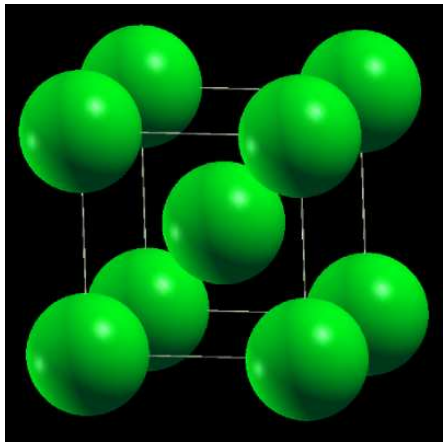
Mackay icosahedron (54 atoms)
center not occupied



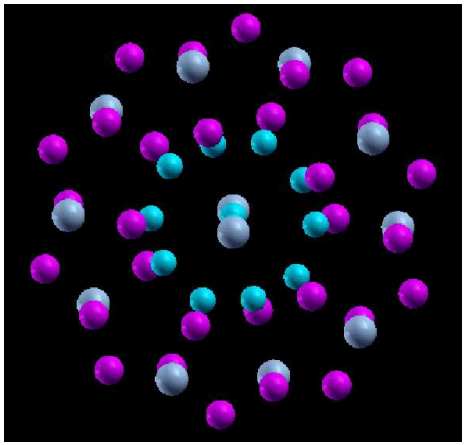
α-AlMn(Si): Planar Mn network

Elser-Henley model (1985)

bcc lattice of MI
and 30 Al glue atoms
(114 Al, 24 Mn)/cell

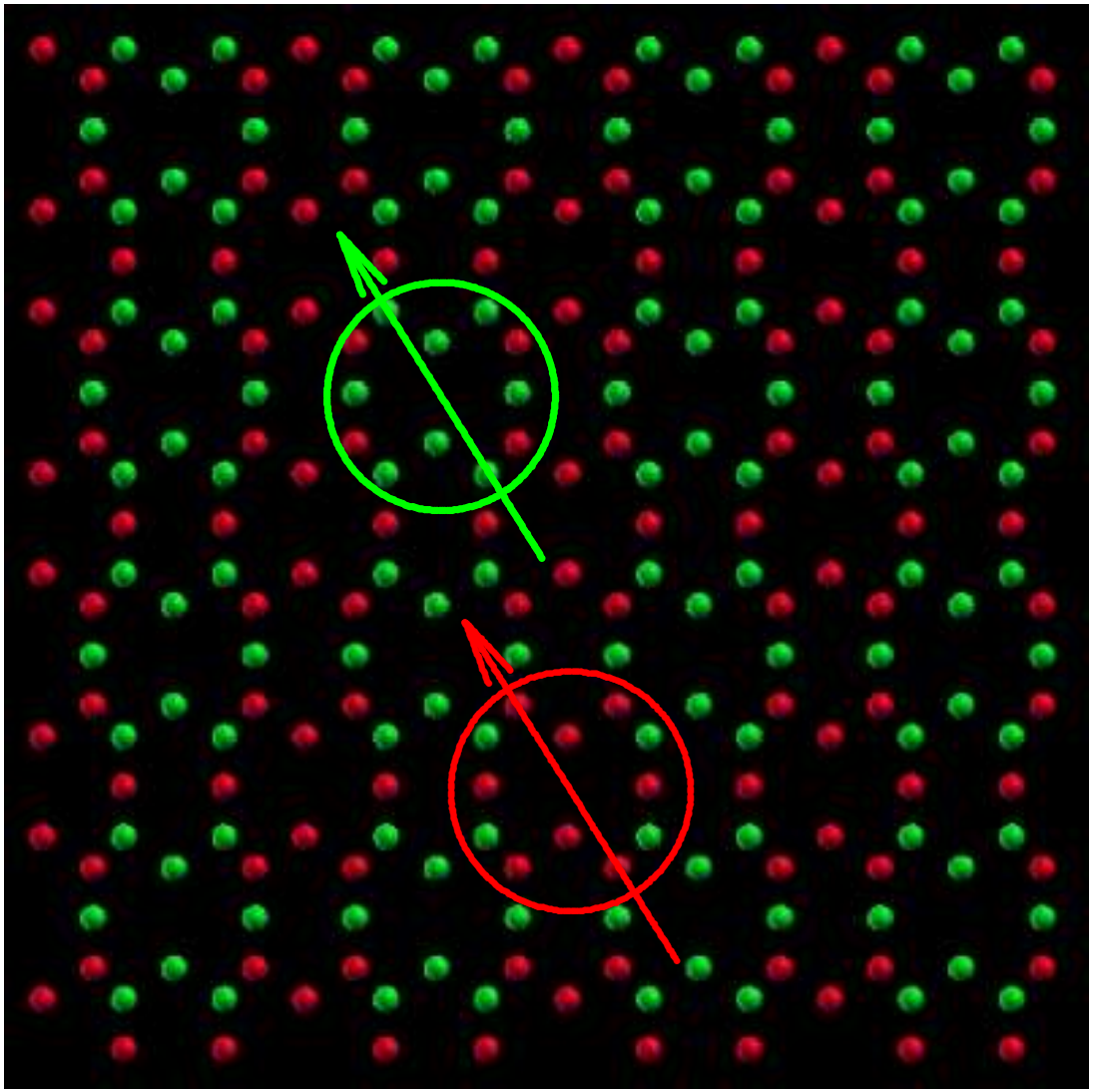


Mackay icosahedron
1st shell (12 Al)
2nd shell (12 Mn, 30 Al)



Mn planes configured by BCC + ICO

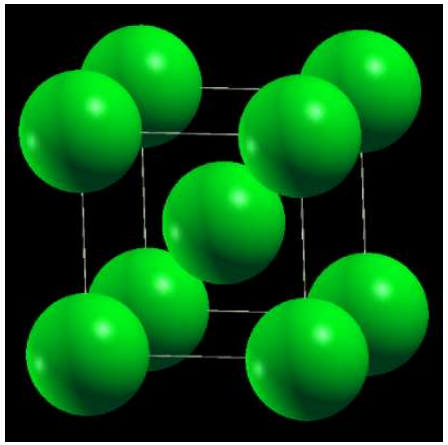
view along (010), Mn from 2 cubic MI-sublattices



α-AlMn(Si): We disturb the planar order of Mn

Elser-Henley model (1985)

bcc lattice of MI
and 30 Al glue atoms
(114 Al, 24 Mn)/cell



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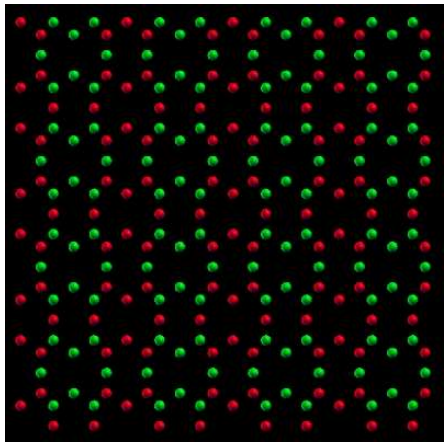

