

Approaching the valence concept:

Crystalline phases of chemical elements

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July 2013

order and diffraction

nearest-neighbor distance

stabilizing a length scale L

trial valance

virtual valance

interference features in the density of states

virtual valence and band structure

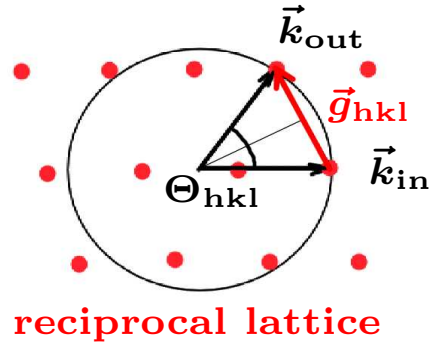
conclusions

Order and diffraction

interference-enhanced valence electrons stabilize the structure
joined planar/radial interference peaks

Planar diffraction peaks

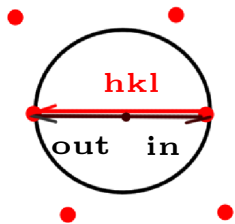
Ewald construction



cubic lattice, side length a , planar spacing d_{hkl} , Miller indices hkl , Bragg peaks at the angles Θ_{hkl} :

$$2 |\vec{k}_{in}| \sin \left(\frac{\Theta_{hkl}}{2} \right) = |\vec{g}_{hkl}| = \frac{2\pi}{d_{hkl}}, \quad \frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

true backscattering



true backscattering by the (hkl) planes: $\Theta_{hkl} = \pi$

first Bragg peak: $2 |\vec{k}_{in}| = \frac{2\pi}{d_{hkl}}$

peak energy due to free-electron dispersion: $\epsilon_{hkl} = \left(\frac{1}{2} \frac{2\pi}{d_{hkl}} \right)^2$

conclusion

- Planar interference peaks emerge at the free-electron energies ϵ_{hkl} . What does this mean for the band electrons?

Radial diffraction peaks

liquid targets:

structure factor $S(q)$, pair correlation $g(r)$,
number density \mathcal{N}_{at}

$$S(q) - 1 = 4\pi\mathcal{N}_{at} \int_0^\infty dr r^2 (g(r) - 1) \frac{\sin(qr)}{qr}$$

suppose: $g(r)-1$ has one peak at R

obtain: peaks of $S(q)-1$ at

$$q = K_n = \frac{5}{4} \frac{2\pi}{R} \left(1 + (n-1)\frac{4}{5}\right), n = 1, 2, \dots$$

due to $x = K_n R = 2\pi (1/4 + n)$

generalizations:

A peak in $S(q)-1$ at K generates the peak sequence

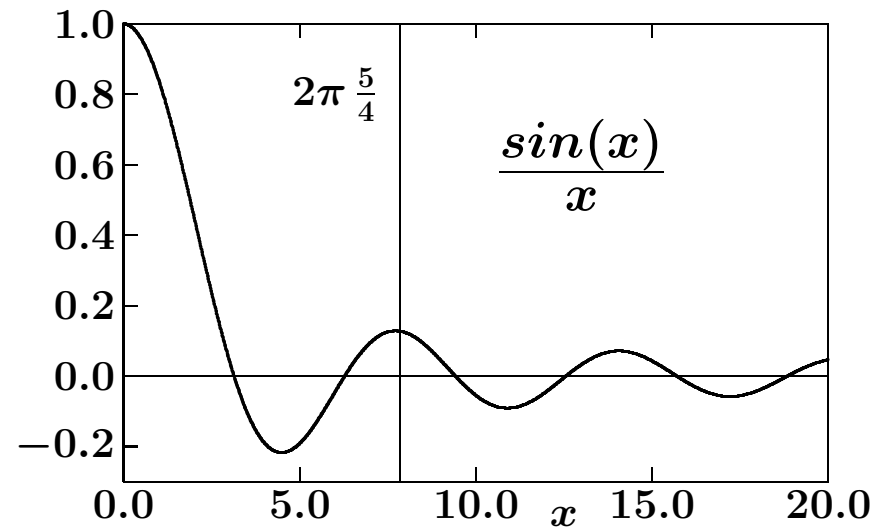
$$R_n = \frac{5}{4} \frac{2\pi}{K} \left(1 + (n-1)\frac{4}{5}\right), n = 1, 2, \dots,$$

in $g(r) - 1$.

