European Network of Exellence

European School in Materials Science

The Hume-Rothery rules for Structurally Complex Alloy Phases

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Complex Metallic Alloys: Surfaces and Coatings
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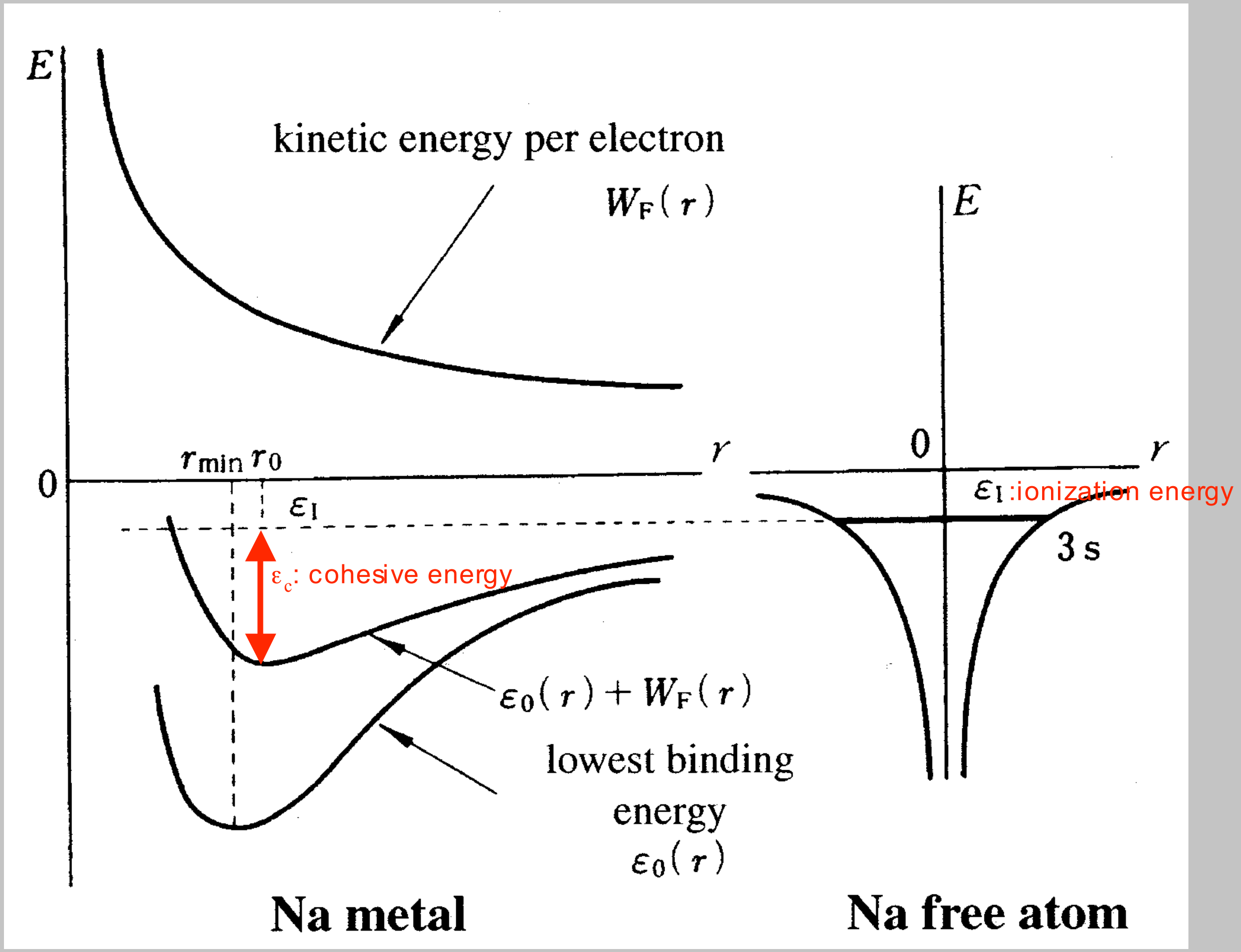
OUTLINE

1. Prior fundamental knowledge for the discussion of phase competition in CMAs
2. What is the Hume-Rothery electron concentration rule?
3. Two different definitions of electron concentration: VEC versus e/a
4. Historical survey
5. Why do we need the first-principles FLAPW band calculations?
6. Why have we chosen a series of gamma-brasses?
7. Hume-Rothery stabilization mechanism
8. Different stabilization mechanisms in Al_8V_5 and Ag_5Li_8 gamma-brasses
9. Stability mechanism in the Al-TM-Cu-Si (TM=Fe and Ru) approximants
10. $2k_F$ versus K_p condition. Issues on VEC versus e/a. Which is more critical parameter to discuss the phase stability of CMA phases?

Concept of a cohesive energy in a solid



The curve $\varepsilon_o(r)$ represents the lowest energy of electrons with the wave vector **k**=0 while the curve ε_{kin} represents an average kinetic energy per electron. ε_I represents the ionization energy needed to remove the outermost 3s electron in a free Na metal to infinity and ε_c is the cohesive energy. The position of the minimum in the cohesive energy gives an equilibrium interatomic distance r_o.

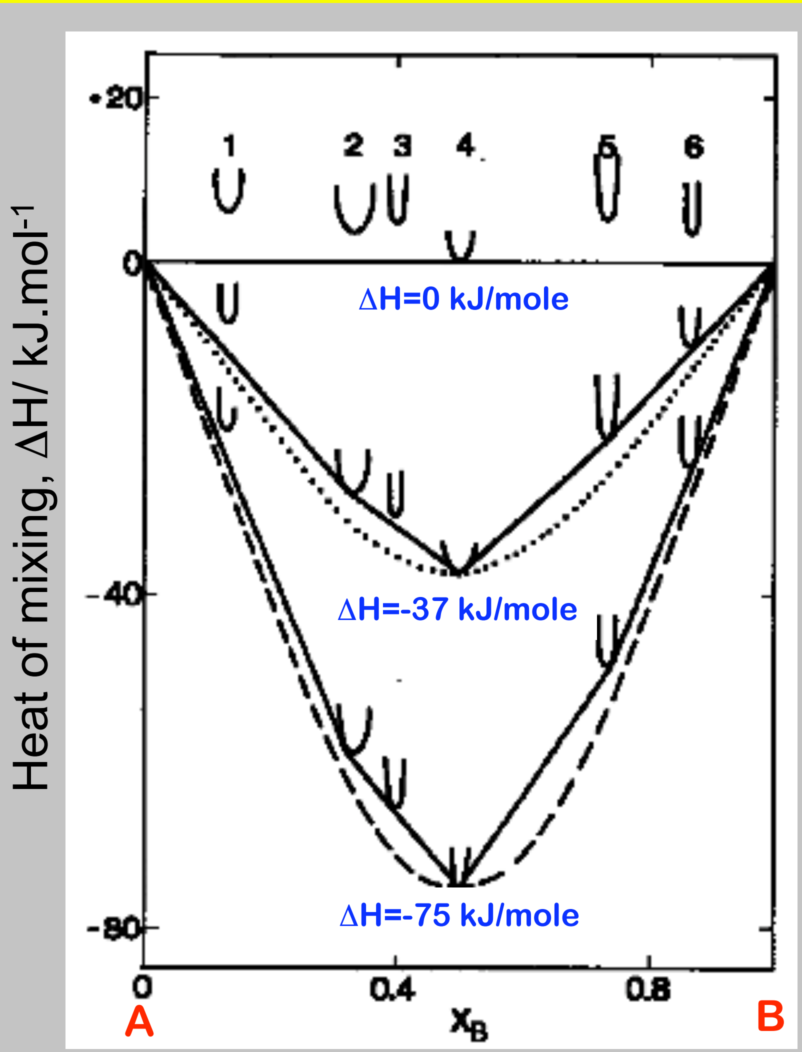
Cohesive energies (kJ/mole) of elements in periodic table

Li 159	Be 322											B 561	C 711	N 477	O 251	F 84	Ne 2.1
Na 108	Mg 148											Al 322	Si 448	P 332	S 277	Cl 135	Ar 7.7
K 91	Ca 176	Sc 379	Ti 469	V 511	Cr 396	Mn 288	Fe 414	Co 424	Ni 428	Cu 338	Zn 130	Ga 269	Ge 374	As 289	Se 206	Br 118	Kr 11
Rb 83	Sr 164	Y 423	Zr 610	Nb 720	Mo 658	Tc	Ru 639	Rh 555	Pd 380	Ag 286	Cd 112	In 247	Sn 301	Sb 259	Te 193	I 107	Xe 15
Cs 80	Ba 179	La 434	Hf 611	Ta 781	W 837	Re 782	Os 783	Ir 670	Pt 565	Au 365	Hg 67	Tl 181	Pb 197	Bi 208	Po 144	At	Rn
Fr	Ra	Ac															

Ce 460	Pr 373	Nd 323	Pm	Sm 203	Eu 174	Gd 399	Tb 393	Dy 297	Ho 293	Er 322	Tm 247	Yb 151	Lu 427
Th 572	Pa 527	U 522	Np 440	Pu 385	Am 251	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Cohesive energy represent an energy needed to separate all atoms in a solid at absolute zero into the assembly of neural atoms. The values underlined refer to those either at 298.15 K or at the melting point. The values are in the units of kJ/mole converted from the values in the units of cal/mole. C.Kittel, “Introduction to Solid State Physics”, (Third Edition, John Wiley & Sons, New York, 1967), Chapter 3.

The number of intermediate phases increases, as ΔH at x_B=0.5 increases. Neighboring phases are competing within ±10kJ/mole.



The number of intermediate phases increases from unity up to five as the heat of mixing increases in a negative direction from zero, -37 and -75 kJ/mole in A-B binary system. [F.R.de Boer, R.Boom, W.C.M.Mattens, A.R.Miedema and A.K.Niessen, “Cohesion in Metals”, (North-Holland 1988)]

Electron theory of metals is an essential ingredient to deepen understanding of an alloy phase competition

The free electron model

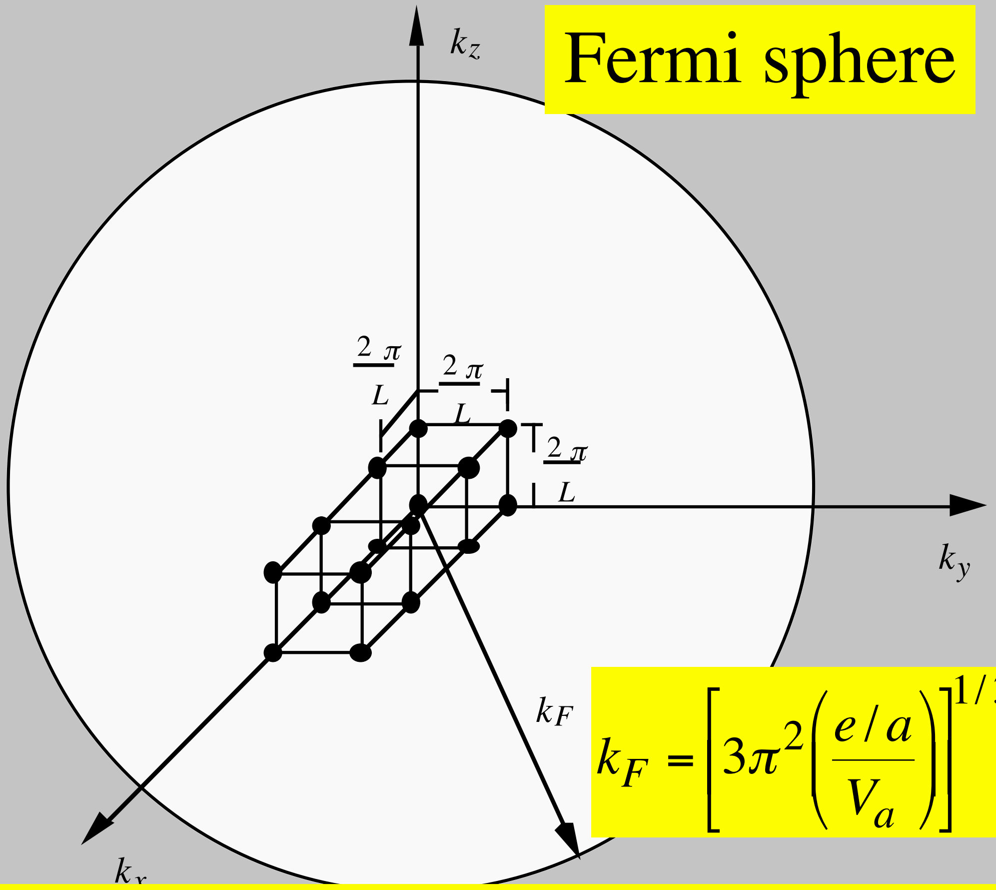
$$-\left(\frac{\hbar^2}{2m}\right)\nabla^2\psi = E\psi$$

$$E = \left(\frac{\hbar^2}{2m}\right)(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}$$

$\psi = e^{i\vec{k}\cdot\vec{r}}$ plane wave

$$k_x = \frac{2\pi n_x}{L} \qquad (n_x = 0, \pm 1, \pm 2, \pm 3 \cdots)$$

Fermi sphere



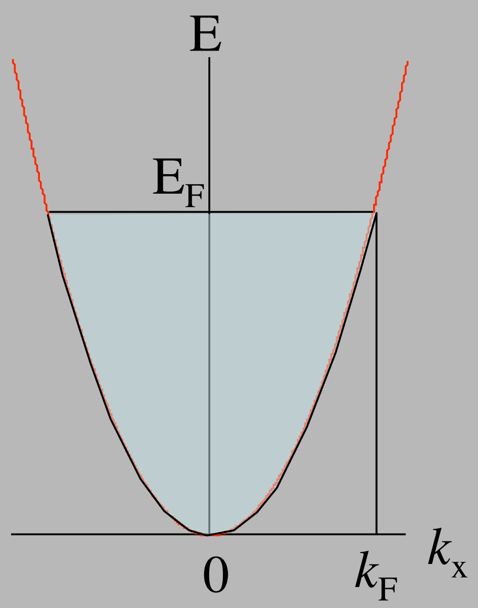
$$k_F = \left[3\pi^2\left(\frac{e/a}{V_a}\right)\right]^{1/3}$$

e/a: electron concentration defined as an average valency of constituent atoms in an alloy.

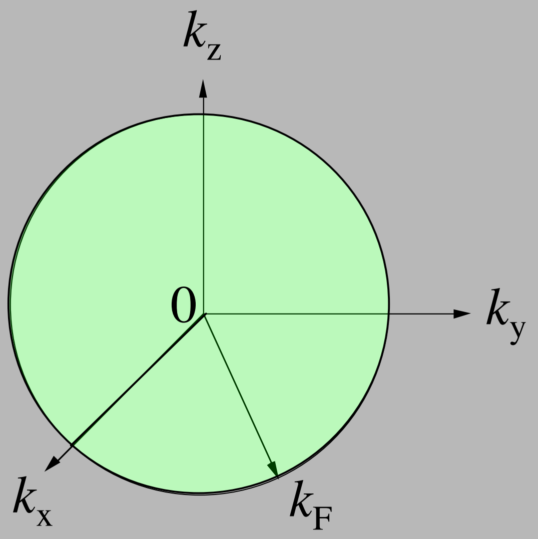
Construction of the Fermi sphere. The reciprocal space is quantized in units of $2\pi/L$ in the k_x-, k_y- and k_z-directions and is made up of cubes with edge length $2\pi/L$ as indicated in the figure. Electrons of up and down spins occupy the corner of each cube or integer set (n_x, n_y, n_z) in accordance with the Pauli principle while making $n_x^2+n_y^2+n_z^2$ as low as possible. The sphere with radius k_F represents the Fermi sphere.

Three representations for the description of the electronic structure

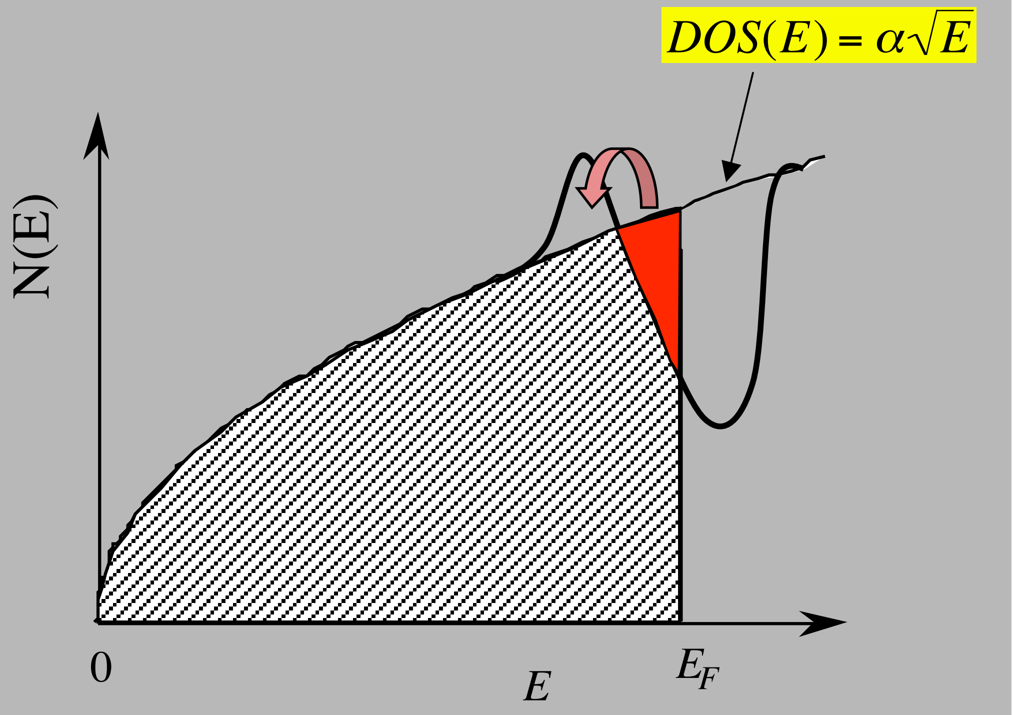
E-k relations (dispersion relation)



Fermi surface



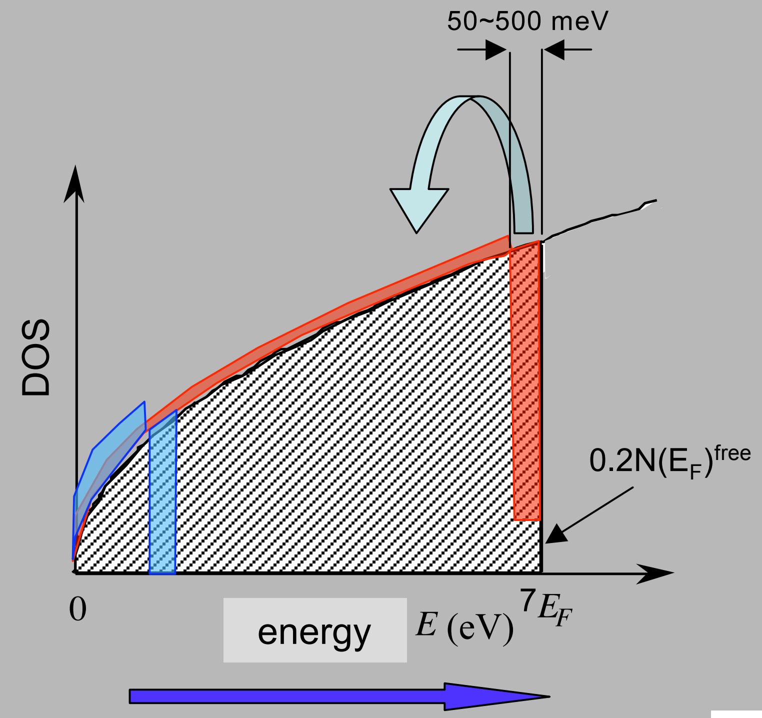
Density of states (DOS)


$DOS(E) = \alpha\sqrt{E}$

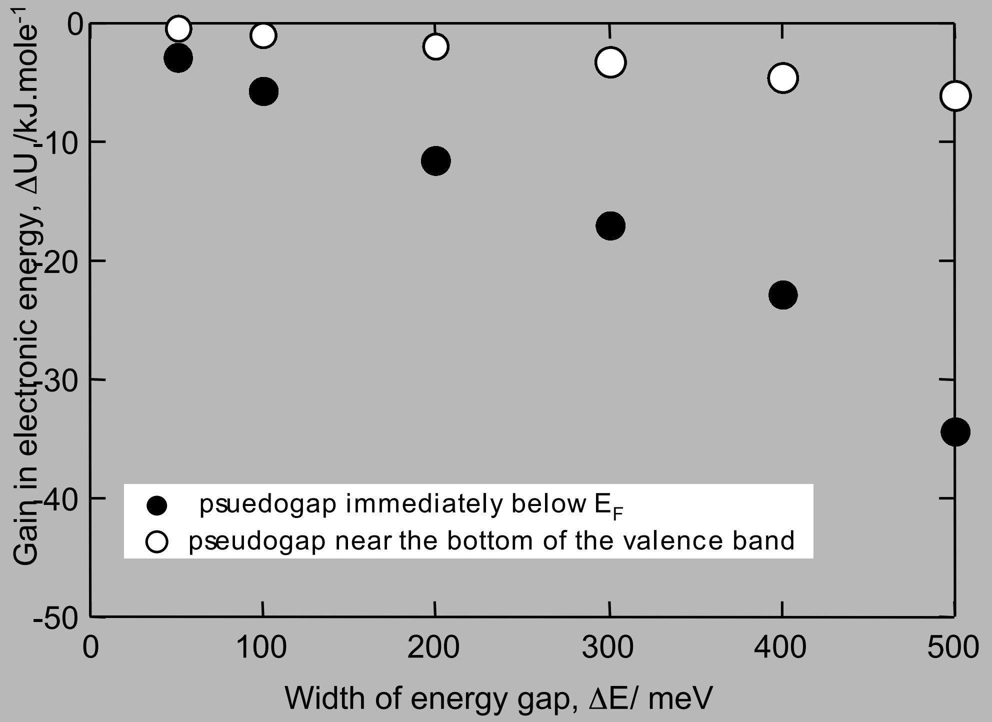
Departure from the free electron model

Nature tries to lower the electronic energy of a system by expelling electrons at the Fermi level. This is nothing but the formation of a true or pseudogap at the Fermi level, as indicated above.