Mackay icosahedron
1st shell (12 Al)
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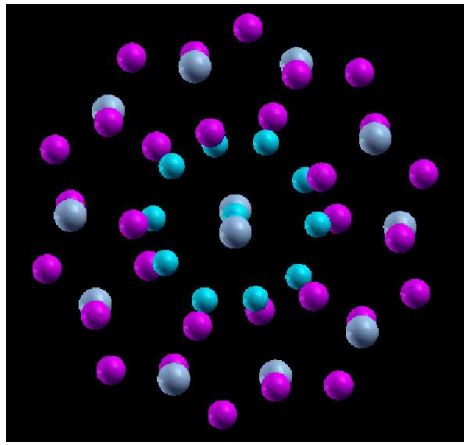
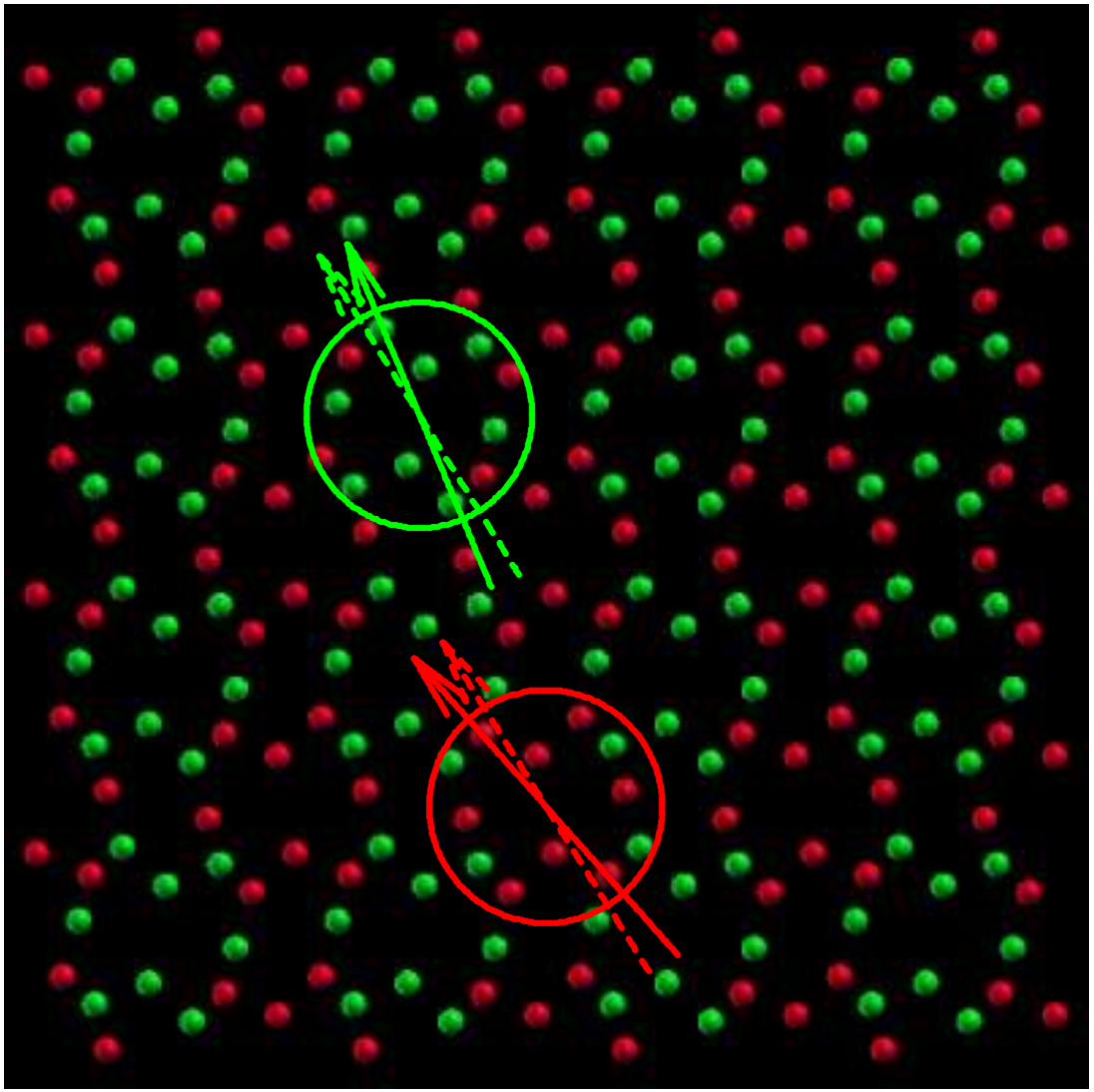


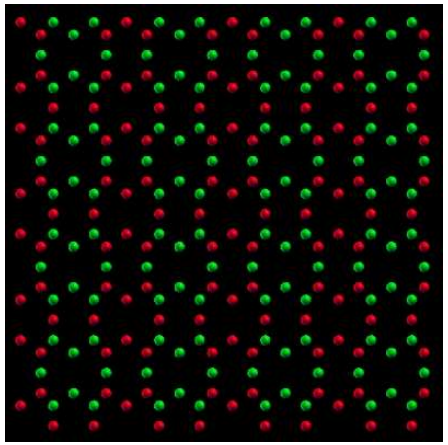
rigid MI tilted $+10^o/-10^o$, axis (010)
planar order decays along (100) and (001)



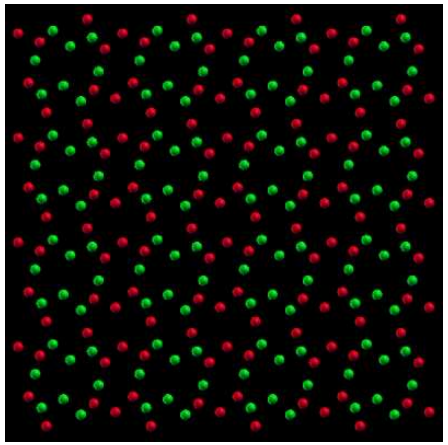
α-AlMn(Si): Does the structure factor change?

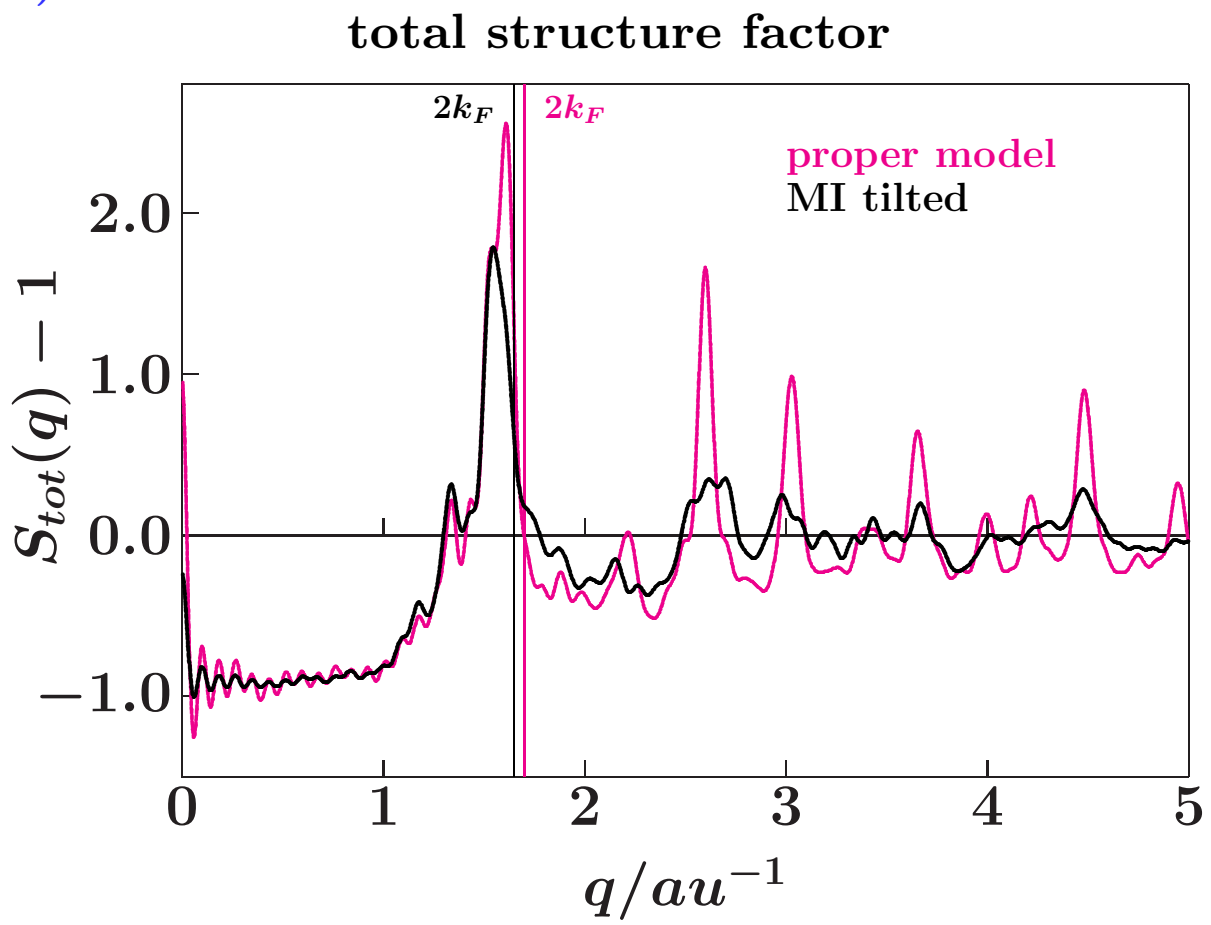
Elser-Henley model (1985)