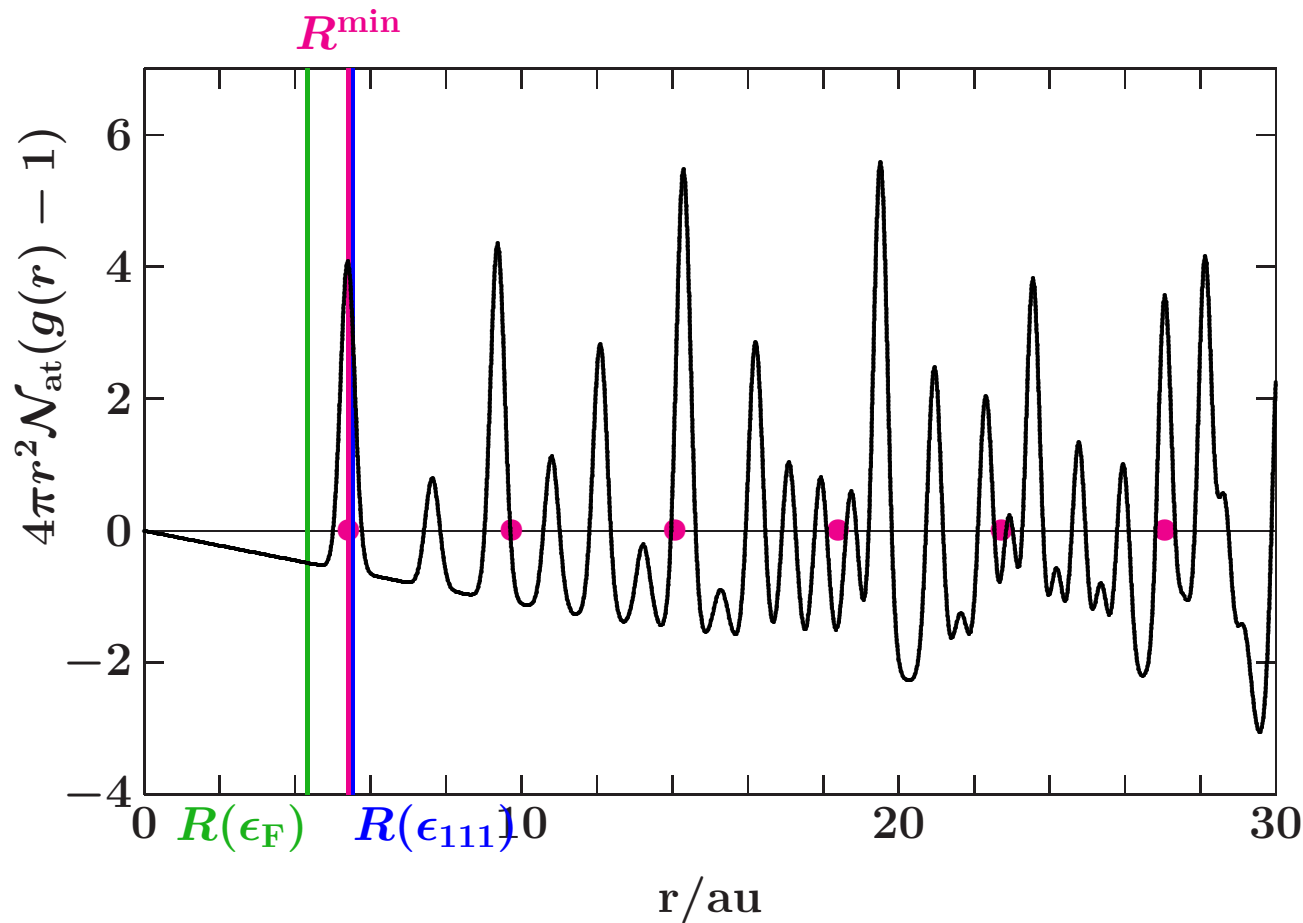
The statements apply to amorphous targets and to the isotropic average of crystal diffraction, as well.

conclusion

- Diffraction with neighbors at the distance R generates the radial main diffraction peak (MDP) at the free-electron energy $\epsilon(R) = \left(\frac{1}{2} \frac{5}{4} \frac{2\pi}{R}\right)^2$ au.