A gain in the electronic energy amounts to several 10 kJ/mol, which is large enough to stabilize a given phase among competing phases



Kinetic energy increases in this direction and becomes the maximum at the Fermi level.



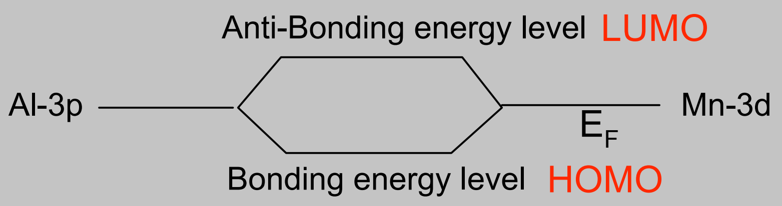
Examples to stabilize a system by formation of (pseudo)gap at E_F

1. A structurally complex phase by increasing the number of atoms in a unit cell
2. A superconductor by forming the superconducting gap
3. A quasi-one-dimensional organic molecular metal by introducing new modulations through deformation of the lattice. This is known as the Peierls transition.

What about the mechanism for the formation of the pseudogap?

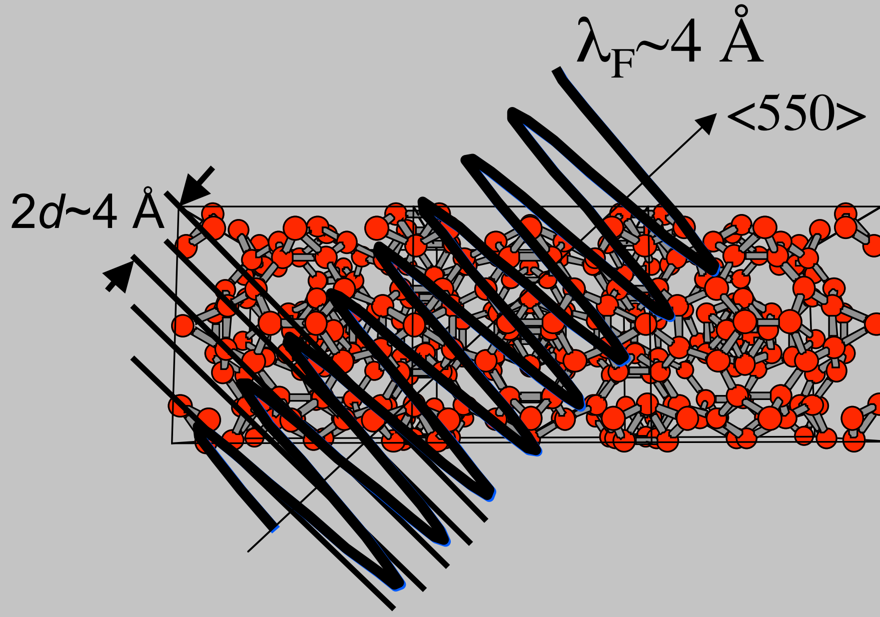
Covalent bondings⇒orbital hybridization between neighboring atoms
Metallic bonding (FsBz interaction)⇒long-range interaction throughout a crystal

Orbital hybridizations



Orbital hybridization effect would occur not only in crystals but also in non-crystalline systems like liquid metals and amorphous alloys.

Fermi surface-Brillouin zone (FsBz) interaction



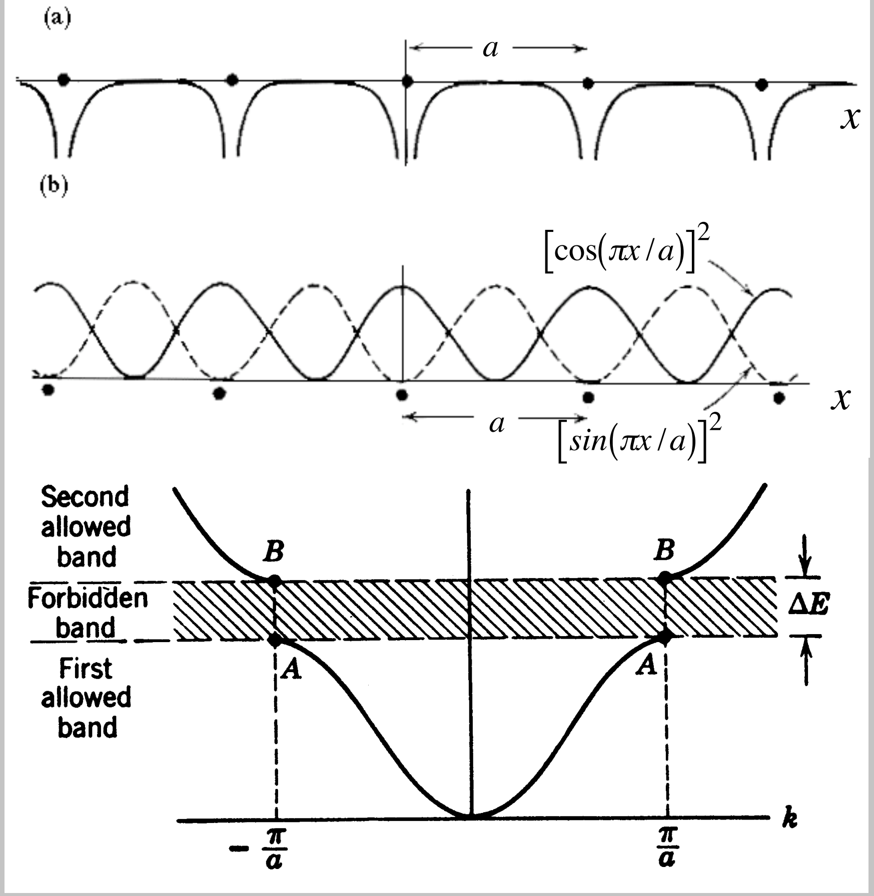
Electrons having the wave length λ_F resonate with a set of lattice planes with lattice spacing 2d.

The FsBz interaction is unique in well-ordered systems like crystals and quasicrystals

$$\lambda_F = \frac{2\pi}{k_F} \propto \frac{1}{(e/a)^{1/3}}$$

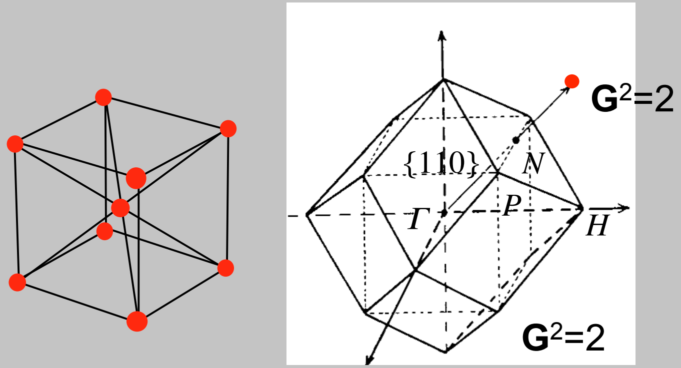
The concept of the Brillouin zone

Stationary waves are formed and an energy gap opens, when the electron wave length matches the lattice periodicity.

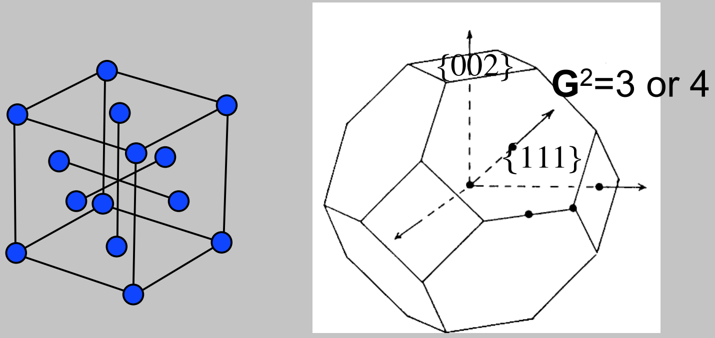


The Brillouin zone is a polyhedron bounded by planes, which are formed by perpendicularly bisecting the relevant reciprocal lattice vectors like **G**=<110> in the reciprocal space. An energy gap opens across each zone face.

I. bcc, N=2, dodecahedron with 12 zone faces

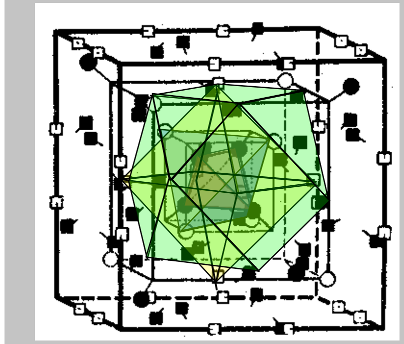


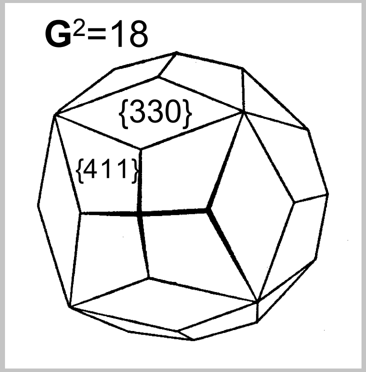
II. fcc, N=4, truncated octahedron with 14 zone faces



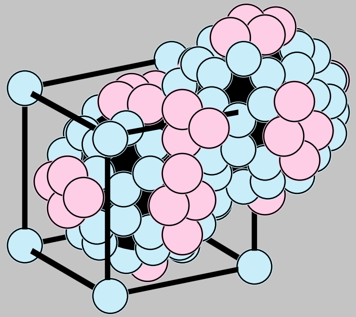
The Brillouin zone of Three Complex Alloy Phases

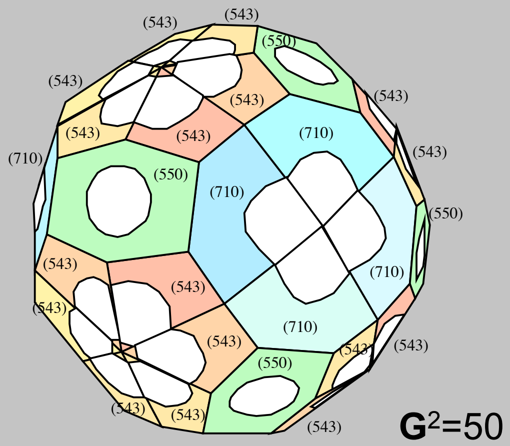
I. gamma-brass, N=52, polyhedron with 36 planes



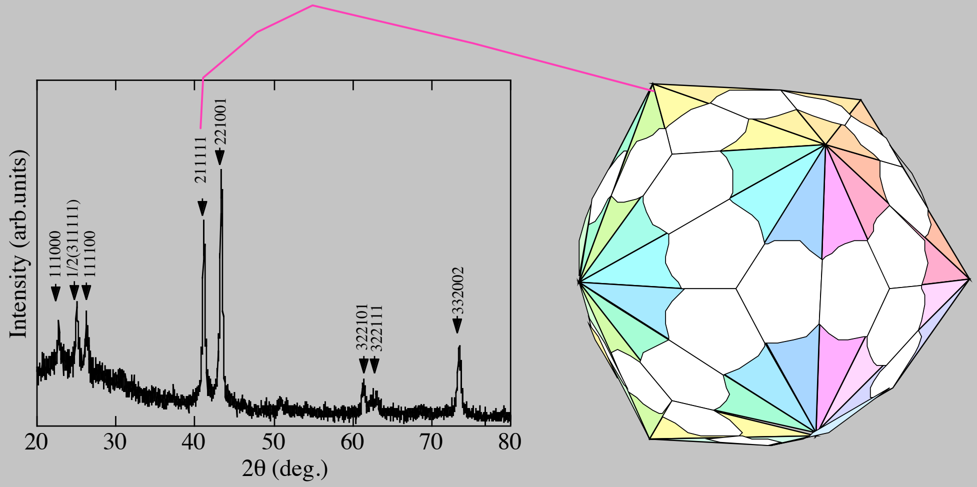


II. 1/1-1/1-1/1 approximant, N=160, polyhedron with 84 planes





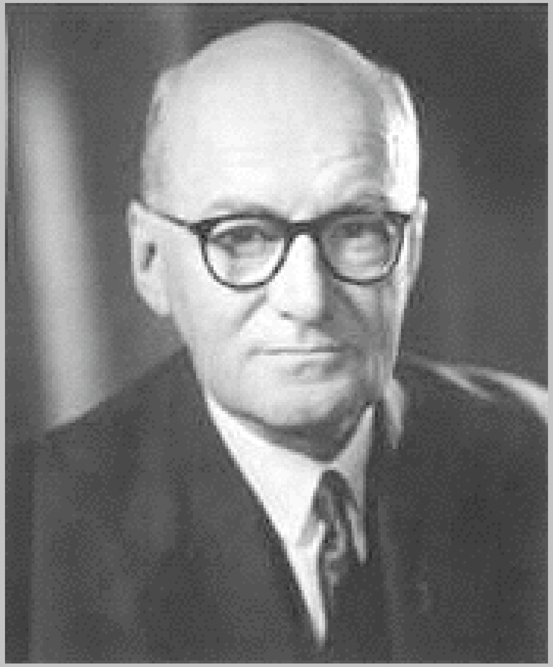
III. Quasicrystal, N is infinite, polyhedron with 60 planes



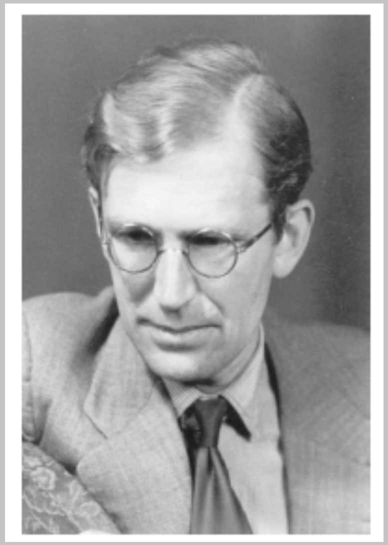
The larger the number of atoms in the unit cell, the more the number of zone faces, across which an energy gap opens. This in turn results in a deeper pseudogap on the DOS. As a result, the electronic energy can be more efficiently lowered by increasing the number of atoms in the unit cell.

What is the Hume-Rothery electron concentration rule？

Hume-Rothery (1926) pointed out a tendency for a definite crystal structure to occur at a particular *electron concentration e/a*. Mott and Jones (1936) made its first interpretation in terms of the Fermi surface-Brillouin zone interaction on the basis of the nearly free electron model.

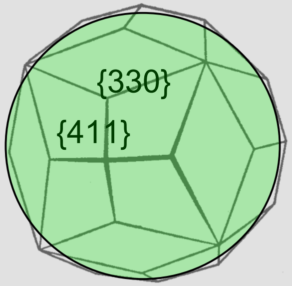


William Hume-Rothery (1899-1968)



N.F.Mott (1905-1996)

H.Jones (1905-1986)



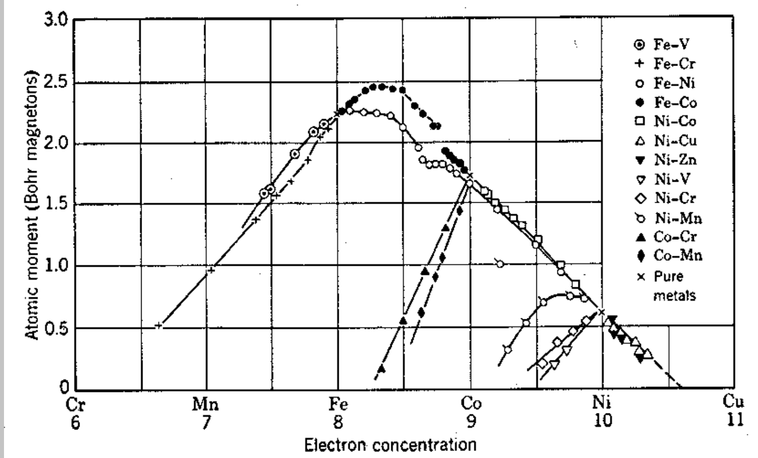
There exist two different definitions for electron concentration:

e/a versus VEC

Various physical properties fall on a universal curve, when plotted against the VEC (number of electrons per atom in the valence band)