Mn planes configured
by BCC + ICO



with tilted MI
planar order decays





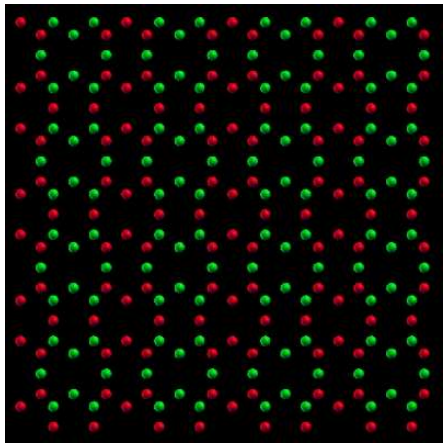
conclusion:

- main diffraction peak less influenced
  $\Longrightarrow$ neighbor-shell sequence also less influenced
  $\Longrightarrow$ s-DOS as well (expected)

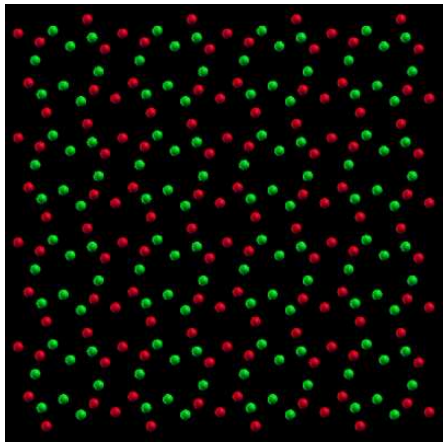
α-AlMn(Si): Does the electronic density of states change?

Elser-Henley model (1985)

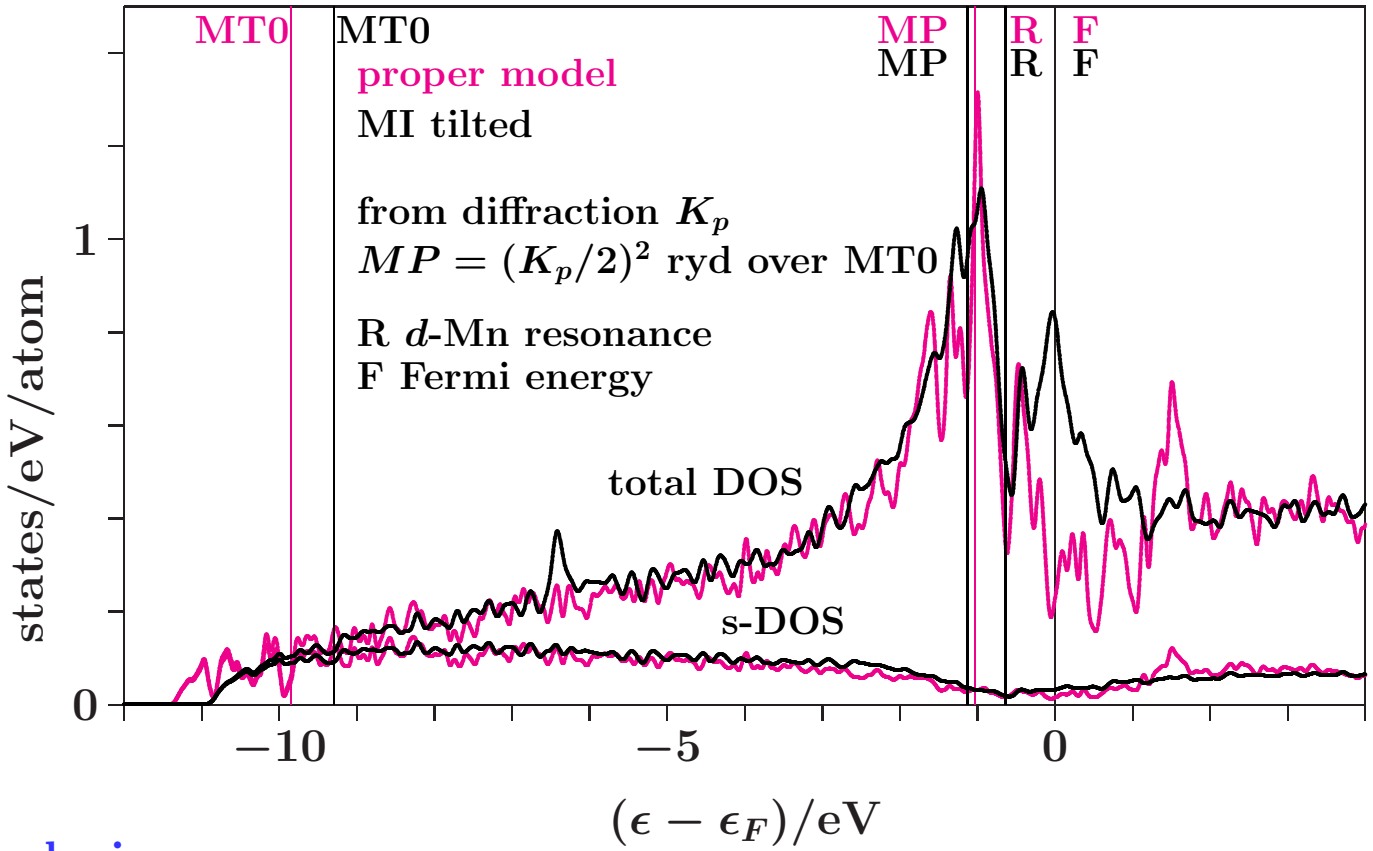
Mn planes configured by BCC + ICO



with tilted MI planar order decays



electronic density of states (DOS)