Al-fcc: Radial and planar interference coexist



plotted: the reduced pair correlation of Al-fcc (gaussian broadening ($\sigma \approx 0.2$ au))

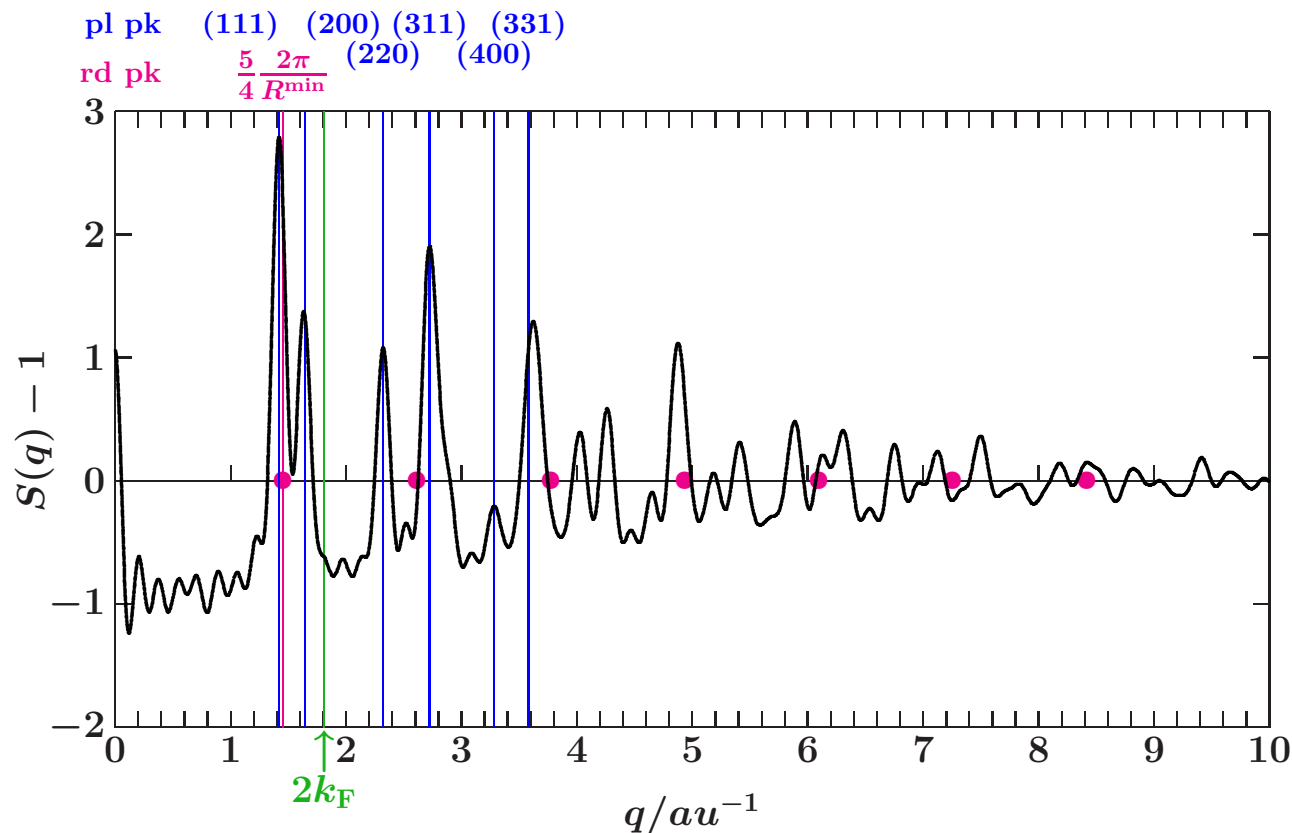
dots (•): $R^{\min}(1 + (n-1)\frac{4}{5})$, the sequence which promotes the radial interference

bars: $R(\epsilon_F)$, $R(\epsilon_{111})$, the shell radii where, if occupied, radial main diffraction peaks could be excited at the indicated energies, ϵ_F (Fermi energy) and $\epsilon_{111} < \epsilon_F$ (planar peak (111)) both with reference to the bottom of the valence band

conclusions:

- The fcc-derived neighbor-shell sequence differs from $R^{\min}(1 + (n-1)\frac{4}{5})$.
- Below ϵ_F both the planar spacing and the lateral positions of the (111) planes can jointly be stabilized.
- With the employed energy reference there is no radial interference at ϵ_F .