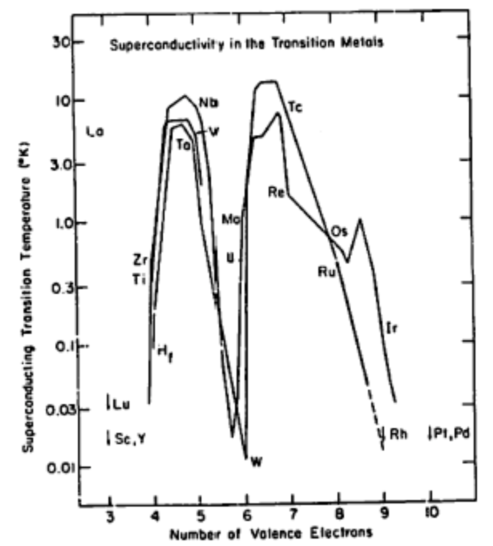
Slater-Pauling curves

Saturation magnetization against VEC



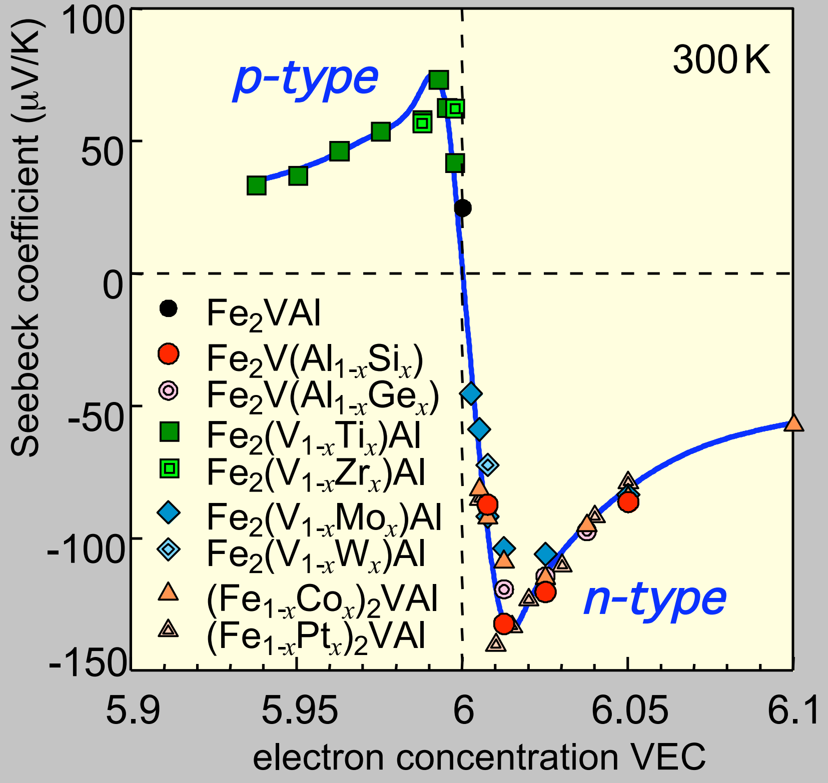
Matthias rule

Superconducting transition temperature against VEC



p- and n-type thermoelectric alloys

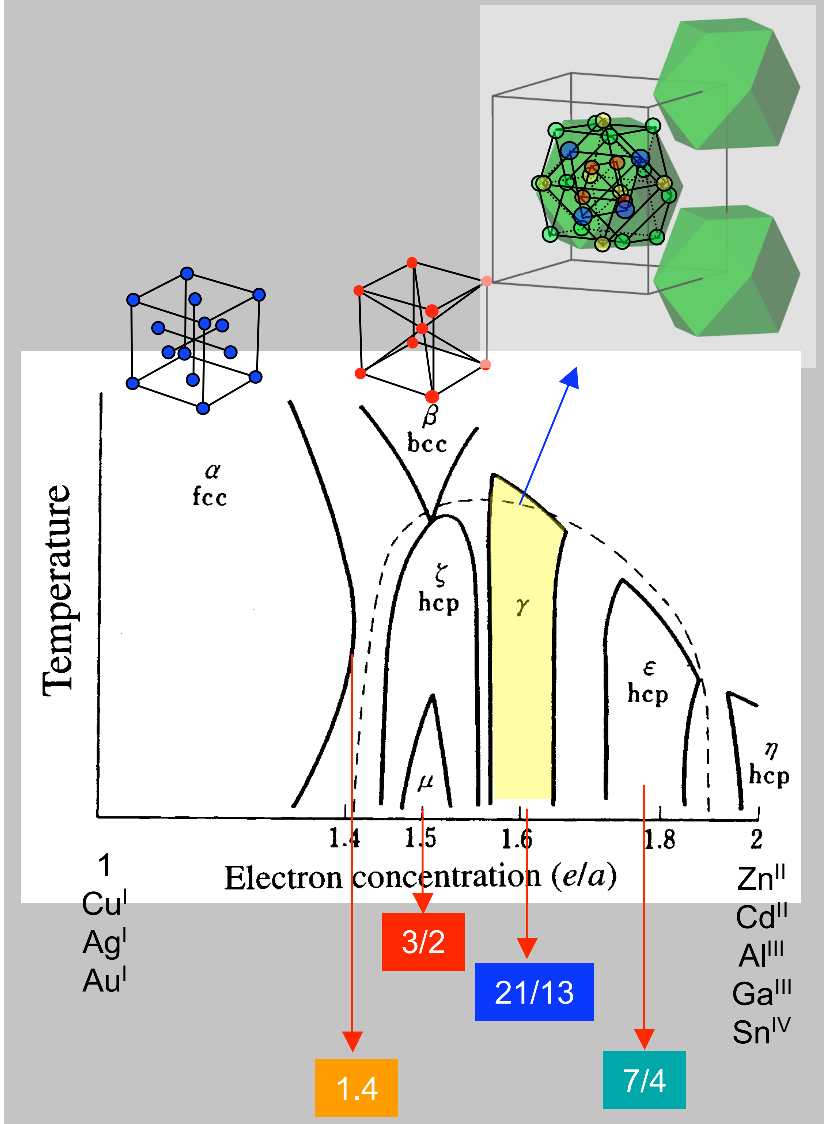
Fe_2VAl doped with various elements

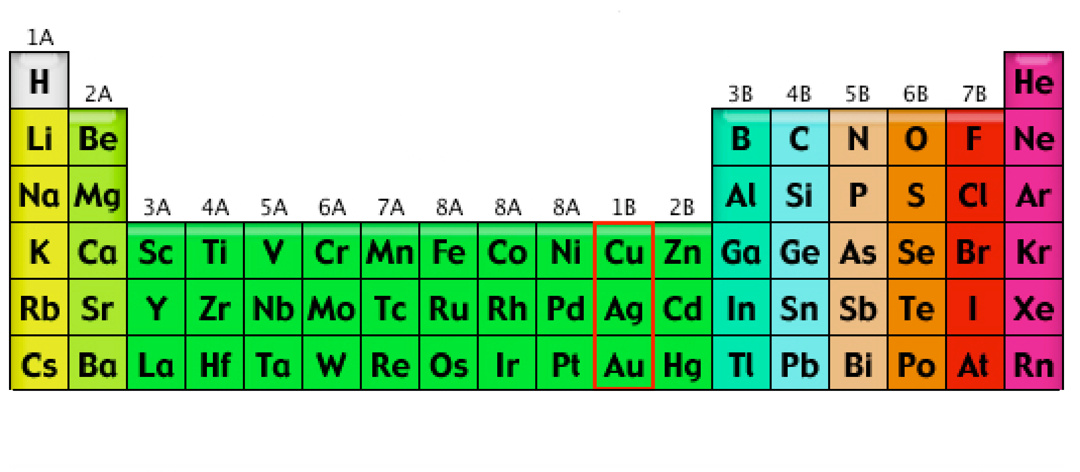


Y.Nishino and U.Mizutani (2005)

$$VEC = \frac{8\times 2 + 5\times 1 + 3\times 1}{4} = 6.0$$

Electron concentration in the Hume-Rothery electron concentration rule is not VEC but should be e/a (averaged number of valencies of constituent atoms).





1A	2A	3A	4A	5A	6A	7A	8A	8A	8A	1B	2B	3B	4B	5B	6B	7B	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

e/a

$$e/a(Cu_5Zn_8)=\frac{1\times 5+2\times 8}{13}=\frac{21}{13}$$

$$e/a(Cu_9Al_4)=\frac{1\times 9+3\times 4}{13}=\frac{21}{13}$$

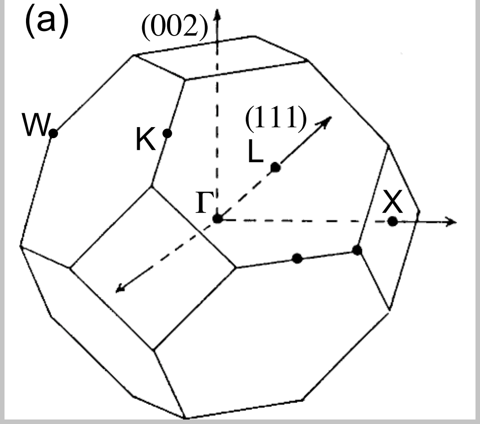
VEC

$$VEC(Cu_5Zn_8)=\frac{11\times 5+12\times 8}{13}=\frac{151}{13}$$

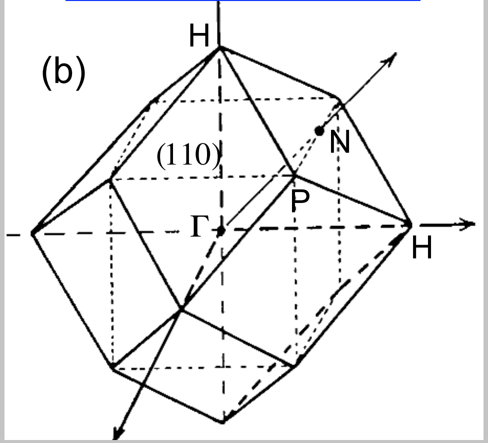
$$VEC(Cu_9Al_4)=\frac{11\times 9+3\times 4}{13}=\frac{111}{13}$$

Model of Jones for the interpretation of the Hume-Rothery rule on α/β phase transformation in Cu-Zn system

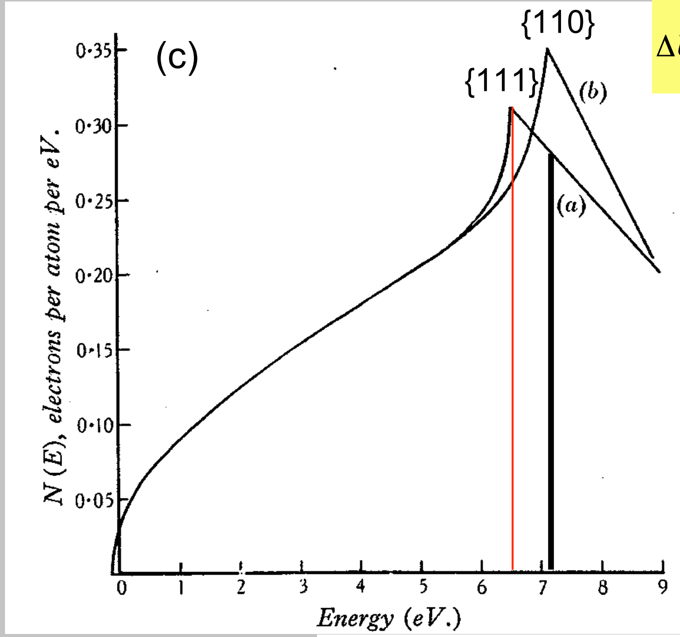
Brillouin zone of fcc

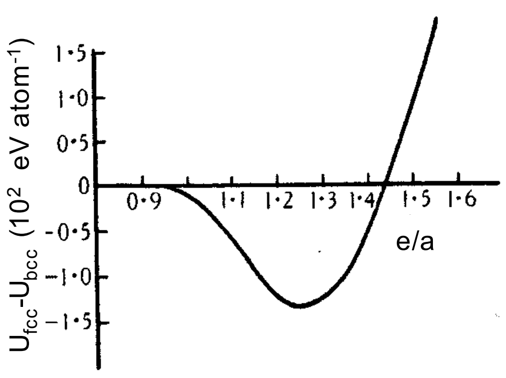


Brillouin zone of bcc



$$\Delta U = U_{fcc} - U_{bcc} = \int_0^{E_F} \{N(E)_{fcc} - N(E)_{bcc}\} E dE$$





H.Jones, Proc.Phys.Soc. A49 (1937) 250

Difficulties in model of Jones

Discovery of the neck in the Fermi surface of fcc-Cu by Pippard in 1957

Ignorance of the Cu-3d band

Hume-Rothery commented in 1961 that “the work of the last ten years has made the theory of alloy structures appear less satisfactory than was the case twenty-five years ago. It is now definitely established that the assumption of a spherical Fermi surface for pure Cu is quite unjustified…”.

Current understanding of fcc/bcc phase transformation of Cu on the basis of the first-principles FLAPW electronic structure calculations in combination with density functional theory

Total energy of a system at absolute zero

W.Kohn and L.J.Sham, Phys.Rev. 140 (1965) A1133

$$U=\sum_i \varepsilon_i-\frac{1}{2}\iint\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+\int n(\mathbf{r})\left[\varepsilon_{XC}\left(n(\mathbf{r})\right)-\mu_{XC}\left(n(\mathbf{r})\right)\right]d\mathbf{r}$$

average interaction energy of electrons known as the Hartree term

exchange-correlation energy

One-electron band structure energy due to both valence and core electrons

electron-electron interaction term

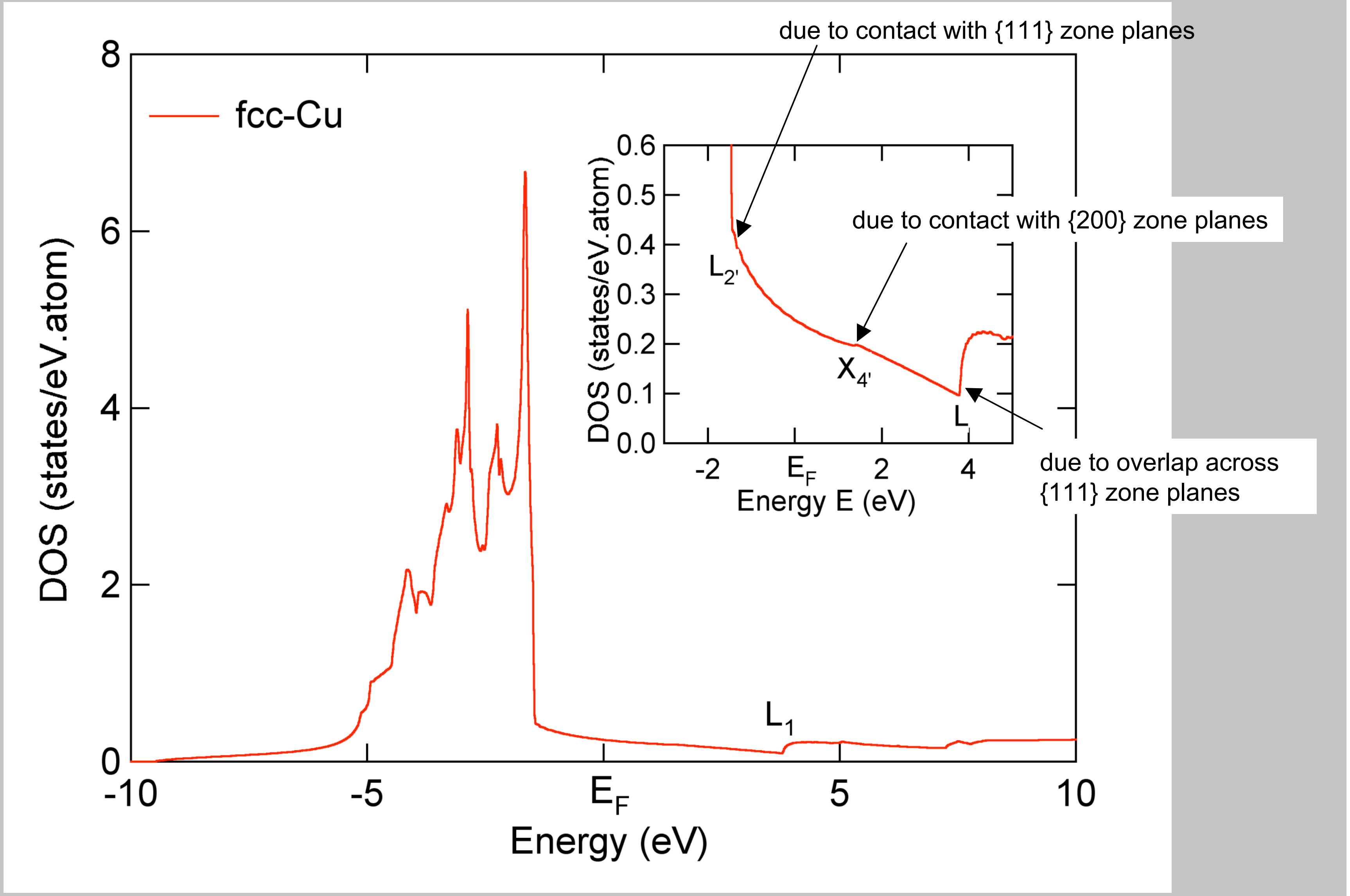
ε_i is the solution of the effective one-electron Schrödinger equation of a system given by

$$\left[-\frac{\hbar^2}{2m}\nabla^2+\mathrm{v}_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})$$

$$U_{valence}=\int_{E_{bottom}}^{E_F}D(E)(E-E_0)dE$$

→ **This is a quantity evaluated by Jones and corresponds to the contribution from the valence electrons in the first term.**

FLAPW valence band structure and van-Hove singularities in fcc-Cu

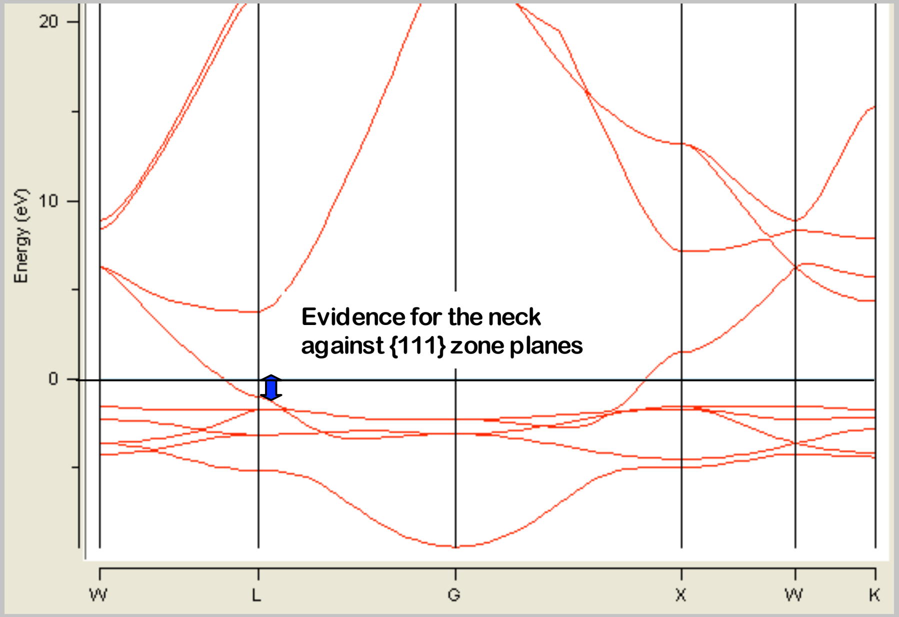


due to contact with {111} zone planes

due to contact with {200} zone planes

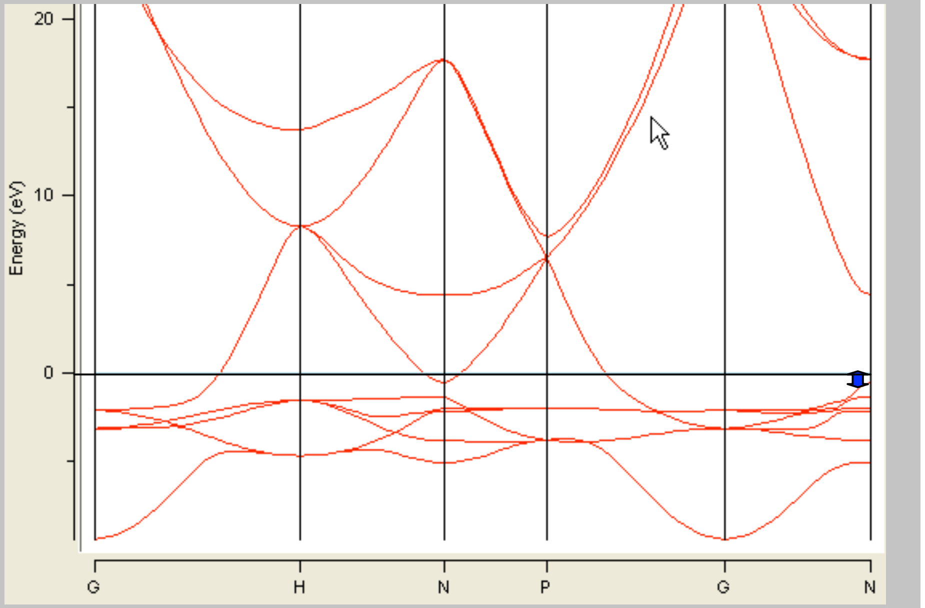
due to overlap across {111} zone planes

Fcc-Cu

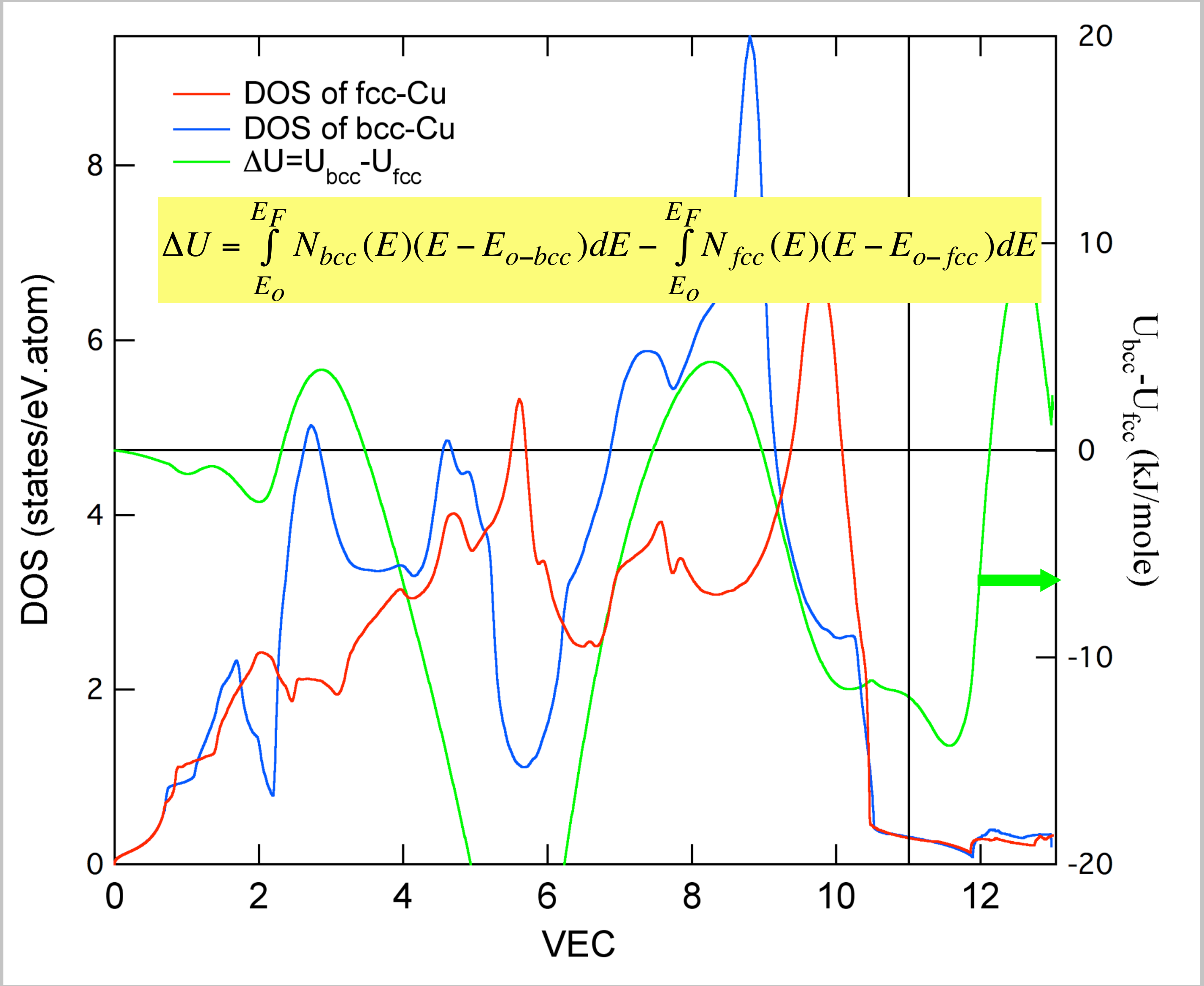


Evidence for the neck against {111} zone planes

Bcc-Cu



The first-principles band calculations prove that the ignorance of the Cu-3d band was a vital failure in the model of Jones. This led him to a wrong location of van-Hove singularities and overestimation of their sizes in both fcc and bcc Cu.



$$\Delta U = \int_{E_o}^{E_F} N_{bcc}(E)(E - E_{o-bcc})dE - \int_{E_o}^{E_F} N_{fcc}(E)(E - E_{o-fcc})dE$$

You can see that the van-Hove singularities are negligibly small in both fcc- and bcc-Cu. The band structure energy difference arises essentially from the difference in Cu-3d bands and amounts to about 10 kJ/mole in favor of the bcc structure.