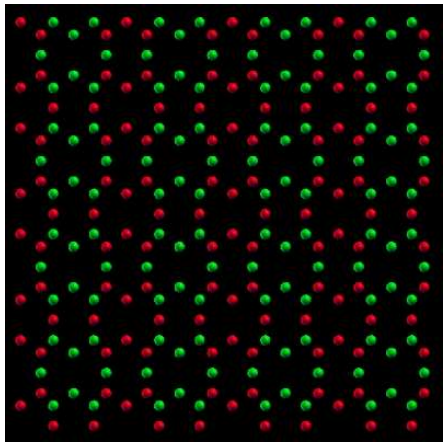
conclusions:

- Mn network destabilized (DOS peak at ϵ_F), s-DOS (neighbor shell sequence) not sensitive about tilting MI
- two competing principles for stable atomic arrangements: neighbor-shell order (weak sp scattering) and network order (strong d scattering)

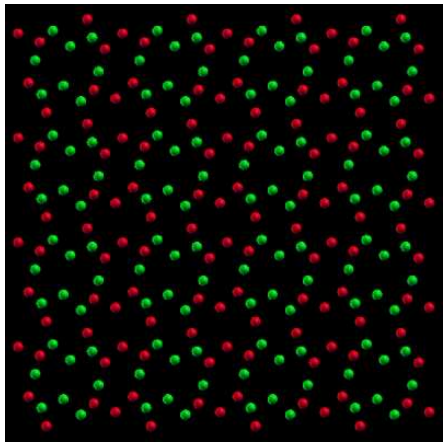
A slab of α-AlMn(Si): Does the resistance change?

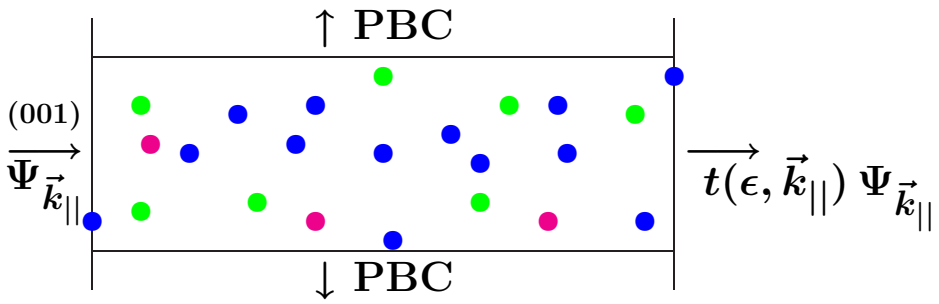
Landauer resistance per unit area at ϵ_F (slab thickness 2.8 nm)

Mn planes configured by BCC + ICO



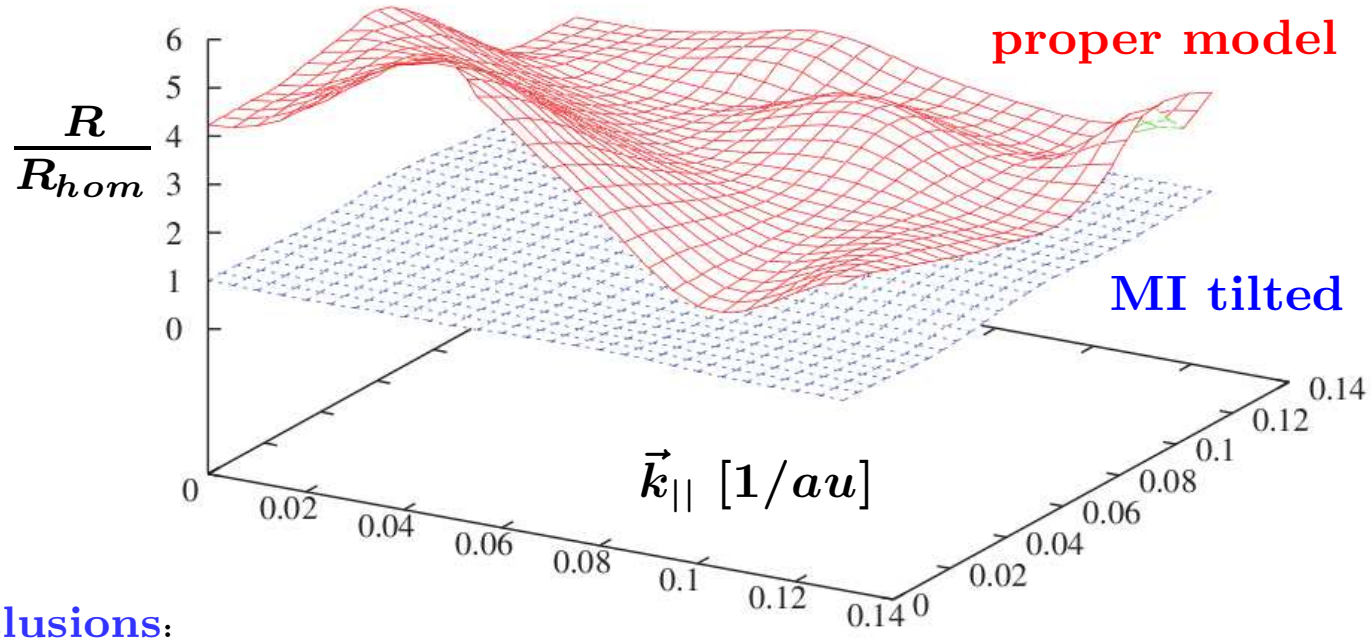
with tilted MI planar order decays





$$R = \left[\frac{2e^2}{h}\, Tr(t^\dagger\, t)\right]^{-1}$$

reference system R_{hom}: homogeneous, 200 $\mu\Omega$cm



conclusions:

- proper model: pronounced dependence on $\vec{k}_{||}$, strong interference
- after tilting MI: resembles a "homogeneous" material