Al-fcc: No planar diffraction around the Fermi level



plotted: the structure factor of Al-fcc as appropriate to powder diffraction (attenuation length 10 Å)

top labels: the observed planar peaks, the calculated radial MDP

dots (•): the expected radial diffraction peaks due to R^{\min}

$2k_F = 2\sqrt{\epsilon_F}$: derived from the Fermi energy with reference to the bottom of the valence band of the LMTO-AS/MT¹ calculation

conclusions:

- The most distinct diffraction peaks are due to planar interference. The radial MDP of R^{\min} joins the planar MDP (111).
- With the present choice of the energy zero there is no strong planar interference around the Fermi energy.

¹ LMTO-ASA extended to the muffin-tin model, R. Arnold, thesis, TU Chemnitz, 1998

Nearest-neighbor distance

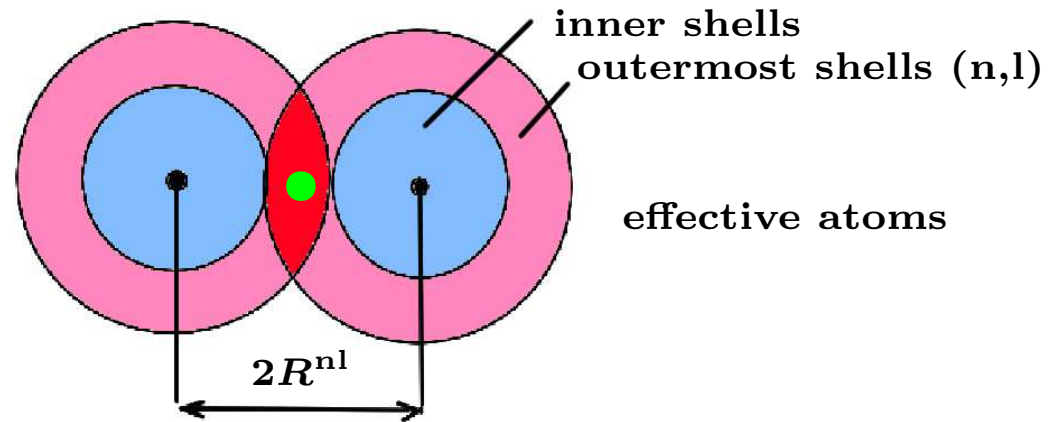
effective atoms in contact feel molecule-like

The role of valence electrons is twofold

nearest-neighbor order:

Nearest-neighbor distances are adjusted to maximum overlap of the outermost electronic shells of the effective atoms (chemical aspect).

The outermost effective-atom orbitals are "sensitive to this length scale".



medium- and long-range order:

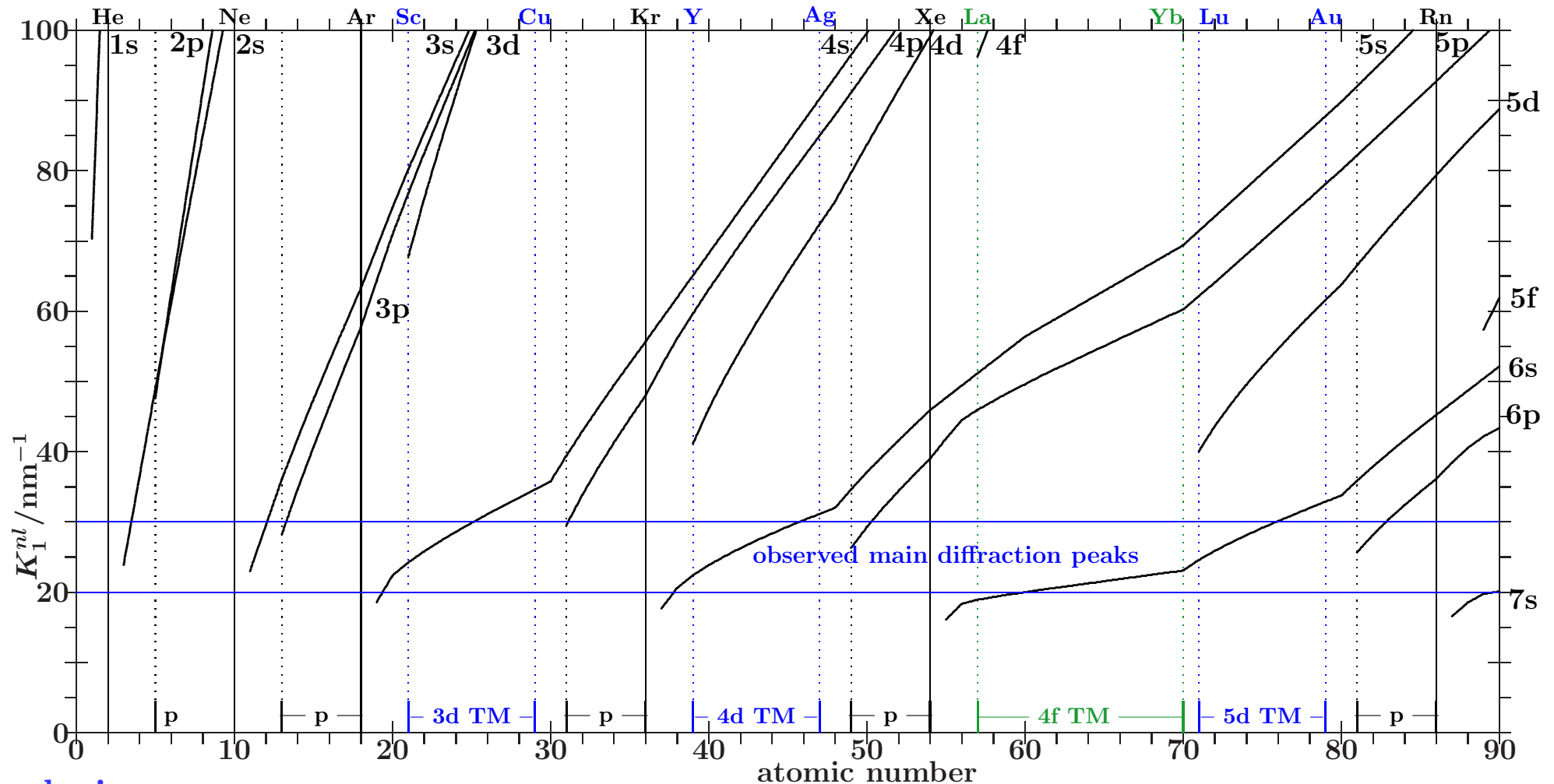
Valence states decompose mainly into the outermost effective-atom orbitals.

The distribution of atoms is driven by the valence electrons towards final structures which enable highly constructive electronic interference (diffraction aspect).

Chemical: If atoms would approach another down to $2R_{nl}$

We employ self-consistent free atoms with a local exchange-correlation potential.

$K_1^{nl} = \frac{5}{4} \frac{2\pi}{2R_{nl}}$, the radial main diffraction peak (MDP) calculated from distance $= 2R_{nl}$