The stability of fcc Cu is correctly predicted, only if the electron-electron term is properly evaluated.

	fcc-Cu	bcc-Cu	$\Delta U=U_{bcc}-U_{fcc}$ (kJ/mole)
lattice constant (A)	3.6048	2.8639	
total energy U (kJ/mole)	-4336455.852	-4336453.49	+2.37 $U_{bcc} > U_{fcc}$
valence-band structure energy U_{bs} (kJ/mole)	5257.9289	5226.4769	-31.45 $U_{bcc} < U_{fcc}$
core electron energy U_{core} (kJ/mole)	-2483799.964	-2483807.338	-7.37
$U_{electron\text{-}electron}$ (kJ/mole)	-1857913.837	-1857872.647	+41.19 $U_{bcc} > U_{fcc}$

$$U = \sum_i \varepsilon_i - \left\{ \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r}) \left[\varepsilon_{XC}(n(\mathbf{r})) - \mu_{XC}(n(\mathbf{r})) \right] d\mathbf{r} \right\}$$

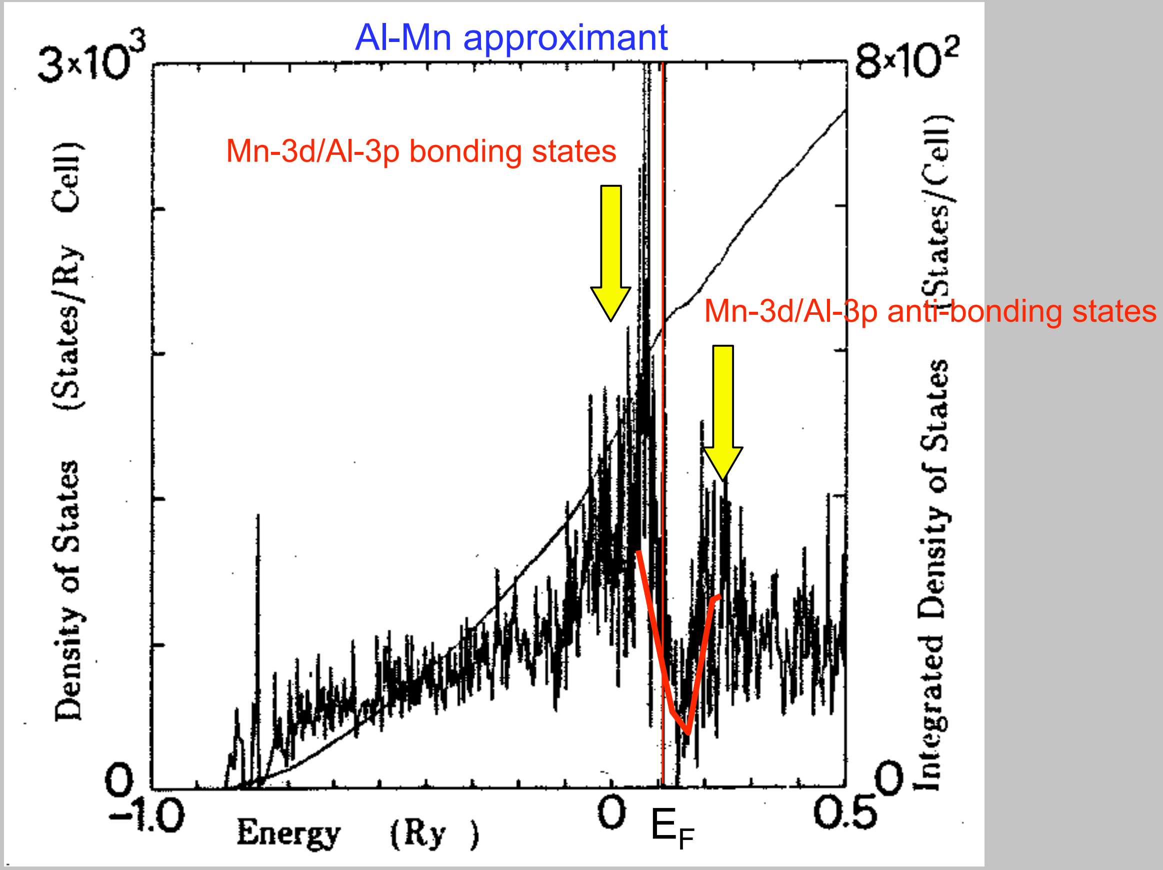
$$= U_{\mathrm{bs}} + U_{core} + U_{electron-electron}$$

$\Delta U = (-31.45) + (-7.37) + 41.19 = +2.37$ kJ/mole

As is clear from the argument above, the interpretation of α/β phase transformation in the Cu-Zn system is still far from our goal.

We believe the situation in complex alloy phases to be different from that in fcc and bcc Cu, where van-Hove singularities are too small to affect the total energy.

A pseudogap across the Fermi level plays a key role in stabilizing a complex alloy phase



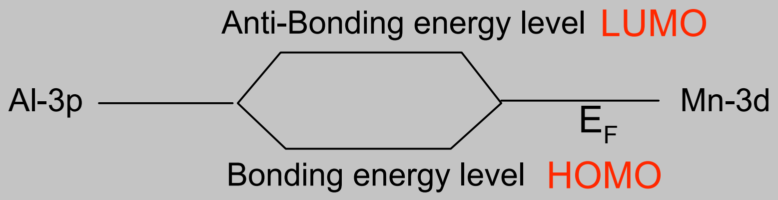
T.Fujiwara, Phys.Rev.B **40** (1989) 942

---First-principles LMTO band calculations---

The origin of the pseudogap was attributed to the Mn-3d/Al-3p orbital hybridizations

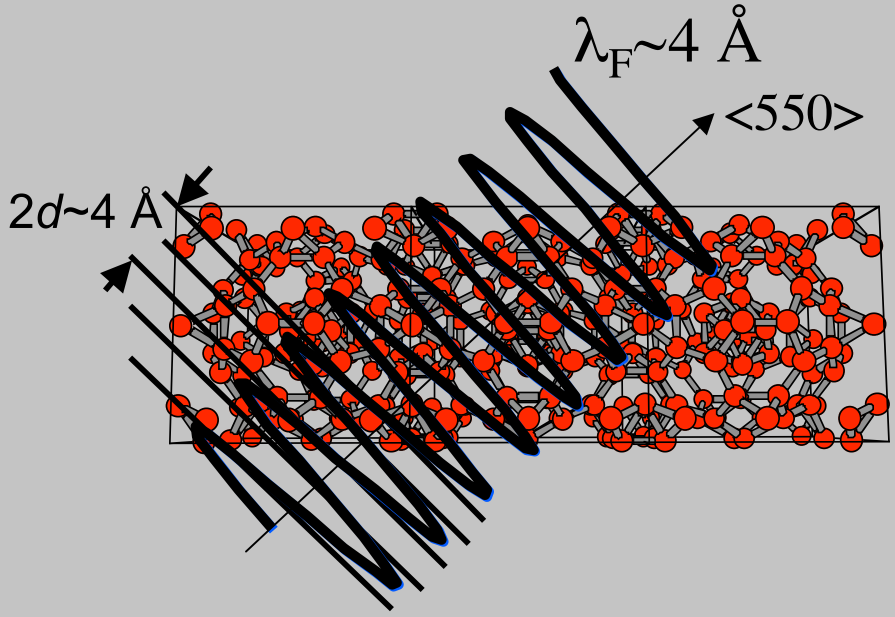
We are interested in e/a-dependent phase stability

Orbital hybridizations



Orbital hybridization effect would occur not only in crystals but also in non-crystalline systems like liquid metals and amorphous alloys.

FsBz interaction



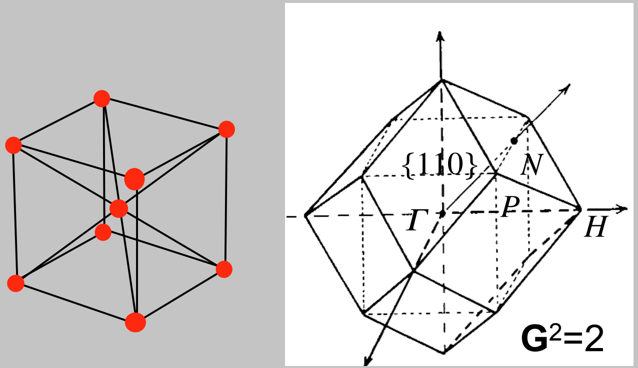
Resonance of electrons having the wave length λ_F with a set of lattice planes with spacing 2d.

FsBz interaction is unique in well-ordered systems like crystals and quasicrystals

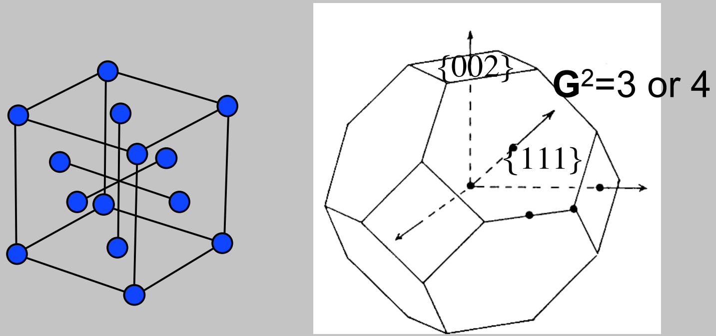
$$\lambda_F = \frac{2\pi}{k_F} \propto \frac{1}{(e/a)^{1/3}}$$

An increase in the number of atoms in unit cell accompanies an increase in Brillouin zone planes

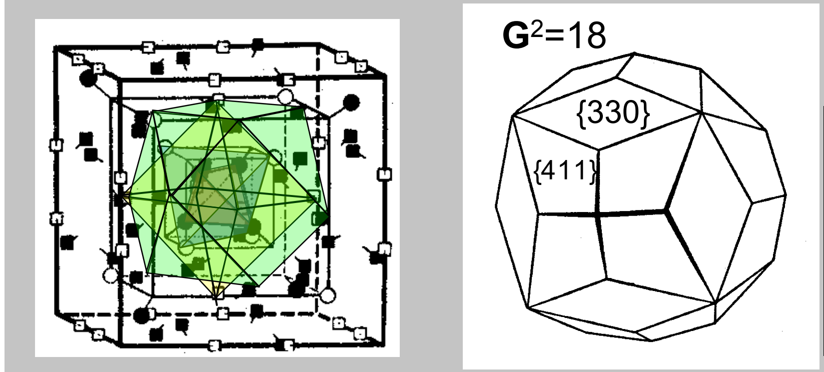
I. bcc, N=2, dodecahedron with 12 planes



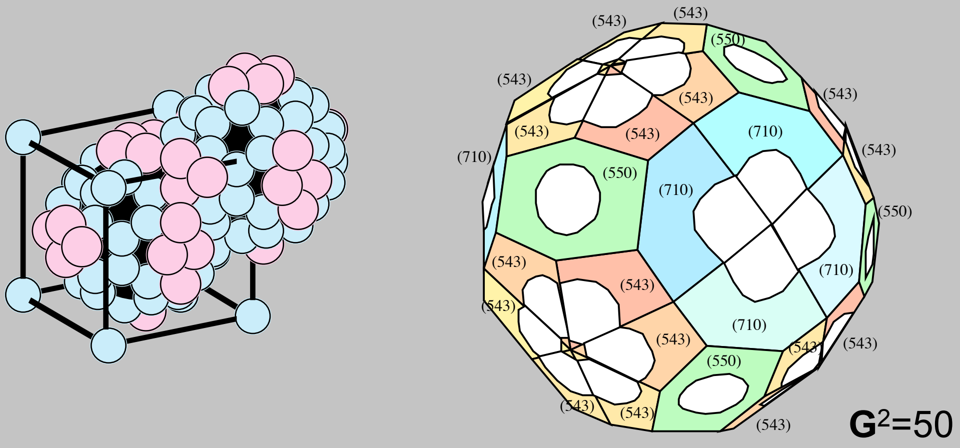
II. fcc, N=4, truncated octahedron with 14 planes



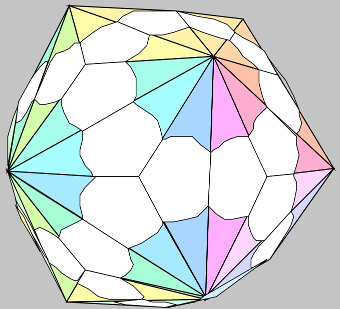
III. gamma-brass, N=52, polyhedron with 36 planes



IV. 1/1-1/1-1/1 approximant, N=160, polyhedron with 84 planes



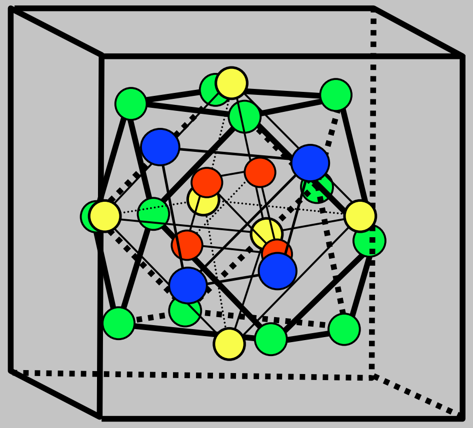
V. Quasicrystal, N is infinite, polyhedron with 60 planes



The gamma-brass is complex enough to produce a sizeable pseudogap at the Fermi level but is still simple enough to perform the FLAPW band calculations with an efficient speed.

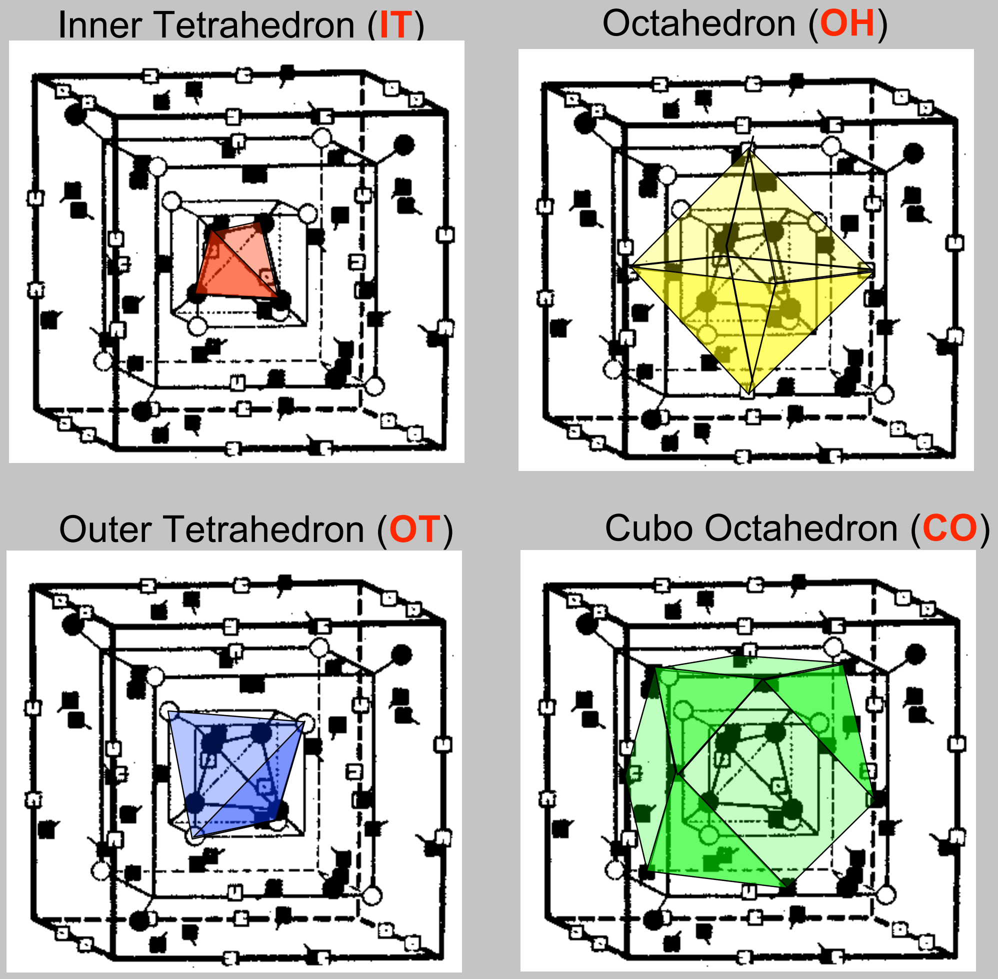
Gamma-brasses with the space group $P\bar{4}3m$ and $I\bar{4}3m$

(a)



26-atom cluster

(b)



Inner Tetrahedron (**IT**)

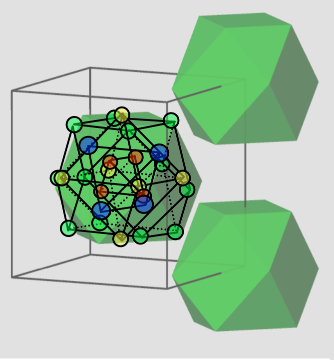
Octahedron (**OH**)

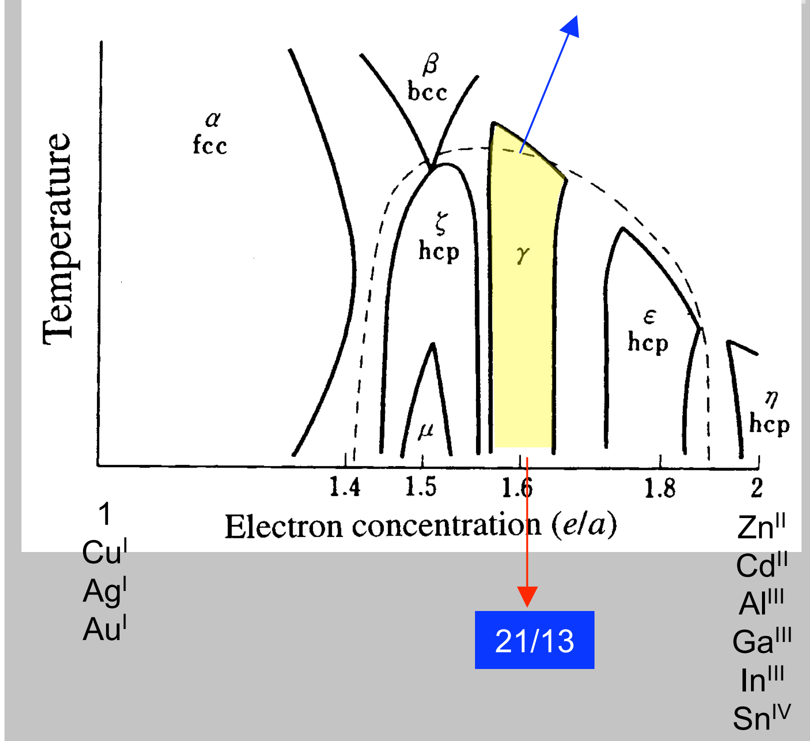
Outer Tetrahedron (**OT**)

Cubo Octahedron (**CO**)

The 26-atom cluster forms either bcc or CsCl-structure and contains 52 atoms in the unit cell.