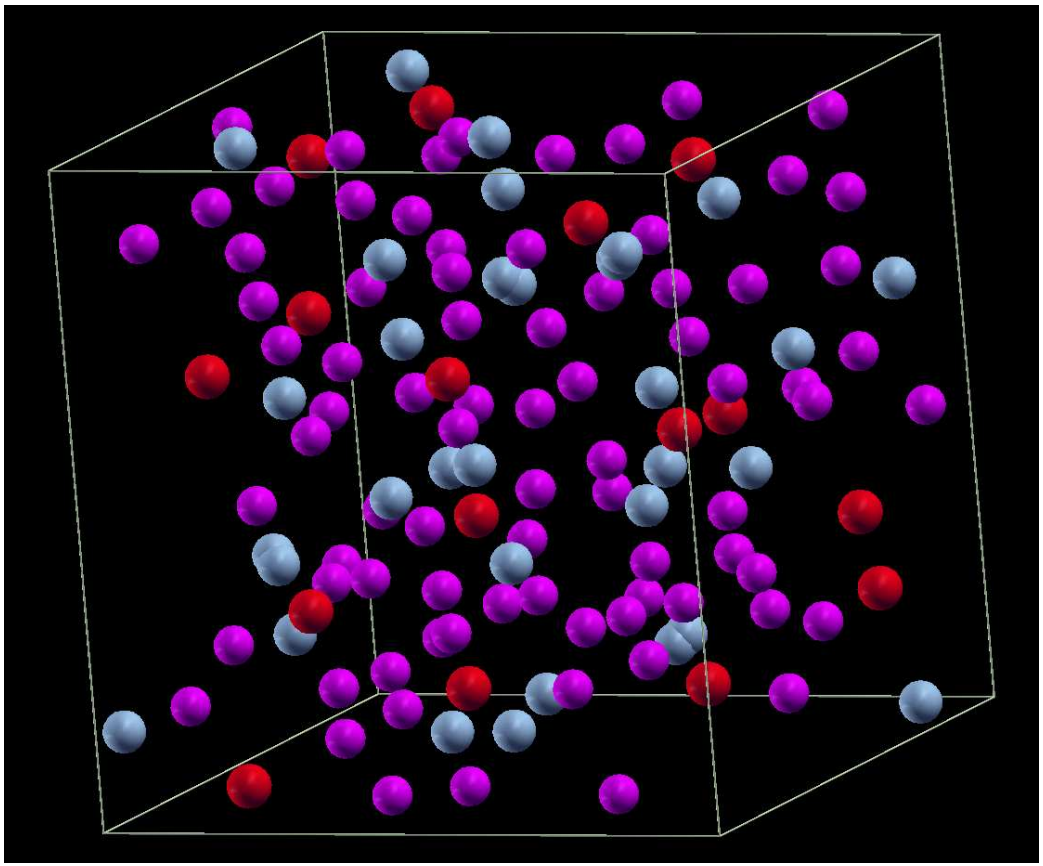
1. spd electron phases
2. α-AlMnSi

3. i-AlCuFe (1/1)

4. Conclusions

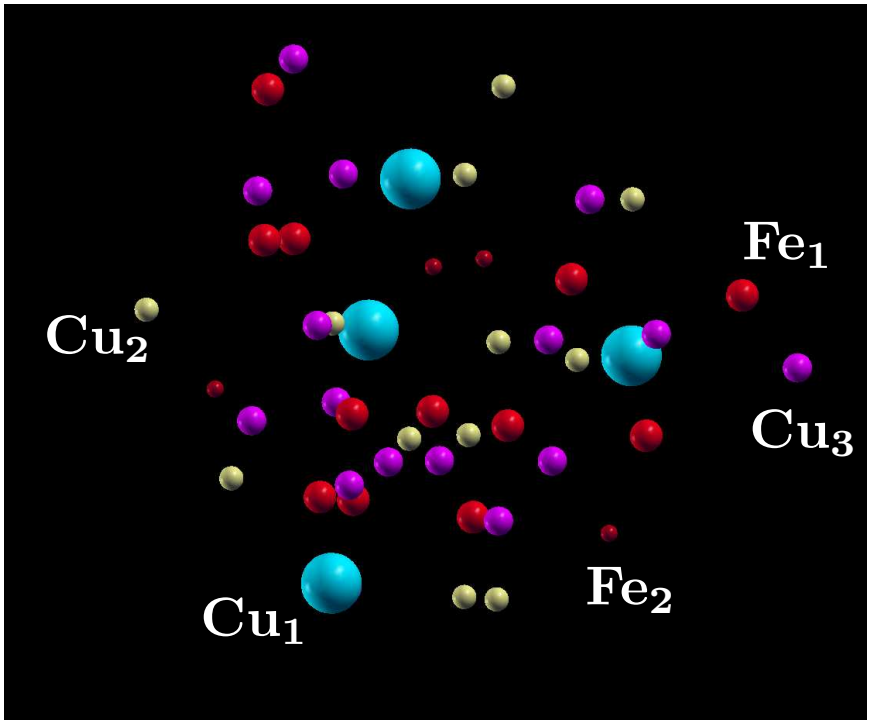
i-AlCuFe-(1/1): 13 types of effective atoms

Cockayne model (1993), the free-atom input:
128 atoms = 80 Al + 32 Cu + 16 Fe



due to different environments
different effective atoms:

8 types Al_{1-8} (not shown) and
4 Cu_1, 12 Cu_2, 16 Cu_3 and
12 Fe_1, 4 Fe_2

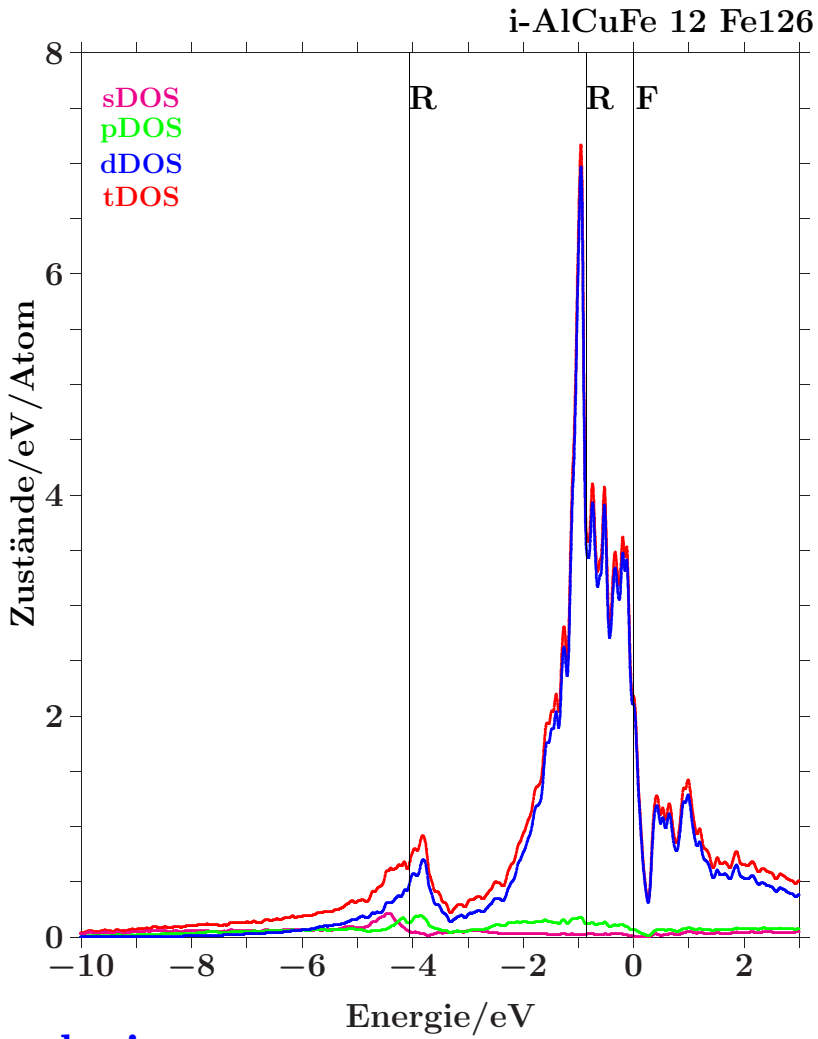


conclusion:

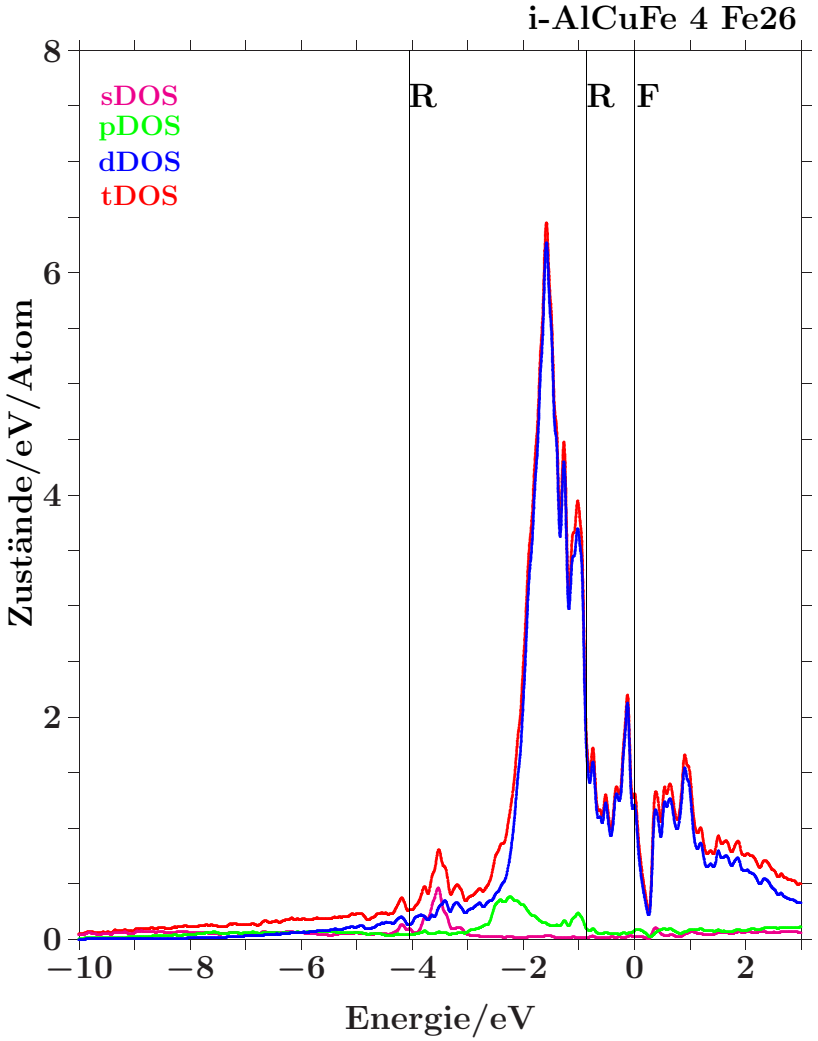
- **Fe_1 close to Cu contrary to Fe_2**

i-AlCuFe-(1/1): More Cu signature at Fe_1 than at Fe_2

DOS at Fe_1



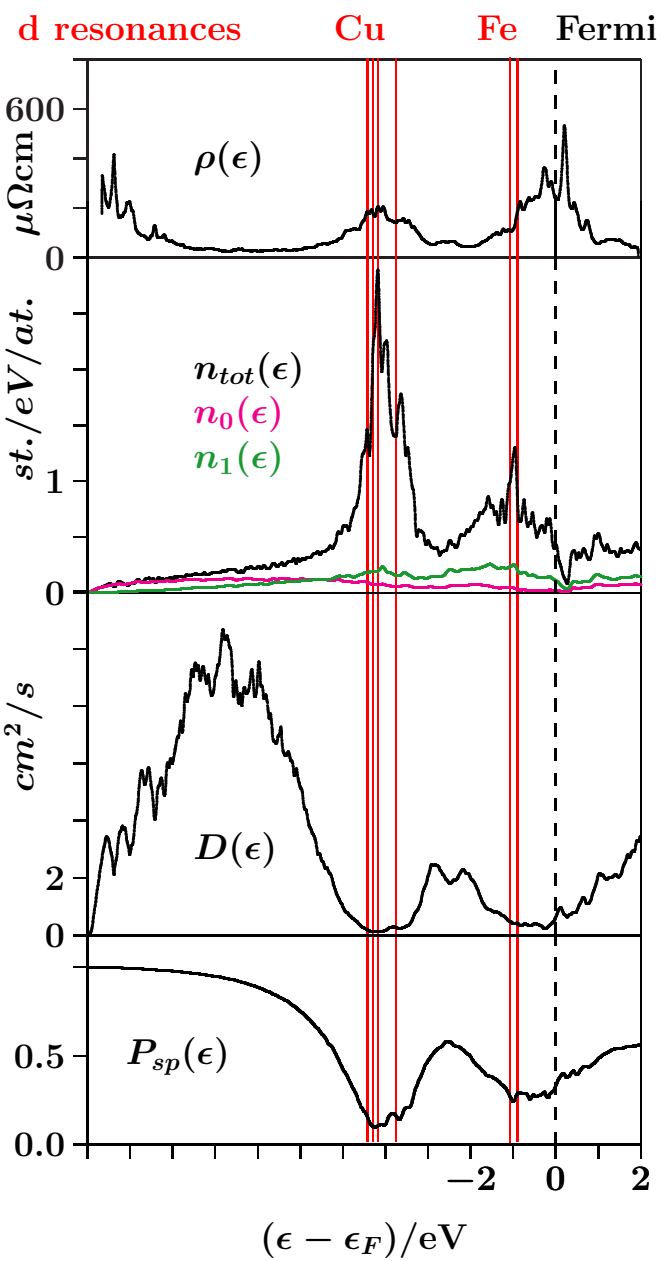
DOS at Fe_2



conclusion:

- **note also: both Fe have Fano profiles at ϵ_F**

i-AlCuFe-(1/1): Spectral curves



structure (Cockayne *et al.* 1993) 128 atoms

spectral resistivity $\rho(\epsilon)$

- 150-meV resistivity peak, thermally stable, aligned with DOS pseudogap

electronic density of states $n(\epsilon)$

- clear signatures of effective-atom d resonances
- Fano profile at ϵ_F

spectral diffusity $D(\epsilon)$

- minimum diffusivity in the d-Cu band

sp content of band states $P_{sp}(\epsilon)$

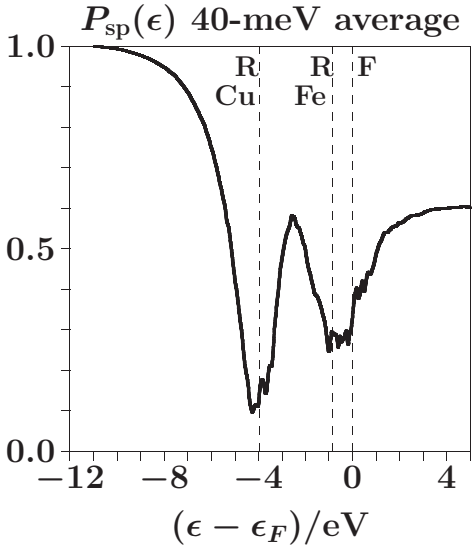
- in the d-Cu band almost pure d-Cu states