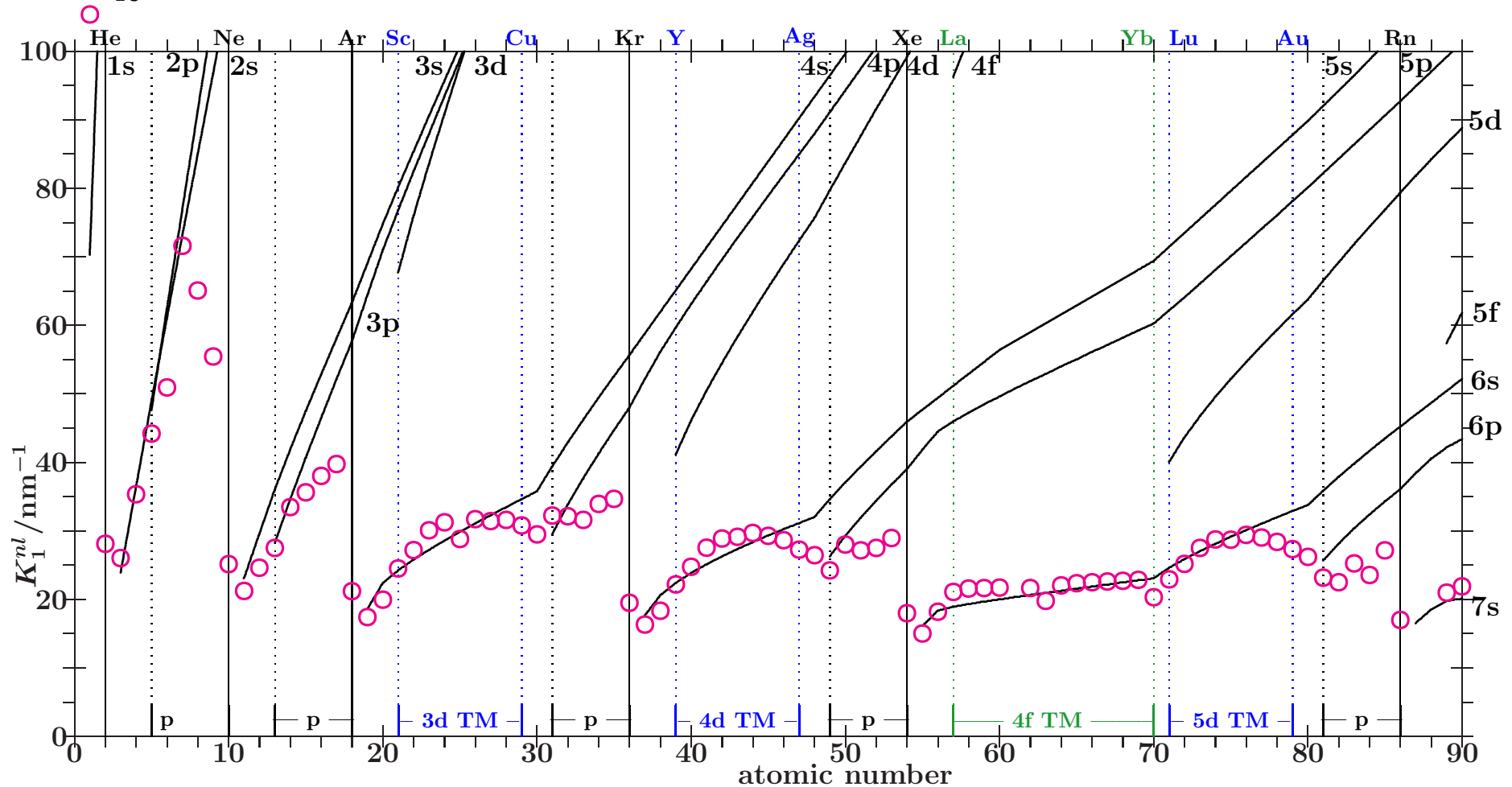
conclusions:

- *ss-/pp*-type nearest-neighbor contacts preferred
- define: "*s/p*-ranges" of the atomic number where the topmost atomic orbitals are *s/p*-type

Crystals: Diffraction from the shortest interatomic distances

$K_1^{nl} = \frac{5}{4} \frac{2\pi}{2R^{nl}}$, the radial MDP calculated from distance $= 2R^{nl}$

$K_1^{\min} = \frac{5}{4} \frac{2\pi}{R^{\min}}$, the radial MDP calculated from the shortest interatomic distance R^{\min}



conclusion:

- Diffraction from the shortest interatomic distances in the element crystals follows the topmost electron density shells of the atoms.

Stabilizing a length scale L

**constructive interference makes electrons strong on a
specific length scale**

Stabilizing the shortest interatomic scale $2\pi/(2k_F)$

- **restrictions:**
alloy components not too different in atomic size and electronegativity
- **empirical finding²:**
Certain AB alloys (concentrations $c_{A/B}$, free-atom valences $Z_{A/B}$) adopt specific structures at specific values of $\bar{Z} = c_A Z_A + c_B Z_B$.
- **explained later on:**
Phase stability is a matter of *sp*-electron diffraction around the Fermi level.
A stabilizing pseudogap is opened around the Fermi energy if the *sp*-electron Fermi sphere encounters Bragg planes of strong diffraction peaks (comprehensive references³).