Our objective is to explore if all gamma-brasses listed here are stabilized via the same mechanism at e/a=21/13



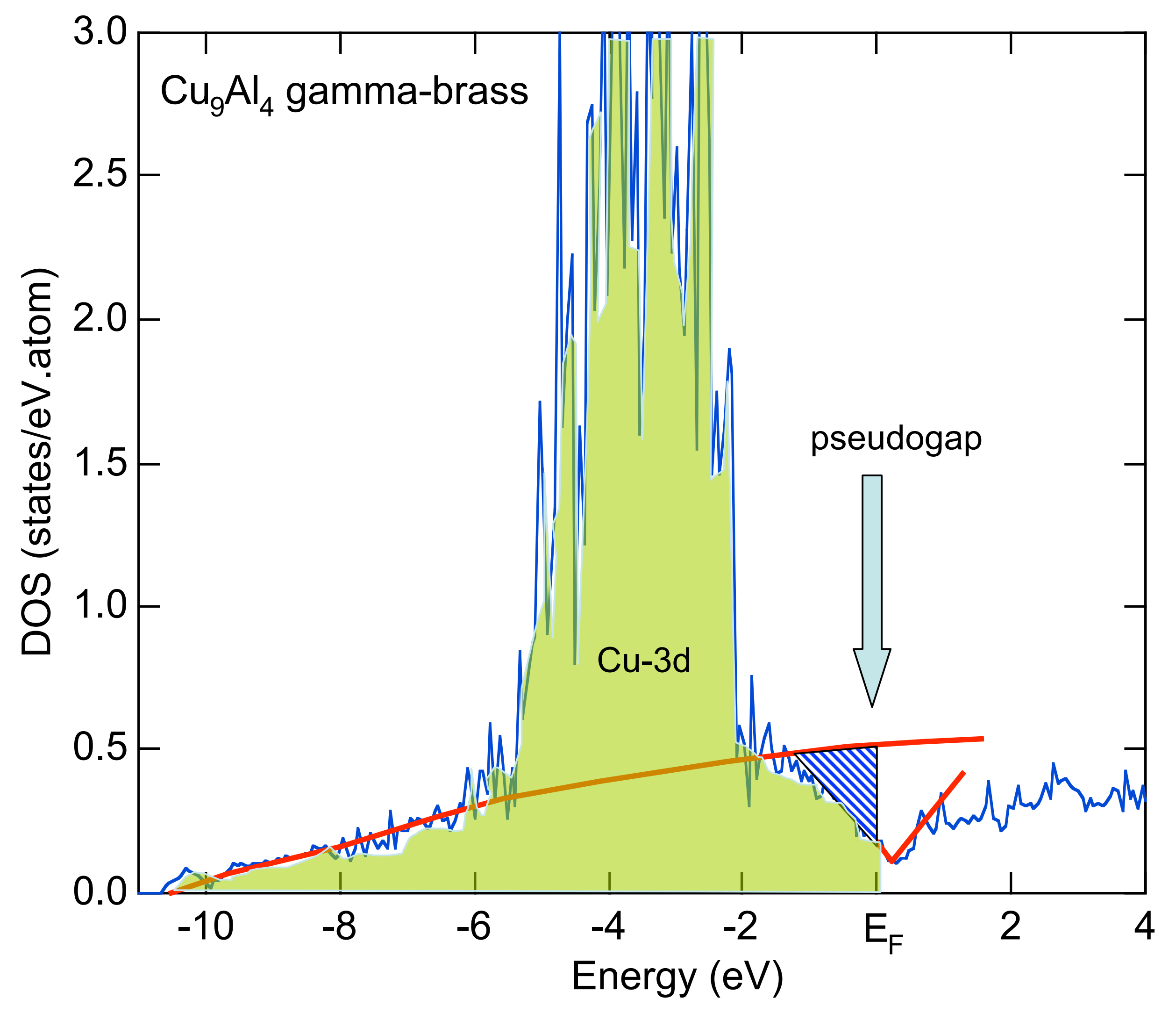


Empirical Hume-Rothery e/a rule for gamma-brasses in the past

	gamma-brass	e/a		gamma-brass	e/a		gamma-brass	e/a
1	Ag_5Cd_8	21/13	1	Cu_9In_4	21/13	2	Ni_2Be_{11}	?
	Ag_5Zn_8	21/13		Ag_9In_4	21/13		Ni_2Cd_{11}	?
	Cu_5Cd_8	21/13		Au_9In_4	21/13		Mn_2Zn_{11}	?
	Cu_5Zn_8	21/13	2	Ni_2Zn_{11}	1.6		Pt_2Zn_{11}	?
	Au_5Cd_8	21/13		Fe_2Zn_{11}	1.6		Al_8V_5	1.46
	Au_5Zn_8	21/13		Co_2Zn_{11}	1.6		Mn_3In	?
	Cu_9Al_4	21/13		Pd_2Zn_{11}	1.6	3	Ag_5Li_8	21/13 ?
	Cu_9Ga_4	21/13		Ir_2Zn_{11}	?			

In literature, all isostructural gamma-brasses above had been implicitly assumed to be stabilized at e/a=21/13 or the valency of the partner element to be forced to take a value to fulfill the total e/a equal to 21/13.

DOS of Cu_9Al_4 gamma-brass



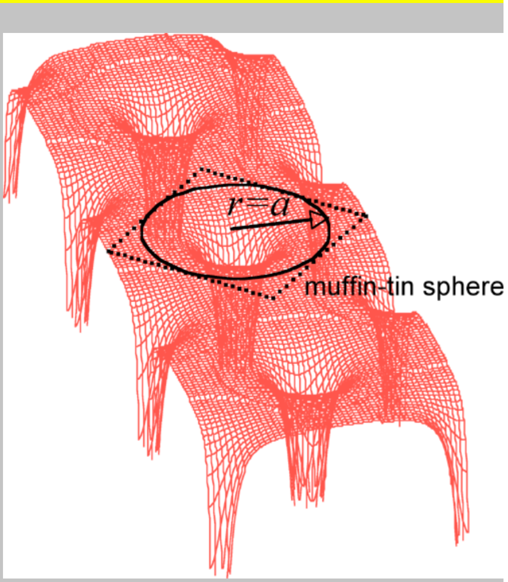
The FsBz interaction is really responsible for the formation of the pseudogap?

Principle for the extraction of the FsBz interaction from the first-principles FLAPW (Full-potential Linearized Augmented Plane Wave method) band calculations

Adoption of spherically symmetric muffin-tin potential

$$r \le a \qquad \chi_{\mathbf{k}}(\mathbf{r}) = \sum_{\ell m}\left[A_{\ell m}^{\mathbf{k}} u_\ell(E_\ell,\mathbf{r}) + B_{\ell m}^{\mathbf{k}} \dot{u}_\ell(E_\ell,\mathbf{r})\right] Y_{\ell m}(\theta,\phi)$$

$$r \ge a \qquad \chi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})$$



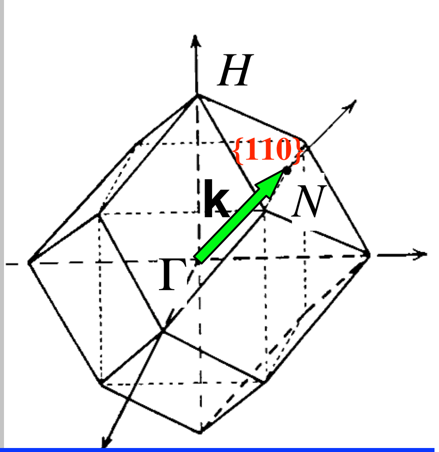
$$\psi_{\mathbf{k}}(E,\mathbf{r}) = \sum_{\mathbf{G}_{hkl}} C(\mathbf{k}+\mathbf{G}_{hkl})\chi_{\mathbf{k}+\mathbf{G}_{hkl}}(E,\mathbf{r})$$

$\chi_{\mathbf{k}+\mathbf{G}_{hkl}}(E,\mathbf{r})$: *FLAPW basis function*

$$\psi_{\mathbf{k}}(E,\mathbf{r}) = \sum_{\mathbf{G}_{hkl}} C(\underbrace{\mathbf{k}+\mathbf{G}_{hkl}})\exp\left[i(\mathbf{k}+\mathbf{G}_{hkl})\cdot\mathbf{r}\right] \qquad (1)$$

E_F

$$\frac{1}{2}(1,1,0)$$



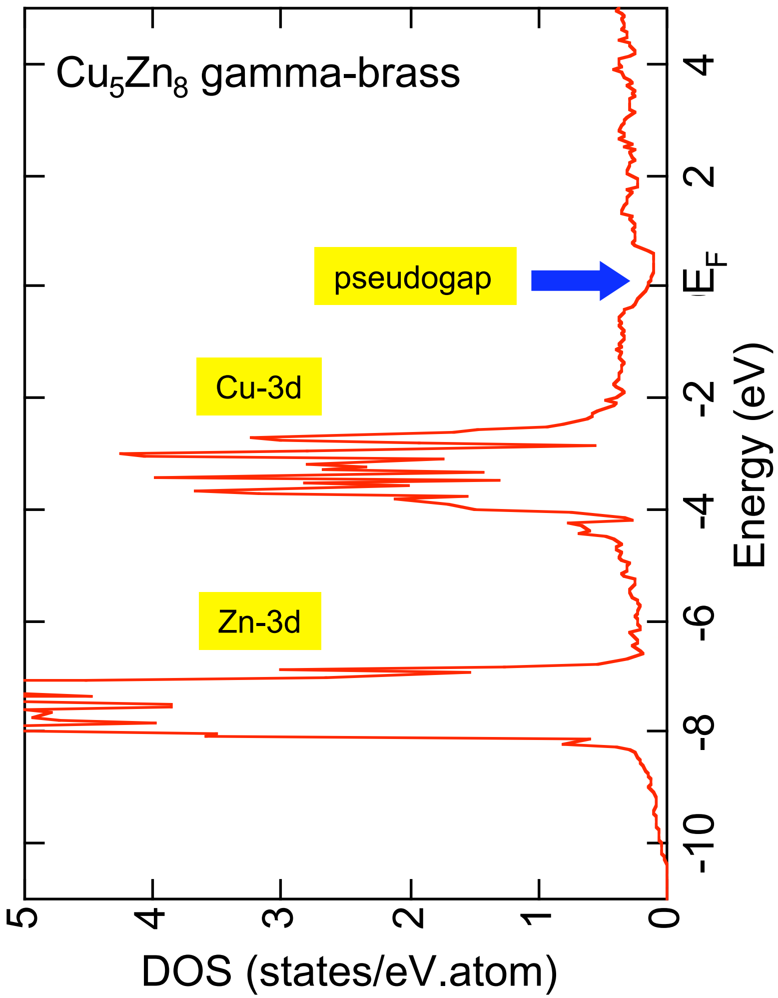
FLAPW-Fourier Analysis

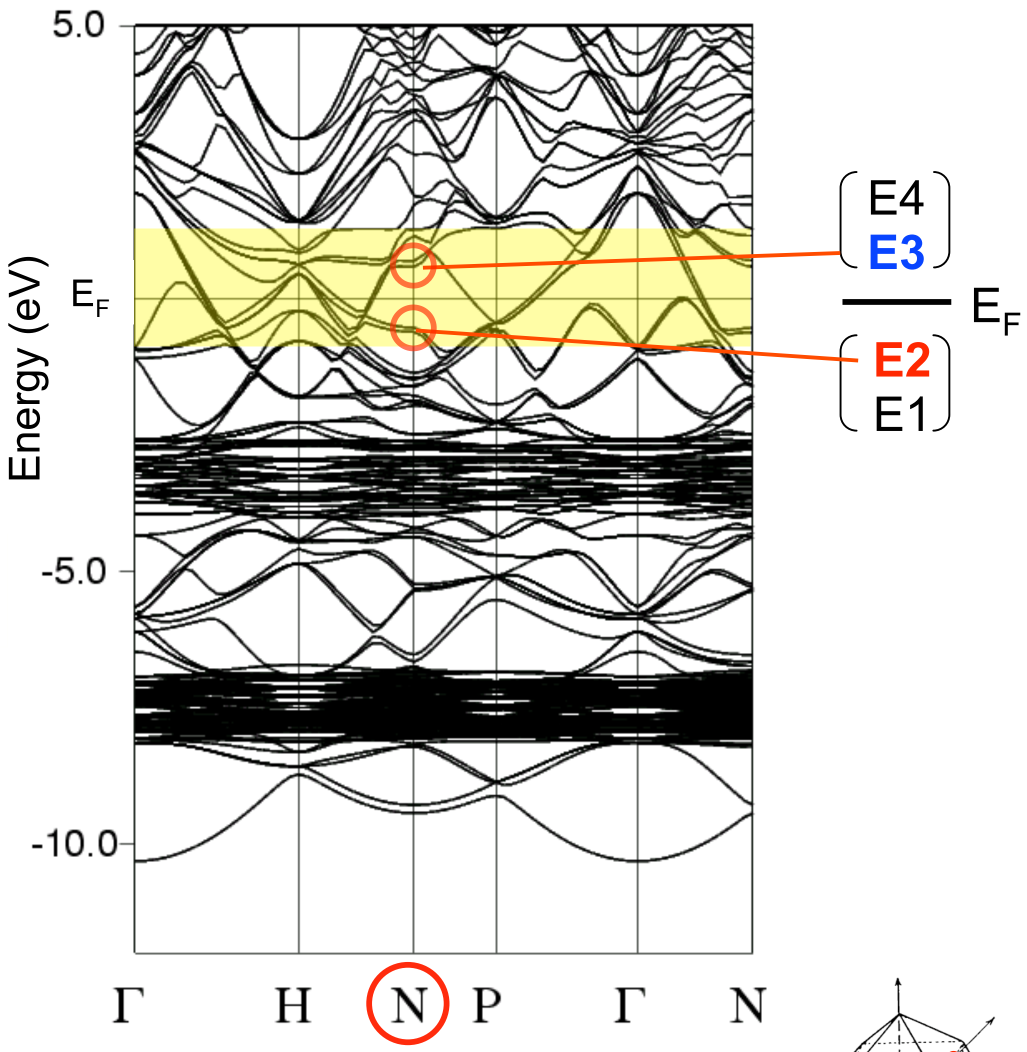
We extract the electronic state **k+G**$_{hkl}$ having the largest Fourier coefficient in wave function (1) at symmetry point N with the energy eigen-value near the Fermi level. This is nothing but the extraction of the set of lattice planes resonating with electron waves.

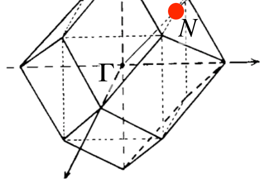
Cu_5Zn_8 and Cu_9Al_4 gamma-brasses in group 1

	gamma-brass	e/a		gamma-brass	e/a		gamma-brass	e/a
1	Cu_5Zn_8	21/13	1	Cu_9In_4	21/13	2	Ni_2Be_{11}	?
	Ag_5Cd_8	21/13		Ag_9In_4	21/13		Ni_2Cd_{11}	?
	Ag_5Zn_8	21/13		Au_9In_4	21/13		Mn_2Zn_{11}	?
	Cu_5Cd_8	21/13	2	Ni_2Zn_{11}	1.60?		Pt_2Zn_{11}	?
	Au_5Cd_8	21/13		Pd_2Zn_{11}	1.60?		Al_8V_5	1.46?
	Au_5Zn_8	21/13		Fe_2Zn_{11}	1.60?		Mn_3In	?
	Cu_9Al_4	21/13		Co_2Zn_{11}	1.60?	3	Ag_5Li_8	21/13 ?
	Cu_9Ga_4	21/13		Ir_2Zn_{11}	?			

E-k dispersions and DOS derived from FLAPW for Cu_5Zn_8 gamma-brass

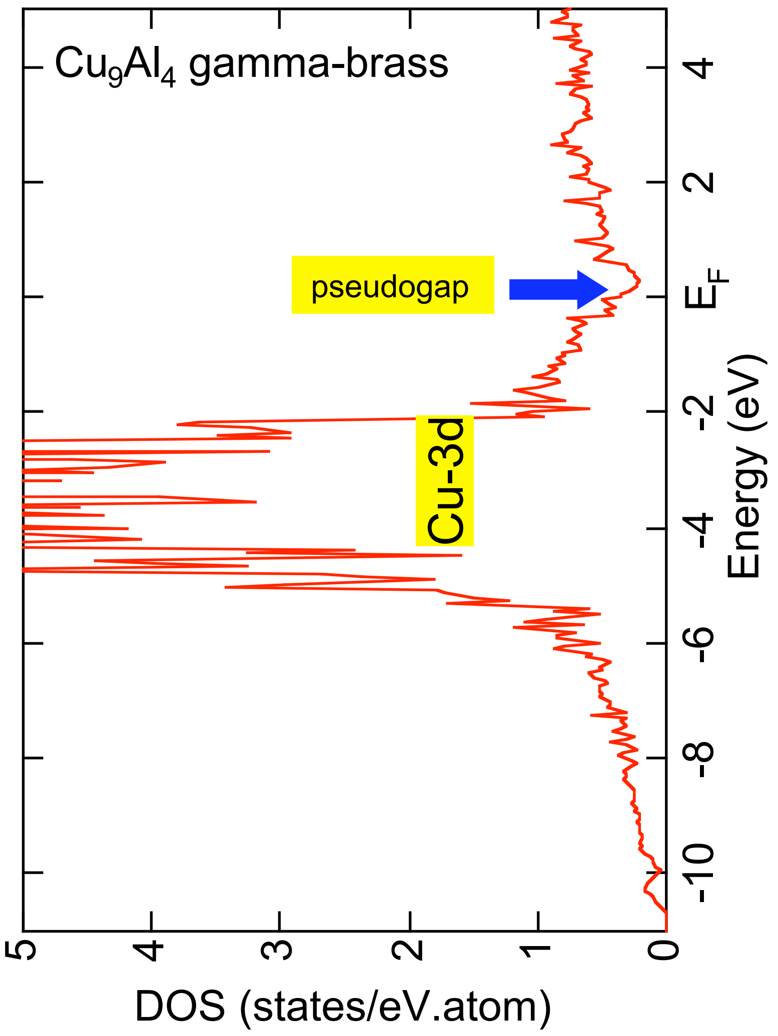


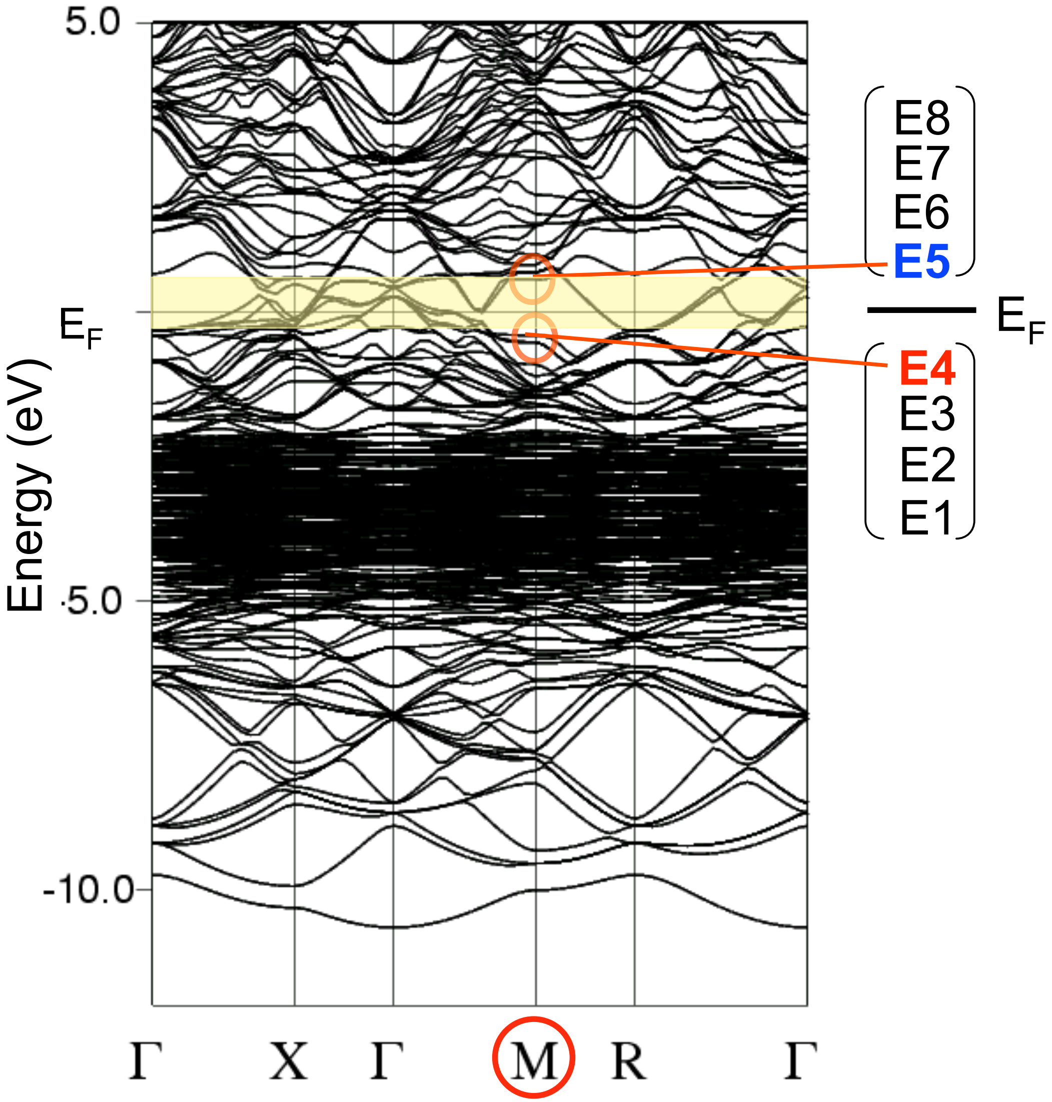




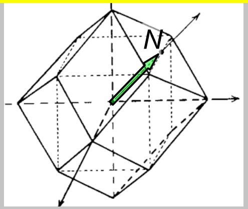
R.Asahi, H.Sato, T.Takeuchi and U.Mizutani, Phys.Rev. B **71** (2005) 165103