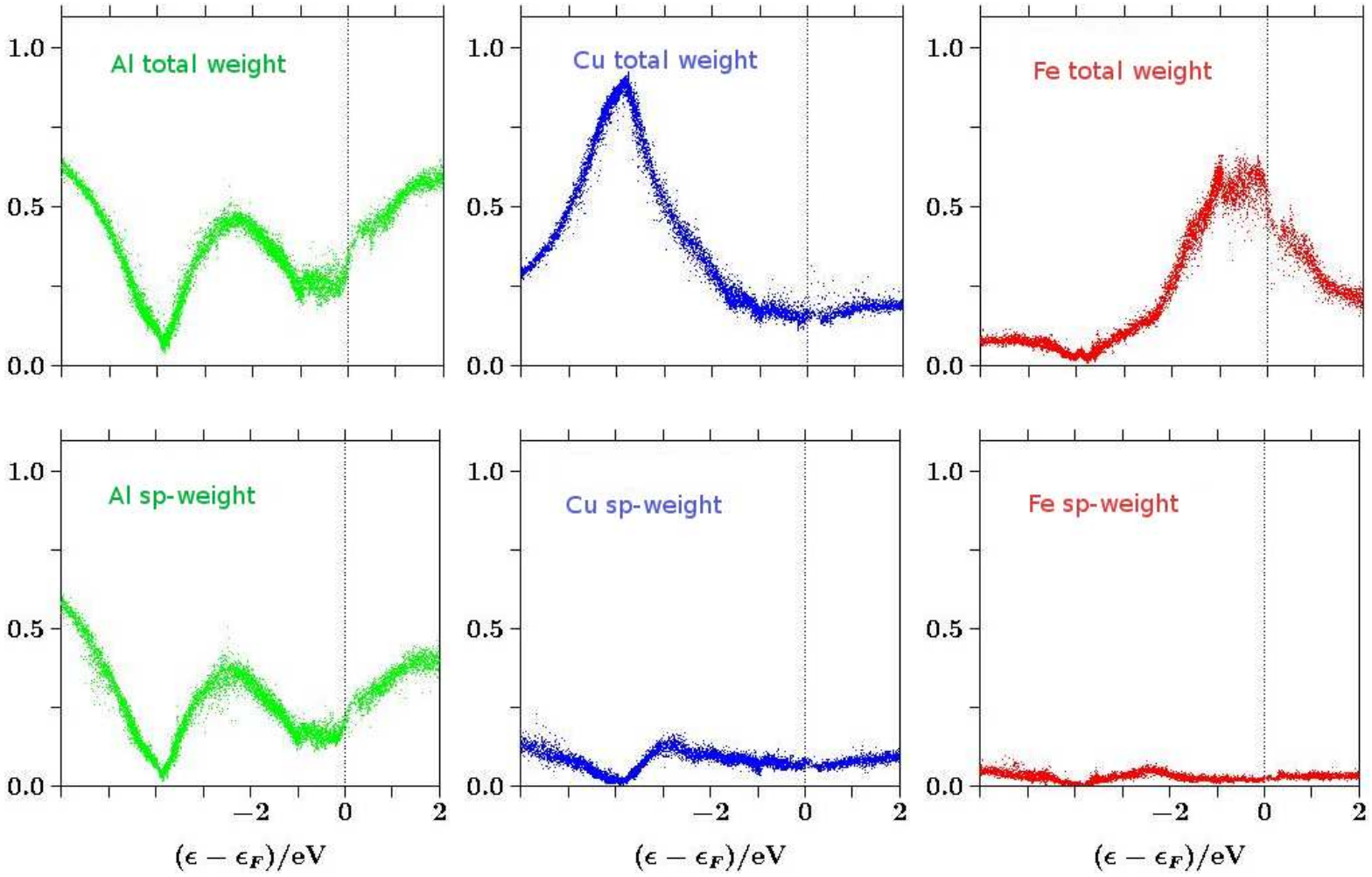
conclusion:

- pronounced spectral fine structures around ϵ_F

i-AlCuFe-(1/1): Decomposition of band states

hybridization status revealed: decomposition with respect to atom / angular momentum





for each band state
a dot

$$\sum_{sl}^{subset} \sum_{m=-l}^{l} |\psi_{slm}|^2$$

conclusion:

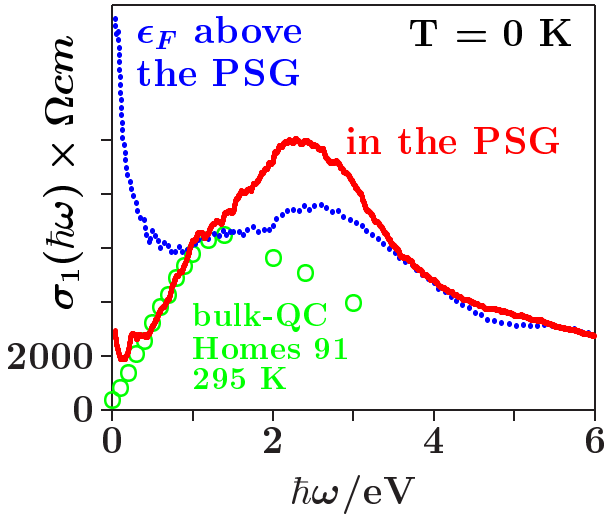
- note the small fluctuation width at given energy
- almost pure *d*-Cu states in the *d*-Cu band, below ϵ_F mainly *d*-Fe and *sp*-Al

i-AlCuFe (1/1): Really approximat of the i-AlCuFe QC ?

ϵ_F in a deep pseudogap (proof: optical conductivity without Drude peak)

$$\sigma_1(\hbar\omega) = \int d\epsilon\, \sigma(\epsilon, \epsilon+\hbar\omega)\, \frac{f^0(\epsilon) - f^0(\epsilon+\hbar\omega)}{\hbar\omega}$$

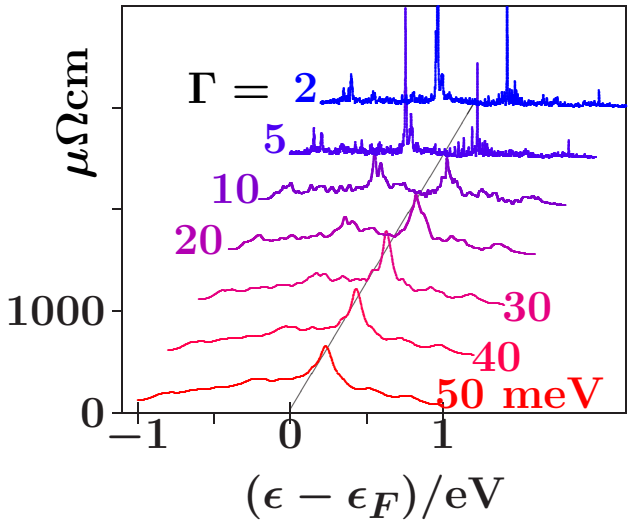
$$\overbrace{\frac{|e|^2 h}{V} \sum_{ij} \langle i|v|j\rangle\langle j|v|i\rangle\, \delta(\epsilon-\epsilon_i)\, \delta(\epsilon+\hbar\omega-\epsilon_j)}$$



only one resistivity peak (pseudogap) is thermally stable

enhanced thermal collision
simulated by Gaussian level broadening (Γ)

scattering time $\tau \approx \frac{\hbar}{\Gamma}$



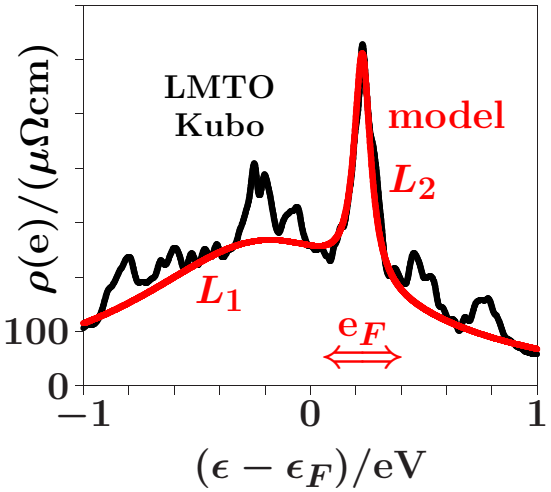
Scaling the spectral resistivity model of the approximant[5]