² W. Hume-Rothery, J Inst Met 35,295(1926)

³ G. Trambly de Laissardière *et al.* Progress in Materials Science 50,679(2005),
Y.M. Zhang, J.R.G. Evans, S. Yang, The prediction of solid solubility of alloys: development and application of Hume-Rothery rules

Stabilizing scales $> 2\pi/(2k_F)$

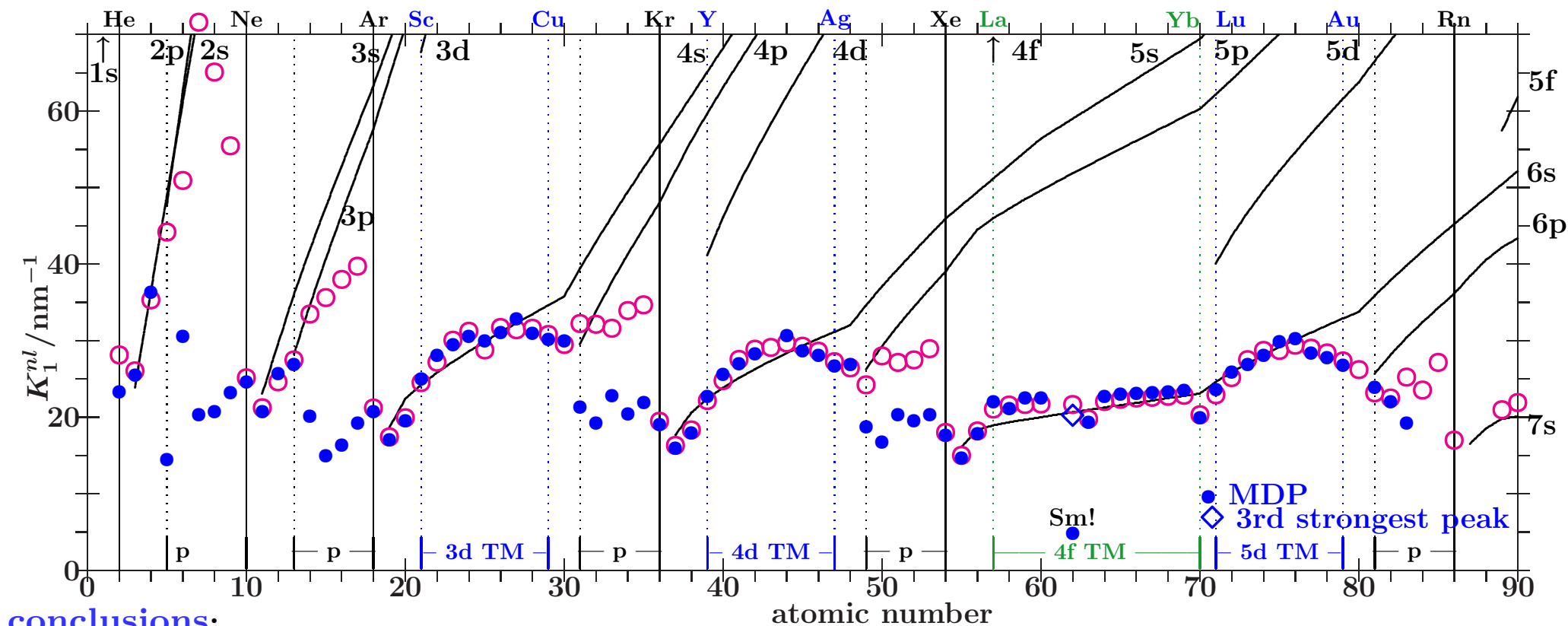
- suppose a stack of lattice planes (spacing L)⁺:
Stability on the scale L must be due to constructive interference in the true backscattering of waves with the momentum $\frac{2\pi}{2L}$ - this ensures $\frac{2\pi}{2L} \times 2L = 2\pi$.
- DOS features below the Fermi level:
Diffraction on length scales $> \frac{2\pi}{2k_F}$ creates DOS features, even far below the Fermi level.

⁺ The corresponding applies to a sequence of neighbor shells.