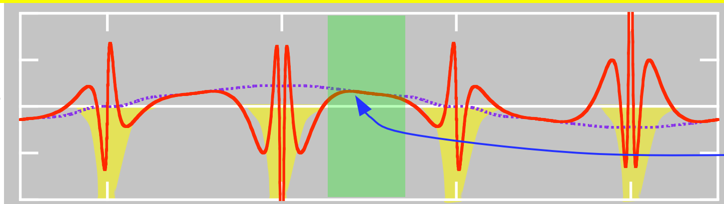
E-k dispersions and DOS derived from FLAPW for Cu$_9$Al$_4$ gamma-brass



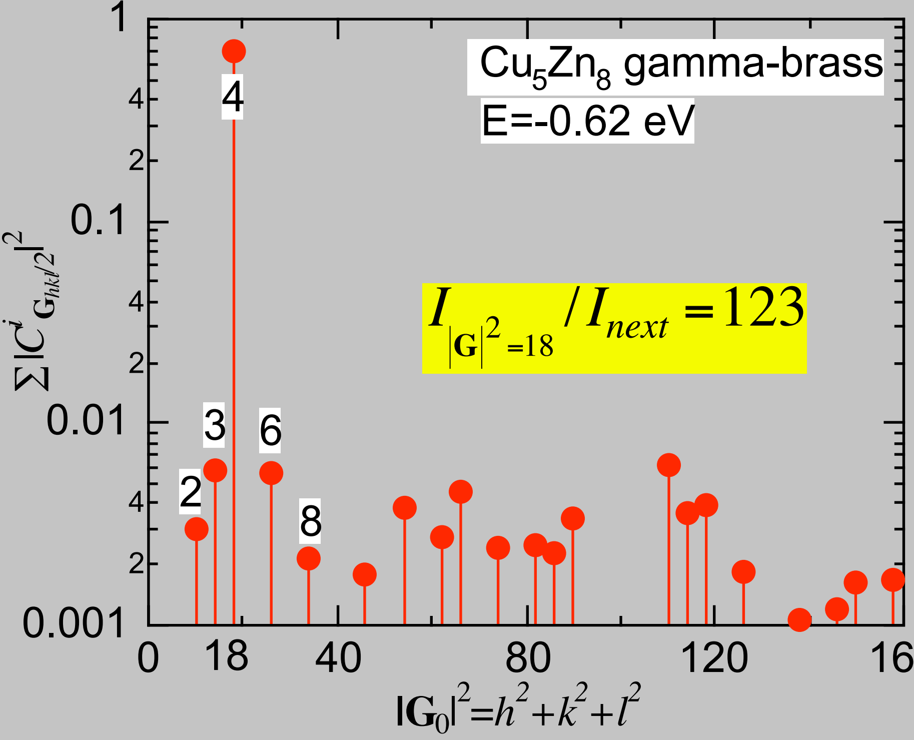


FLAPW-Fourier spectra for the wave function outside the MT sphere at the point *N* at energies immediately below the Fermi level

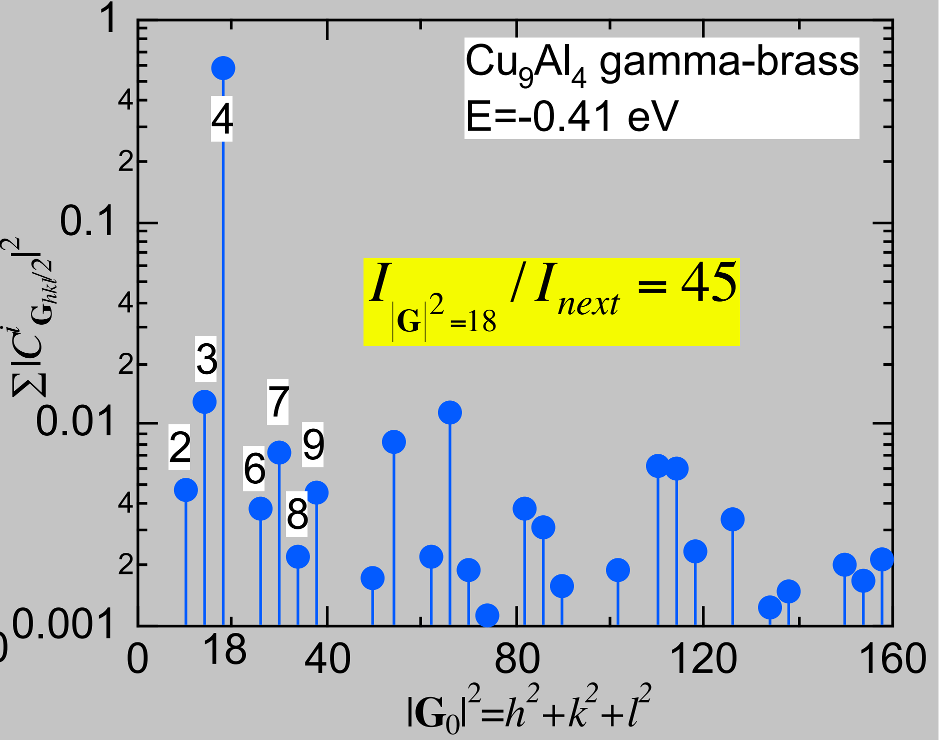




$$\psi_{\mathbf{k}}(E,\mathbf{r}) = \sum_{\mathbf{G}_{hkl}} C(\mathbf{k}_N+\mathbf{G}_{hkl})\exp\left[i(\mathbf{k}_N+\mathbf{G}_{hkl})\cdot\mathbf{r}\right]$$



$I_{|\mathbf{G}|^2=18}/I_{next}=123$



$I_{|\mathbf{G}|^2=18}/I_{next}=45$

1: {211}, 2: {310}, 3: {321}, 4: {411}+{330}, 5: {332}, 6: {510}+{431}, 7: {521}, 8: {530}+{433}, 9: {611}+{532}

The Fourier coefficient is extremely large at G^2=18. This implies that electron waves near the Fermi level exclusively resonate with the set of {411} and {330} lattice planes with G^2=18, resulting in the formation of the pseudogap.

Evaluation of the e/a value by means of the FLAPW-Fourier method

---Hume-Rothery plot---

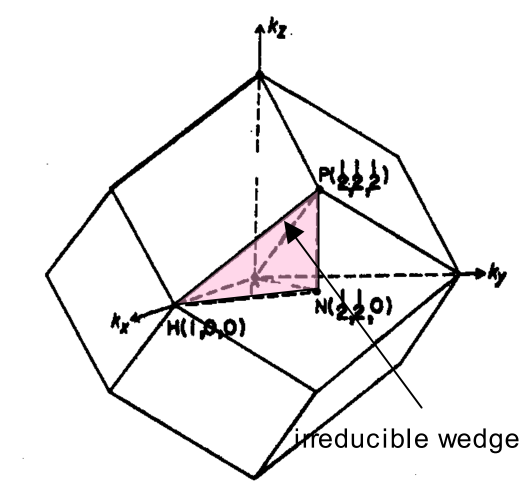
We have so far limited ourselves to the extraction of the largest plane wave component of the FLAPW wave function only near the Fermi level and only at the symmetry point N.

This technique is now extended to a whole valence band. We need to do this only in the irreducible wedge of the Brillouin zone. The wedge is divided into 200 elements and the electronic state ($\mathbf{k}_i+\mathbf{G}$) having the largest Fourier coefficient for the wave function at energy E in the *i-th* element is extracted. This is done for all elements over i=1 to 200 and an average value of $(\mathbf{k}_i+\mathbf{G})_{av}$ is calculated. In this way, a new single-branch dispersion relation E-$(\mathbf{k}_i+\mathbf{G})_{av}$ for electrons extending outside the MT sphere is derived in the extended zone scheme.

$$\left|\mathbf{k}+\mathbf{G}\right|_E \equiv \sum_{i=1}^{N=200} \omega_i \left|\mathbf{k}_i+\mathbf{G}\right|_E$$

The variance σ must be small to validate this approach.

Once the E-(k+G) is determined, the Fermi diameter $2k_F$ is obtained from the value of 2(k+G) at E_F.



The e/a is immediately calculated by inserting the Fermi diameter $2k_F$ into the relation below:

$$(e/a)_{total} = \frac{\pi}{3N}\left(2k_F\right)^3$$

N=52:number of atoms in the unit cell

E-$\{2(k+G)\}^2$ relations for itinerant electrons for Cu_5Zn_8 and Cu_9Al_4 gamma-brasses

---Hume-Rothery plot---

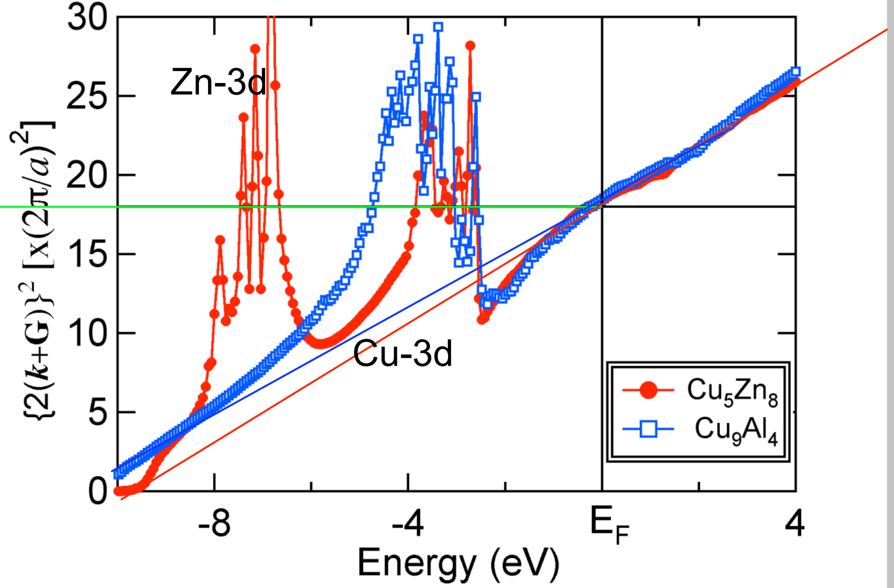
$(2k_F)^2=18.47$ for Cu_5Zn_8

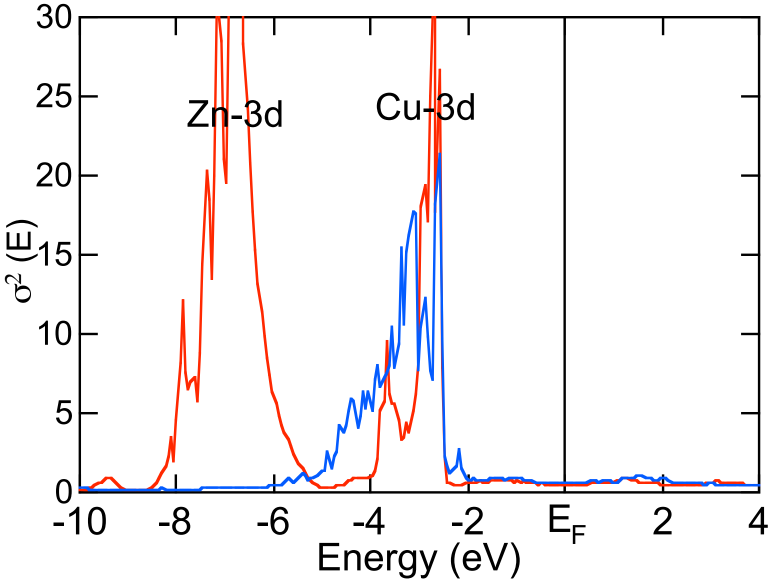
$(2k_F)^2=18.45$ for Cu_9Al_4

$$(e/a)_{total} = \frac{\pi}{3N}(2k_F)^3$$

N=52

e/a=1.60 for both gamma-brasses





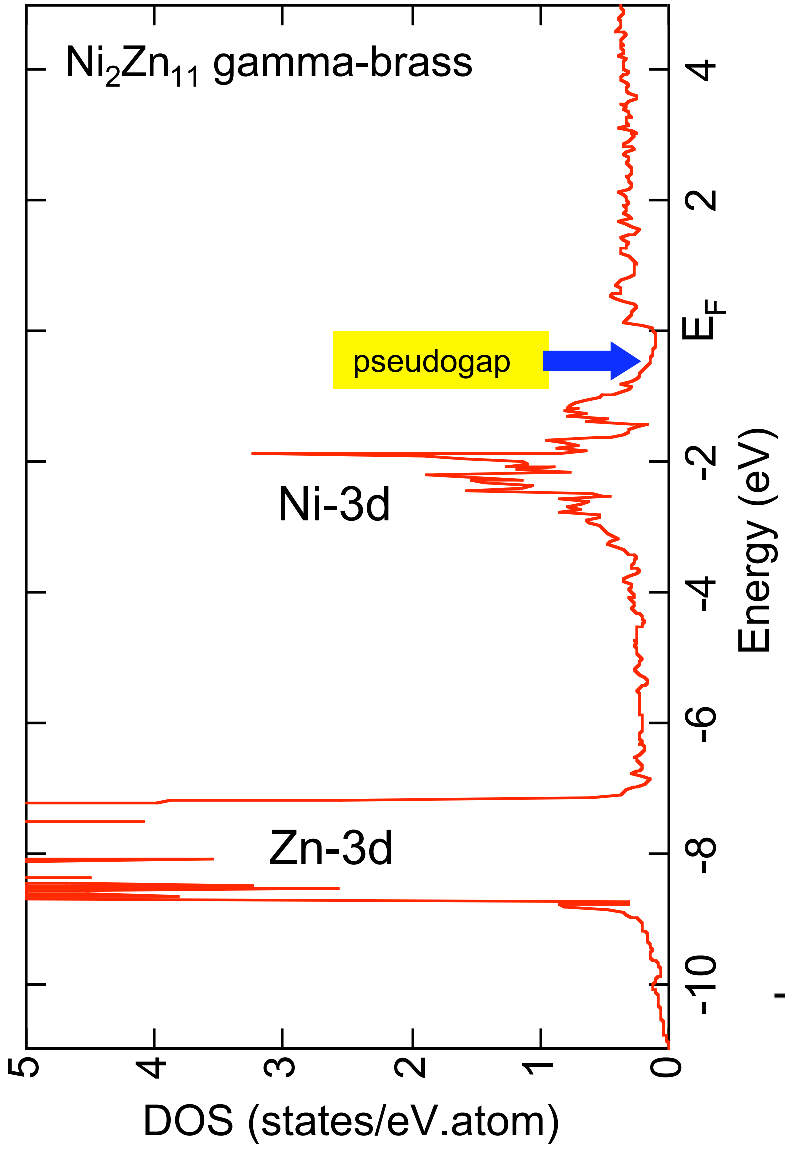
Studies of TM_2Zn_{11} (TM=Ni, Pd, Fe, Co) gamma-brasses in group 2

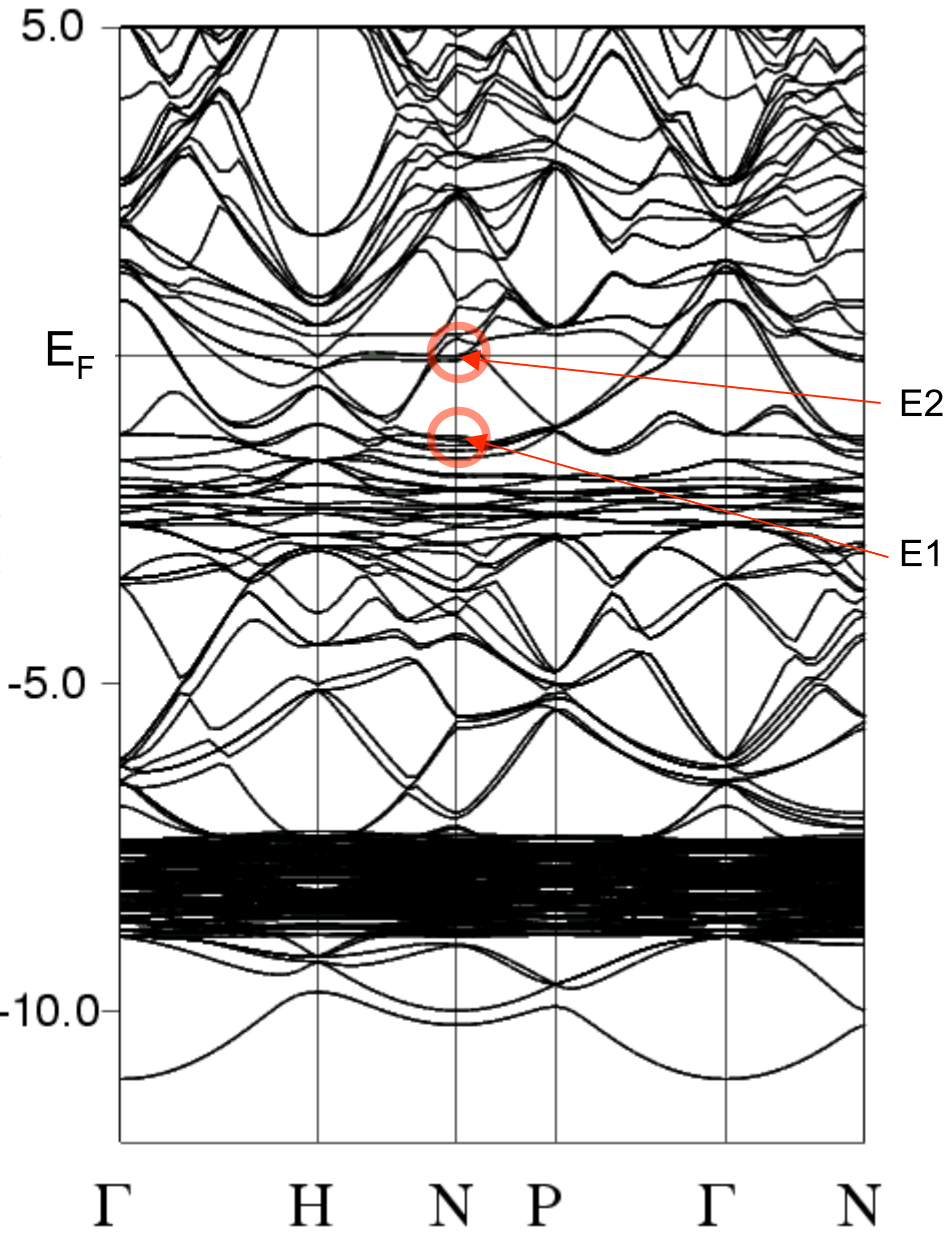
	gamma -brass	e/a		gamma -brass	e/a		gamma-brass	e/a
1	Cu_5Zn_8	21/13	1	Cu_9In_4	21/13	2	Ni_2Be_{11}	?
	Ag_5Cd_8	21/13		Ag_9In_4	21/13		Ni_2Cd_{11}	?
	Ag_5Zn_8	21/13		Au_9In_4	21/13		Mn_2Zn_{11}	?
	Cu_5Cd_8	21/13	2	Ni_2Zn_{11}	1.60?		Pt_2Zn_{11}	?
	Au_5Cd_8	21/13		Pd_2Zn_{11}	1.60?		Al_8V_5	1.46?
	Au_5Zn_8	21/13		Fe_2Zn_{11}	1.60?		Mn_3In	?
	Cu_9Al_4	21/13		Co_2Zn_{11}	1.60?	3	Ag_5Li_8	21/13 ?
	Cu_9Ga_4	21/13		Ir_2Zn_{11}	?			