2 Lorentzians required for the Cockayne model

L_1, width eV, atomic-scale processes
L_2, width 100 meV, cluster-scale processes

$$\rho(\epsilon) = \sigma^{-1}(\epsilon) = A\left[L_1(\epsilon) + \alpha L_2(\epsilon)\right]$$

$$L_j(\epsilon) = \frac{\gamma_j/\pi}{[(\epsilon-(\epsilon_F+\delta_j)]^2+\gamma_j^2}$$



fit A, α, γ_2 to approximate the measured thermopower $S^{exp}(T)$, ρ_{4K}^{exp}

Phase	ρ_{4K}^{exp} $\mu\Omega$ cm	$\frac{\alpha/\gamma_2}{1/\gamma_1}$	A $\mu\Omega$cmeV	δ_1 eV	γ_1 eV	α	δ_2 eV	γ_2 meV
(1/1)-APP[1]	610	1.6	580	-0.2	0.7	0.1	0.23	44
thin film[2]	2333	7.8	1047	-0.2	1.35	0.32	0.23	55
poly[3] $Al_{63}Cu_{25}Fe_{12}$	4957	11	1400	-0.2	1	0.45	0.23	41
poly[3] $Al_{62}Cu_{25.5}Fe_{12.5}$	7241	31	1047	-0.2	1.35	0.98	0.23	43
bulk[4] $Al_{62.5}Cu_{25}Fe_{12.5}$	8078	34	1047	-0.2	1.35	1.0	0.23	40

[1] Cockayne *et al.* 93, [2] C. Madel 00, [3] Bilušić *et al.* 01, [4] Pierce *et al.* 93, [5] Landauro *et al.* 01

conclusion:

high 4K-resistivity if the small Lorentian predominates

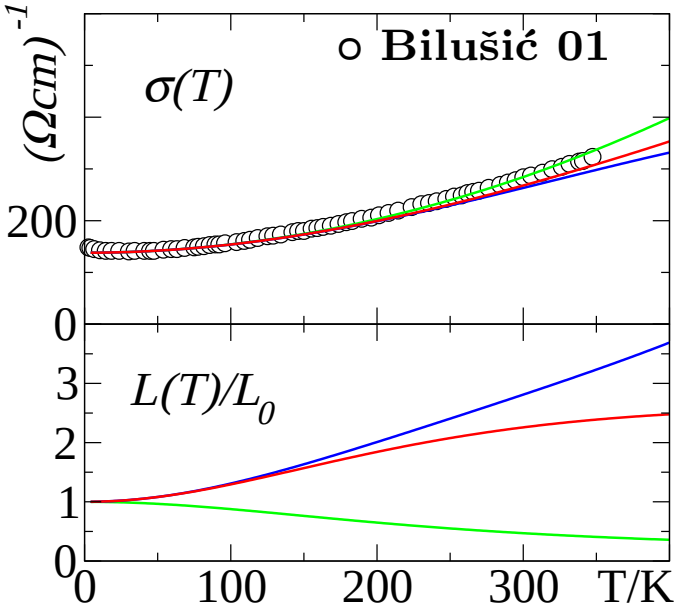
Application to the poly-quasicrystal i-$Al_{62}Cu_{25.5}Fe_{12.5}$

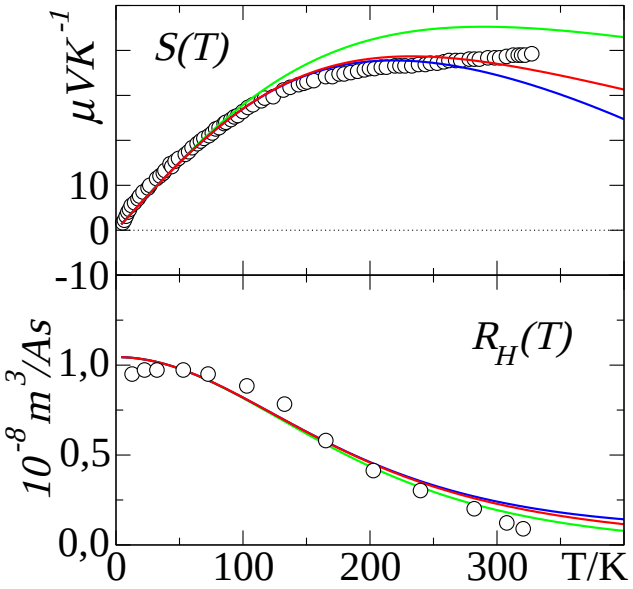
elec. cond. $\sigma(T) = \mathcal{L}^{11}(T)$ **therm. cond.** $K(T) = \frac{\mathcal{L}^{22}(T)}{|e|^2 T} - T\sigma(T)\, S(T)^2$

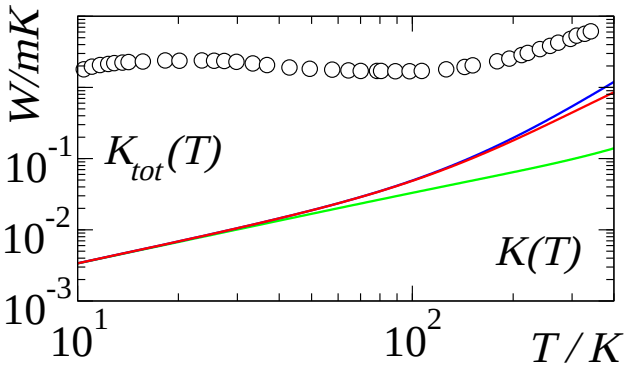
thermopower $S(T) = \frac{1}{|e|T}\frac{\mathcal{L}^{12}(T)}{\sigma(T)}$ **Lorenz number** $L(T) = \frac{K(T)}{T\,\sigma(T)}, L_o = \left(\frac{k_B}{e}\right)^2 \frac{\pi^2}{3}$

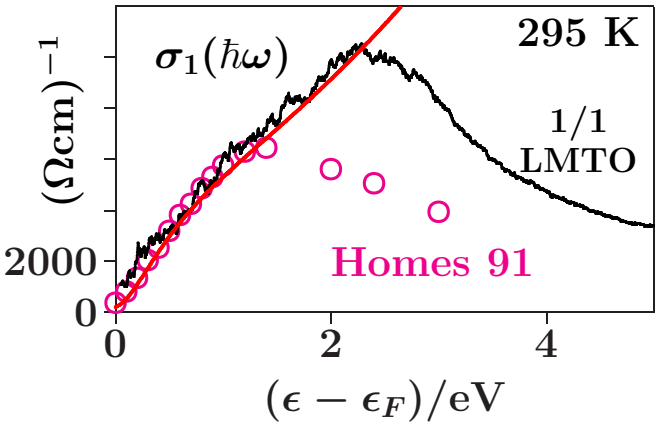
Hall coefficient $R_H(T) = \frac{|e|}{\sigma(T)^2}\int d\epsilon \left(-1.13\times 10^{-5}\mathrm{Am}^2\, \frac{d}{d\epsilon}\widehat{\sigma}(\epsilon)\right)\left(-\frac{\partial f^0(\epsilon,\mu,T)}{\partial \epsilon}\right)$

with kinetic coefficients $\mathcal{L}^{ij}$ integrated numerically, expanded up to T^4 or T^6









$$\widehat{\sigma}(\epsilon, \epsilon+\hbar\omega) \approx 1.8\sqrt{\widehat{\sigma}(\epsilon)\,\widehat{\sigma}(\epsilon+\hbar\omega)}$$

General Conclusions

Properties of complex alloys depend substantially on the
electron-ion interrelations
in the medium order range (nanometers).

Complex Al-TM alloys demonstrate that a general neighbor-shell order
can coexist
with a TM-based network order.

Shell order is mainly supported by
FE-like band electrons
whereas
***d*-TM hybridized band electrons**
support network order.

Shell order forms spectral structures on the
1-eV scale
whereas those on the
0.1-eV scale
are due to network order.