Ekman (1931) studied the TM-Zn gamma-brasses and proposed that they obey the Hume-Rothery electron concentration rule with e/a=1.60, provided that the valency of the TM element is zero.

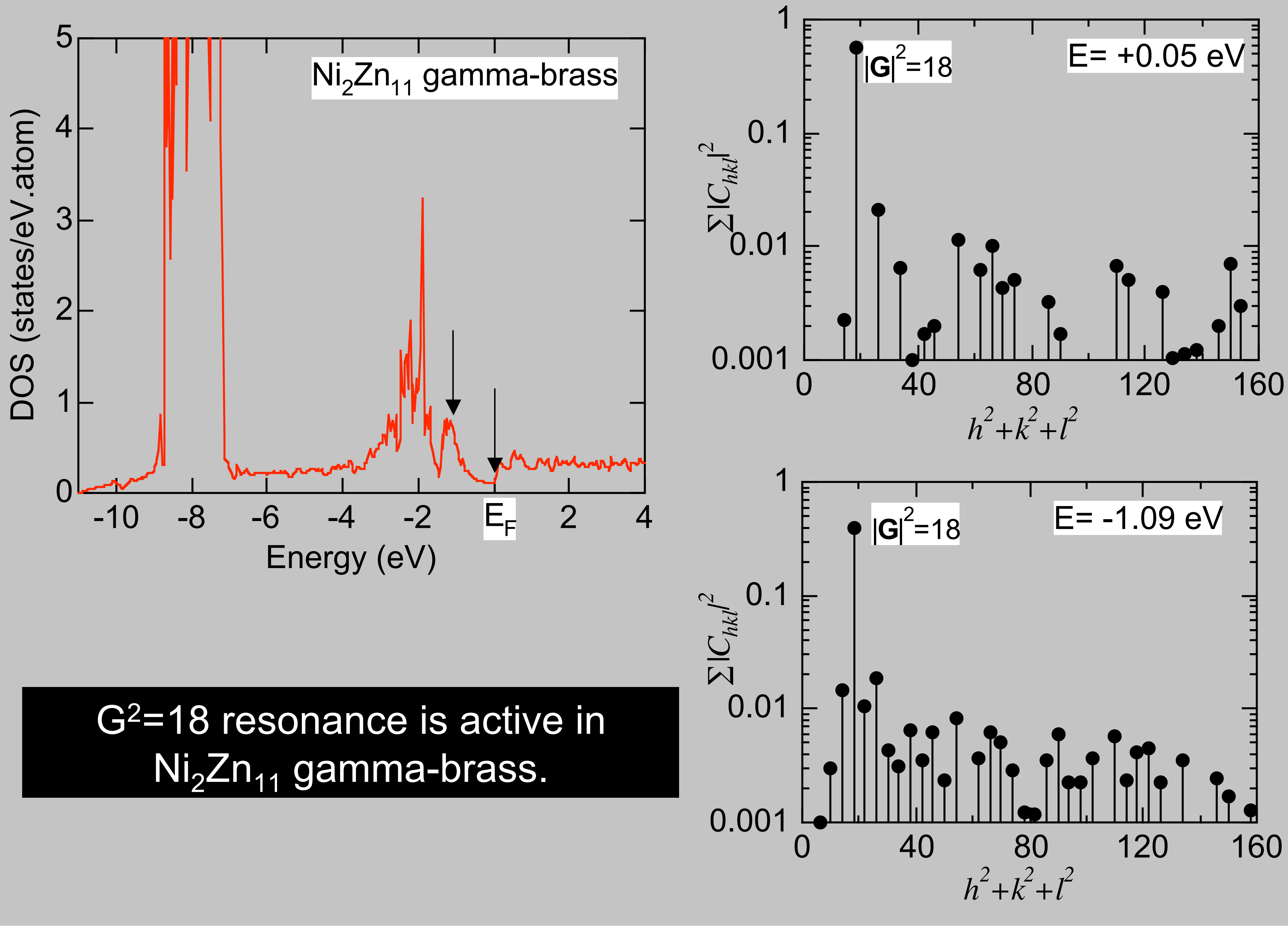
W.Ekman, Z.Physik.Chem. B 12 (1931) 57

FLAPW-derived E-k relations and DOS for Ni_2Zn_{11} gamma-brass



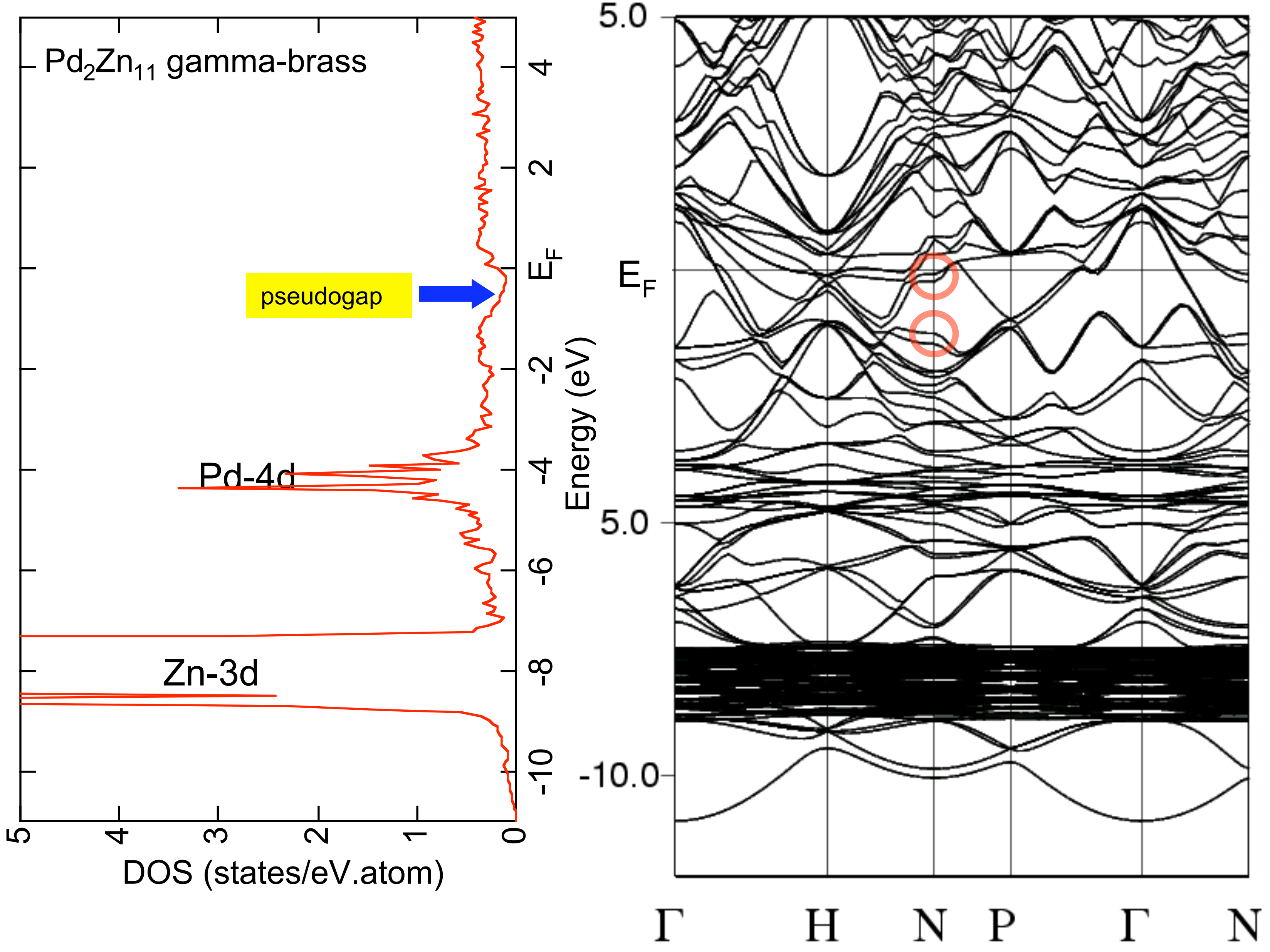


FLAPW-Fourier spectra just below and above the pseudogap in Ni_2Zn_{11} gamma-brass

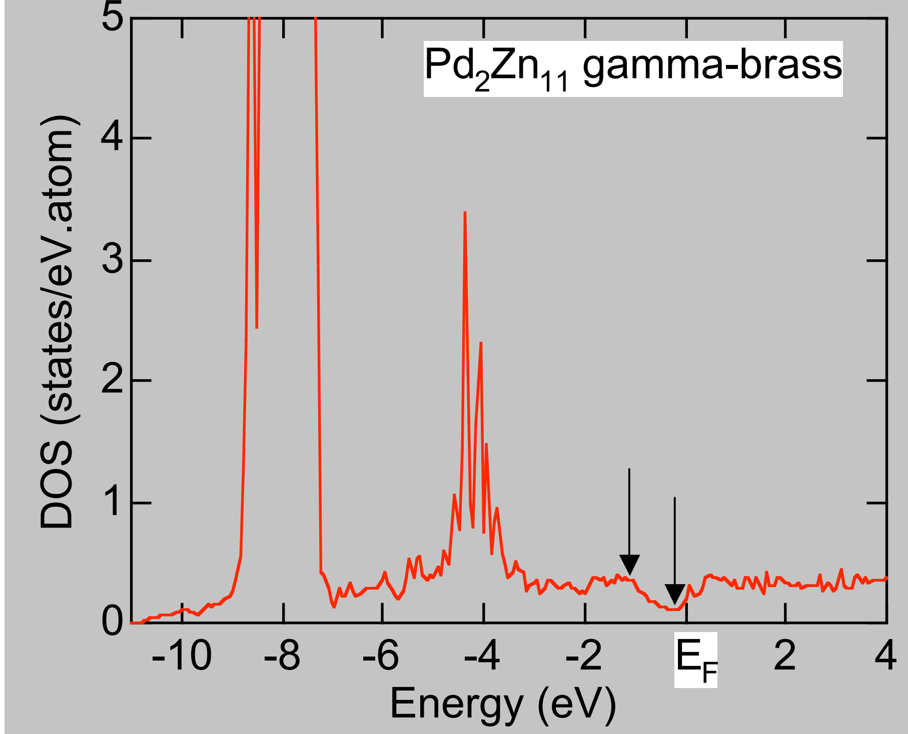


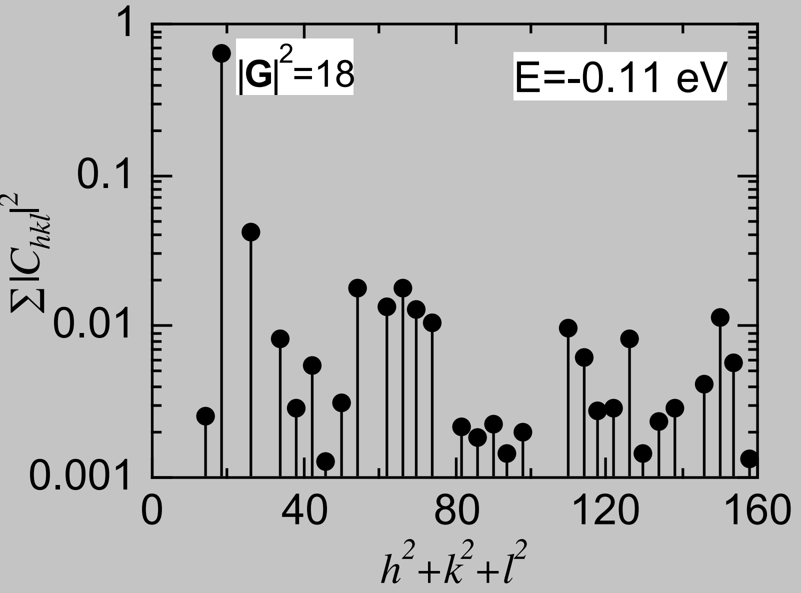
$G^2=18$ resonance is active in Ni_2Zn_{11} gamma-brass.

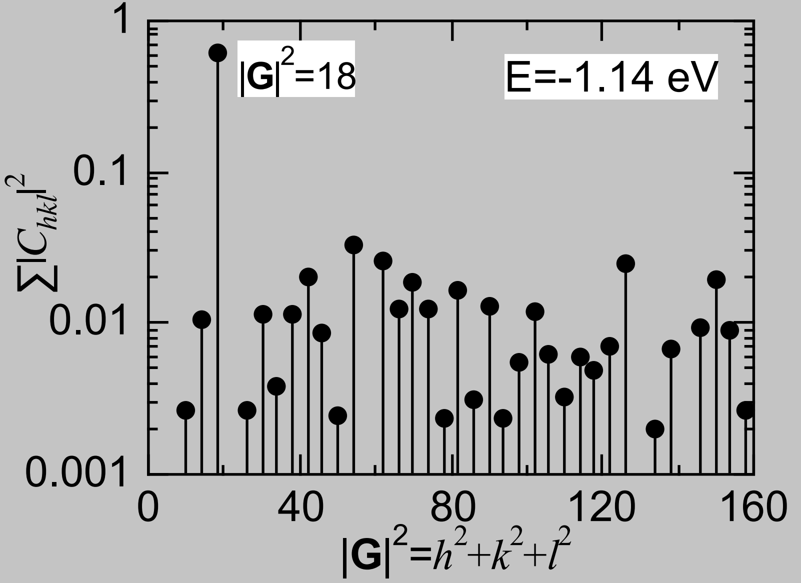
FLAPW-derived E-k relations and DOS for Pd_2Zn_{11} gamma-brass



FLAPW-Fourier spectra just below and above the pseudogap in Pd_2Zn_{11} gamma-brass

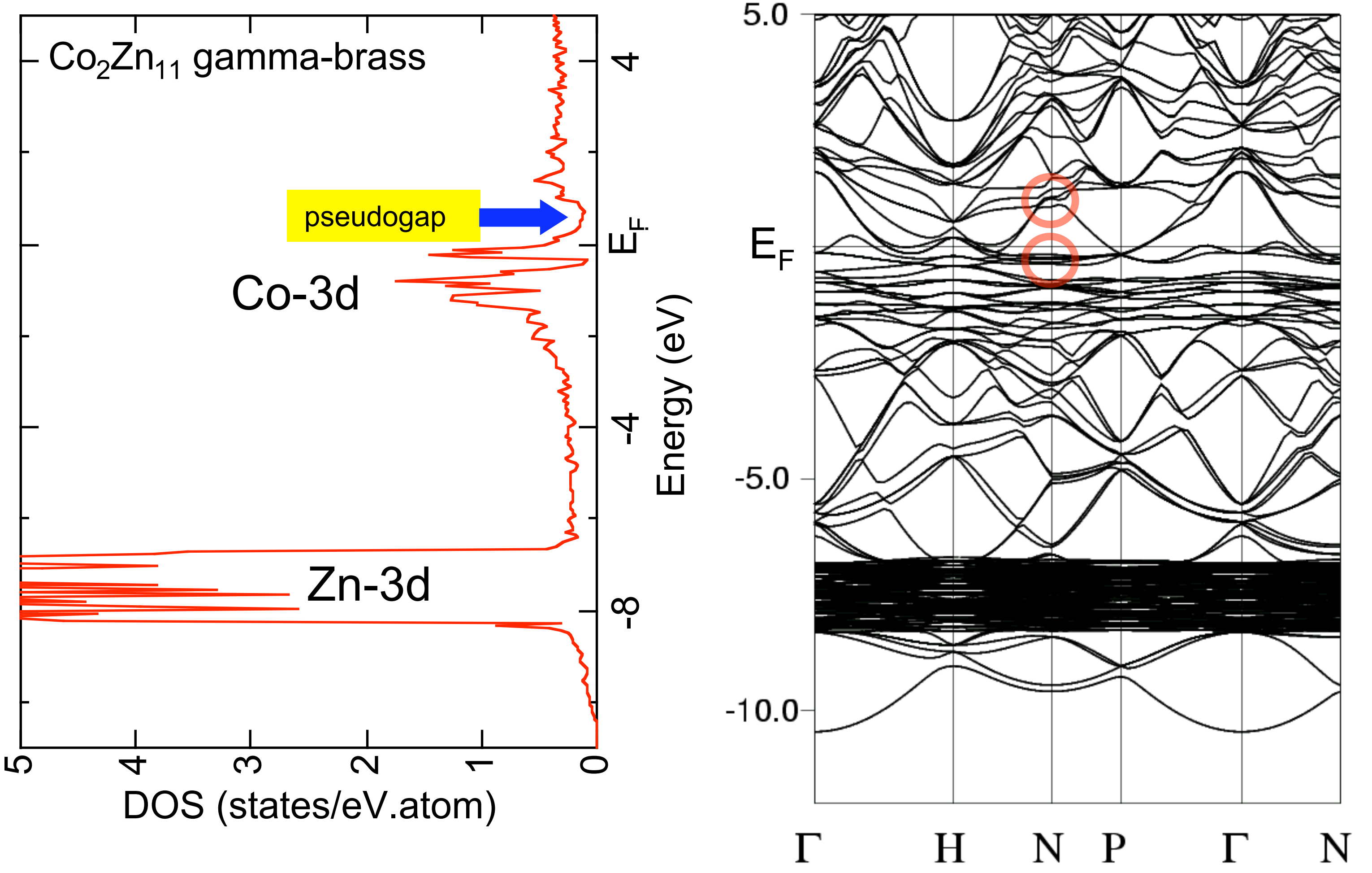




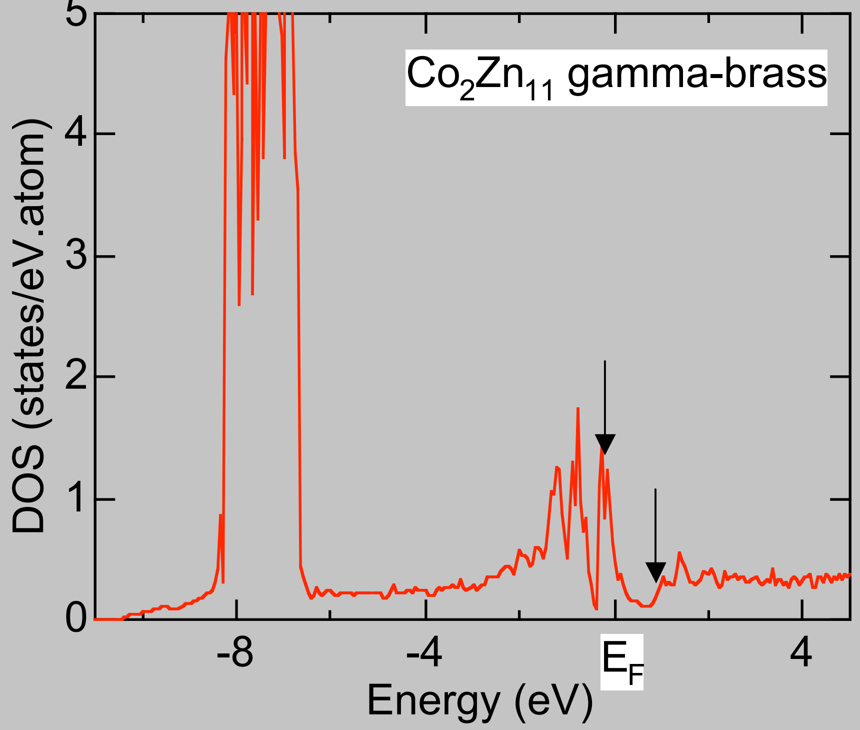


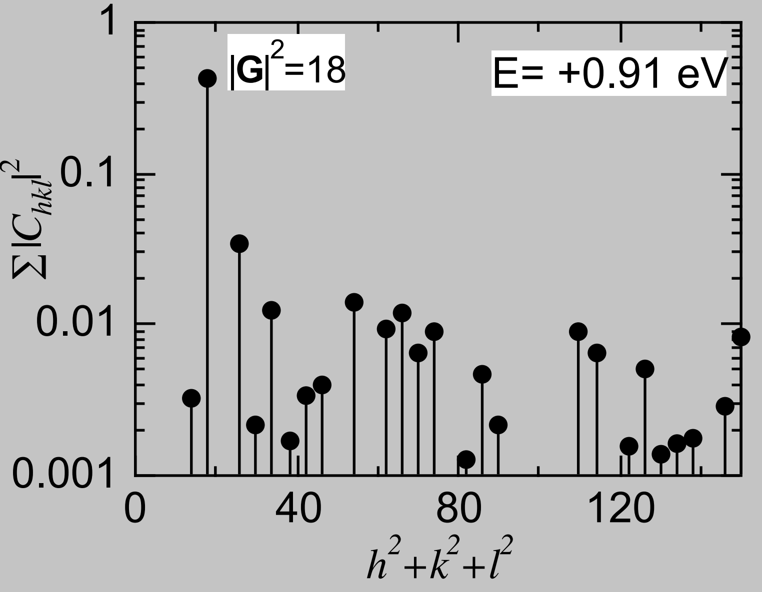
$G^2=18$ resonance is active in Pd_2Zn_{11} gamma-brass.

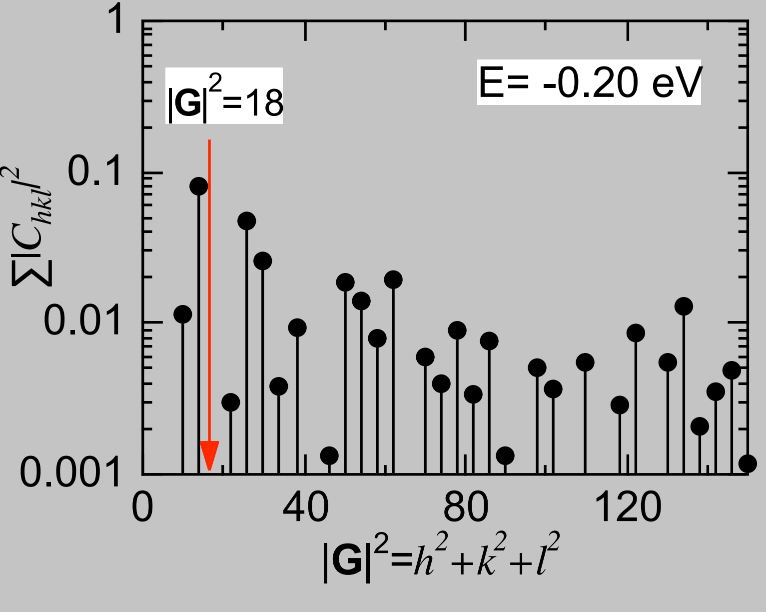
FLAPW-derived E-k relations and DOS for Co_2Zn_{11} gamma-brass



FLAPW-Fourier spectra just below and above the pseudogap in Co_2Zn_{11} gamma-brass

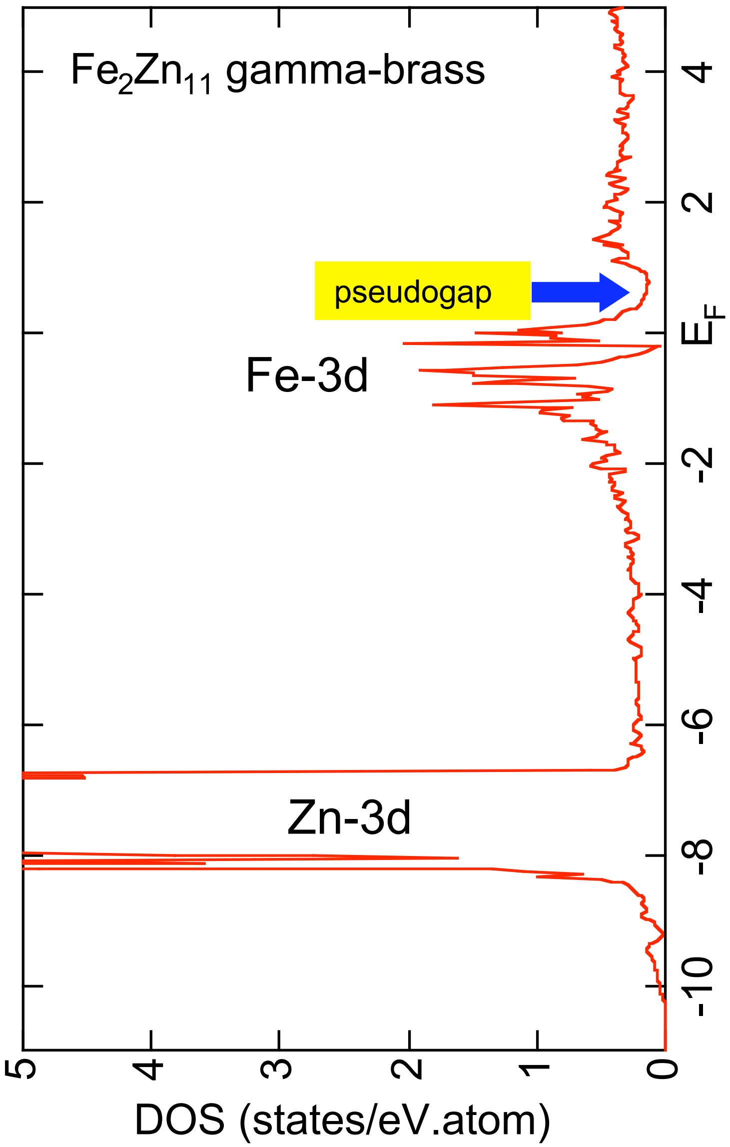


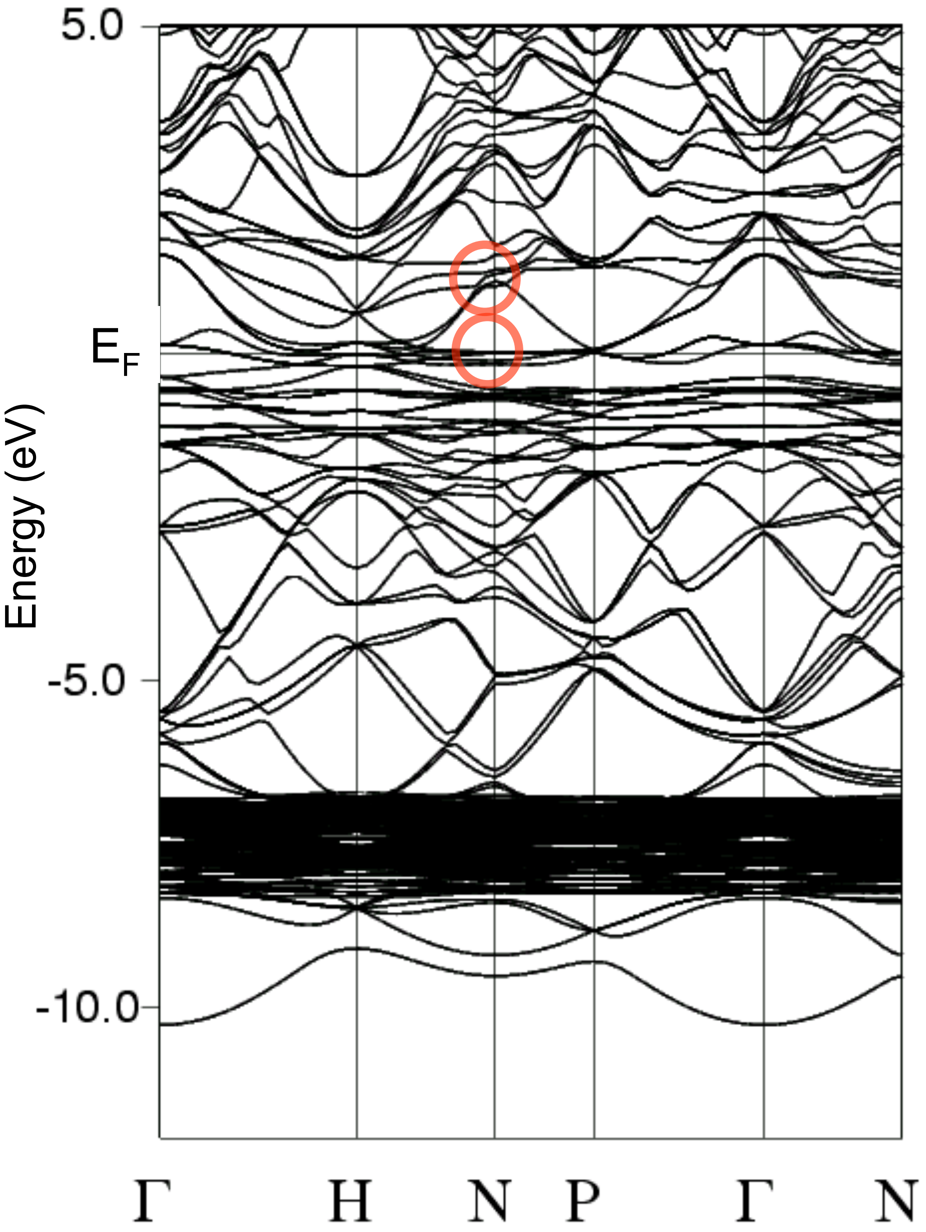




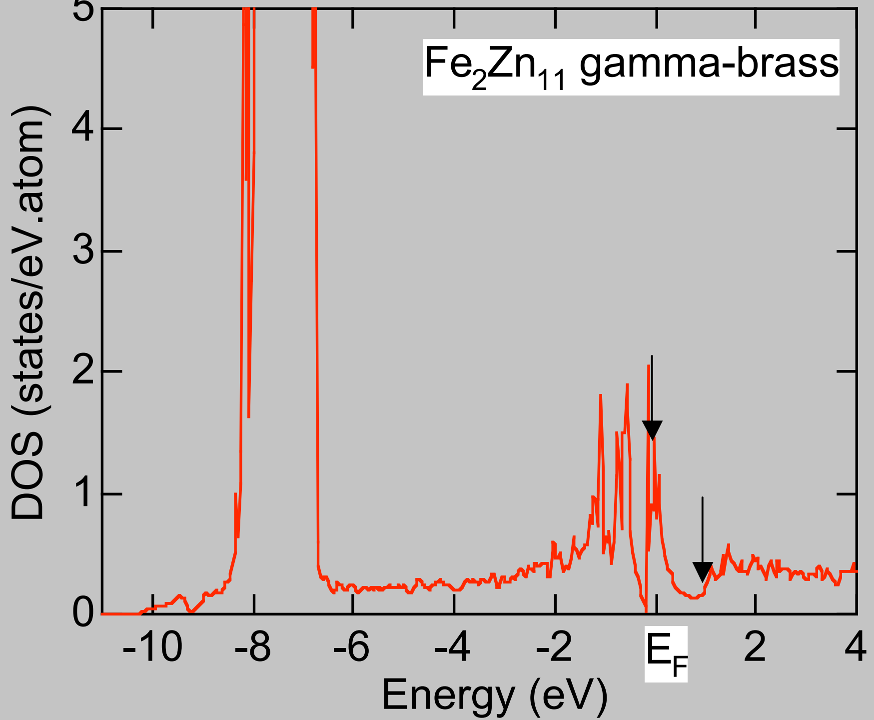
The G^2=18 resonance still survives only above the Fermi level in Co_2Zn_{11}.

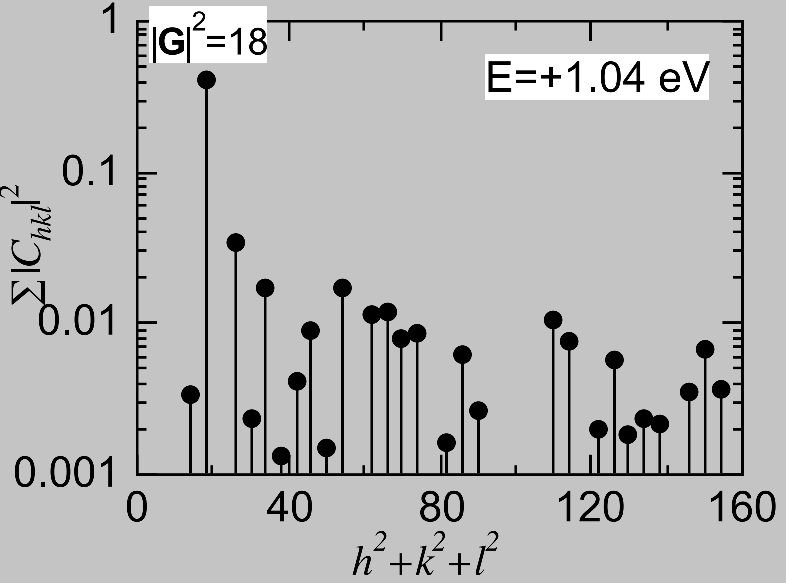
FLAPW-derived E-k relations and DOS for Fe_2Zn_{11} gamma-brass

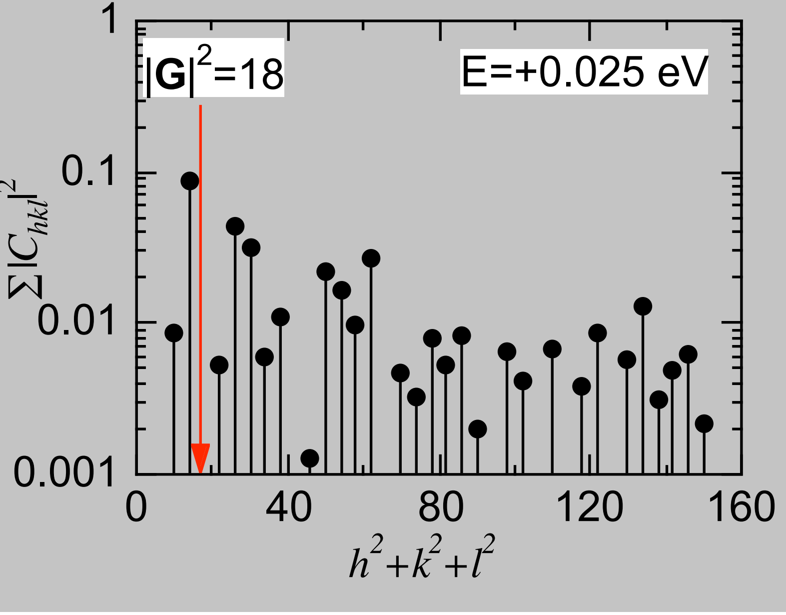




FLAPW-Fourier spectra just below and above the pseudogap in Fe_2Zn_{11} gamma-brass



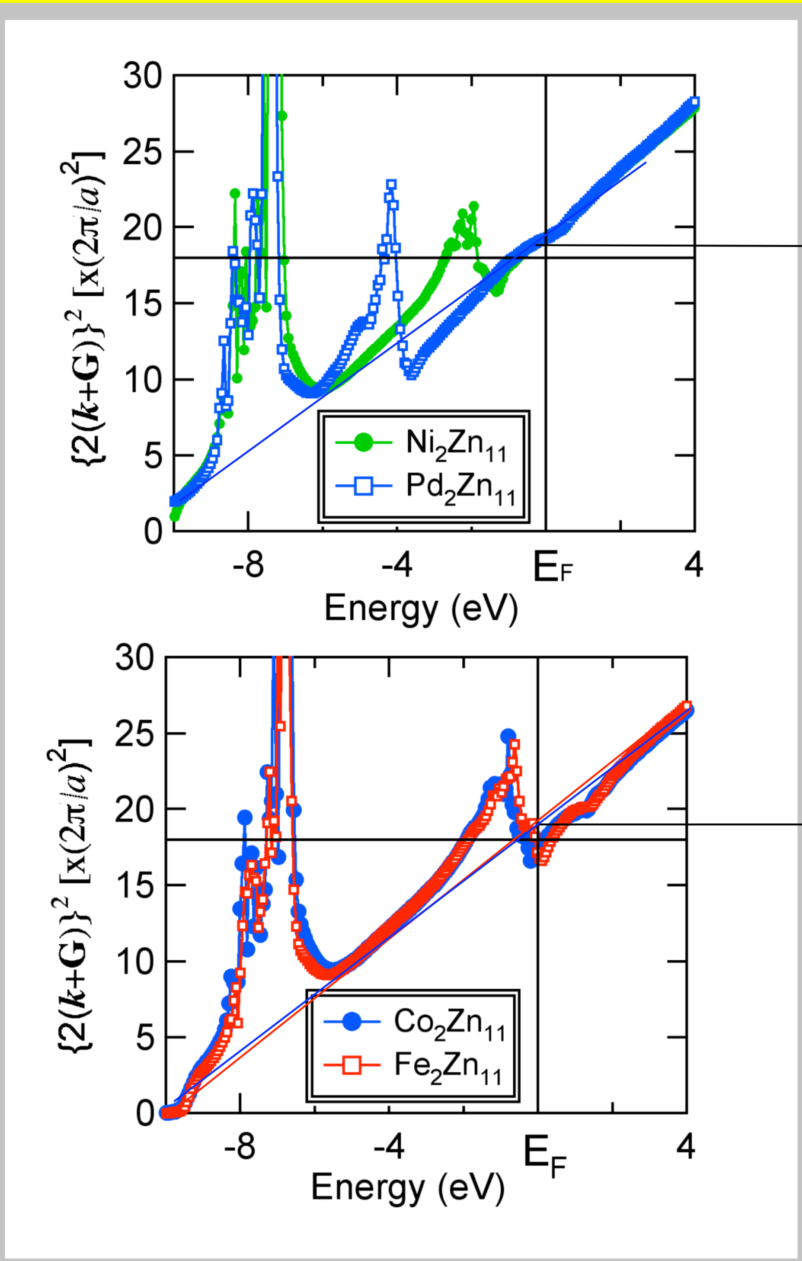




The $G^2=18$ resonance still survives only above the Fermi level in Fe_2Zn_{11}.

E-$(k+G)^2$ relations for itinerant electrons for TM_2Zn_{11} (TM=Ni, Pd, Co, Fe) gamma-brasses

---Hume-Rothery plot---



$(2k_F)^2$=19.36 for Ni_2Zn_{11}
=19.27 for Pd_2Zn_{11}

$$(e/a)_{total} = \frac{\pi}{3N}(2k_F)^3$$

N=52

$e/a_{Ni\text{-}Zn}$=1.72
$e/a_{Pd\text{-}Zn}$=1.70

$(2k_F)^2$=19.5 for Co_2Zn_{11}
=20.0 for Fe_2Zn_{11}

$$(e/a)_{total} = \frac{\pi}{3N}(2k_F)^3$$

N=52

$e/a_{Co\text{-}Zn}$=1.73
$e/a_{Fe\text{-}Zn}$=1.80

Gamma-brasses in group 1 obey the Hume-Rothery e/a law with e/a=21/13

	Cu_5Zn_8	Cu_9Al_4	Ni_2Zn_{11}	Pd_2Zn_{11}	Co_2Zn_{11}	Fe_2Zn_{11}
A pseudogap formed below E_F	○	○	○	○	X	X
$\lvert G\rvert^2$ deduced from the FLAPW-Fourier method	18	18	18	18	—	—
$(2k_F)^2$ deduced form the H-R plot	18.47	18.45	19.36	19.27	19.5	20.0
$(e/a)_{total}$	1.60	1.60	1.72	1.70	1.73	1.80
$(e/a)_{TM}$	0.96	0.97	0.15	0.07	0.26	0.70
VEC	11.6	8.5	11.7	11.7	11.538	11.385
	group (1)				group (2)	

The Hume-Rothery stabilization mechanism refers to the mechanism, in which a pseudogap is formed across the Fermi level as a result of electron waves resonating with a particular set of lattice planes and thereby the particular e/a value is specified.

Summary for gamma-brasses in groups 1 and 2

	gamma -brass	e/a		gamma -brass	e/a		gamma-brass	e/a
1	Cu_5Zn_8	1.60	1	Cu_9In_4	21/13	2	Ni_2Be_{11}	?
	Ag_5Cd_8	21/13		Ag_9In_4	21/13		Ni_2Cd_{11}	?
	Ag_5Zn_8	21/13		Au_9In_4	21/13		Mn_2Zn_{11}	?
	Cu_5Cd_8	21/13		Ni_2Zn_{11}	1.72		Pt_2Zn_{11}	?
	Au_5Cd_8	21/13		Pd_2Zn_{11}	1.70		Al_8V_5	1.46?
	Au_5Zn_8	21/13	2	Fe_2Zn_{11}	1.80		Mn_3In	?
	Cu_9Al_4	1.60		Co_2Zn_{11}	1.73	3	Ag_5Li_8	21/13 ?
	Cu_9Ga_4	21/13		Ir_2Zn_{11}	?			