Crystals: In *p*-ranges two length scales to be stabilized

K_1^{cry} = $4\pi \frac{\sin(\Theta/2)}{\lambda}$, the measured strongest planar peak (MDP), data from AMS⁴

K_1^{min} , the radial MDP calculated from the shortest interatomic distance R^{min}



conclusions:

- K_1^{cry} and K_1^{min} are momentum transfers where certain **planar** respectively **radial** interferences produce MDPs. Coincidence indicates that the valence electrons may stabilize an interplanar distance **together** with an assigned interatomic distance (stable lateral shift).
- *p*-ranges: K_1^{min} belongs to stabilized subunits. K_1^{cry} arises from the scale of a correlation length of subunits which is almost the scale of the *ss*-contacts at the beginning of the next *s*-range. Note Sm with $\sim 5 \text{ nm}^{-1}$ due to long hexagonal structure units.

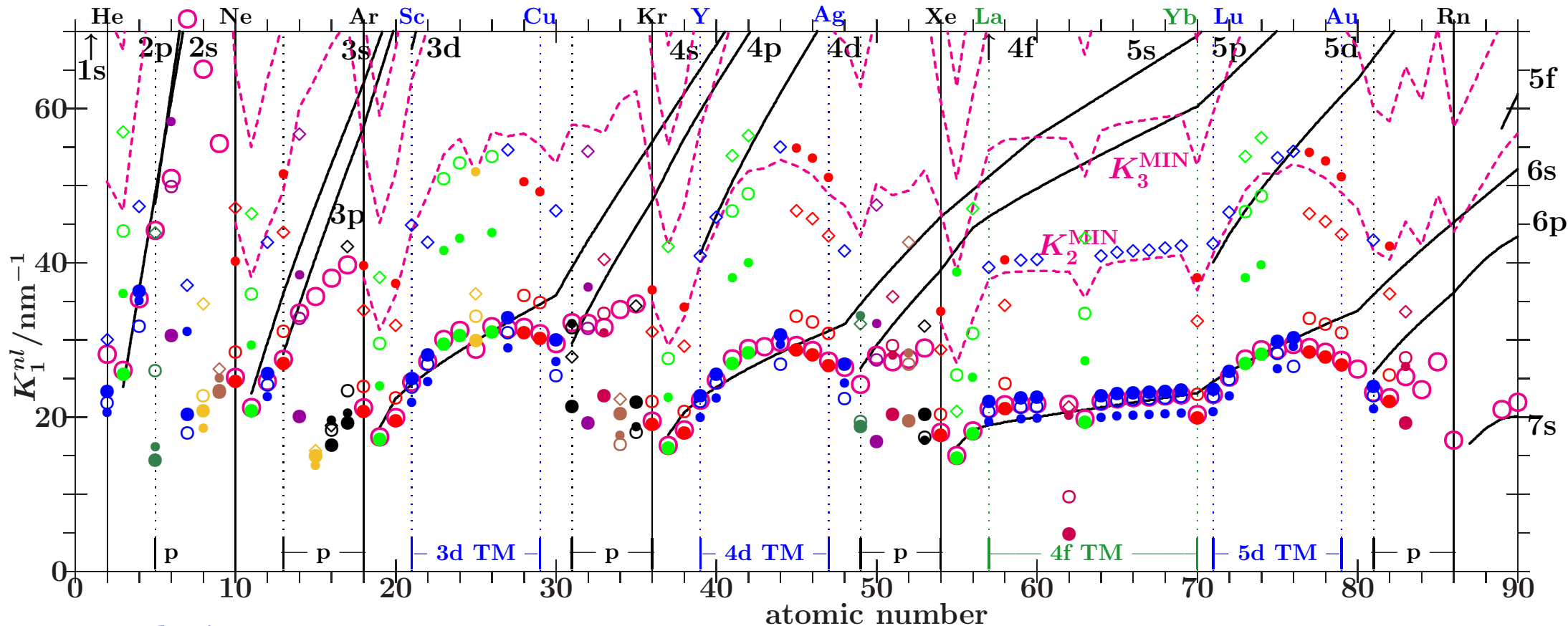
⁴ AMS American Mineralogical Society, $\lambda = 1.541838 \text{ \AA}$

Crystals: Diffraction peaks for two length scales

$$K_{hkl} = 4\pi \frac{\sin(\Theta_{hkl}/2)}{\lambda}, \text{ observed planar peaks}^4$$

$$K_n^{\text{MIN}} = K_1^{\text{min}} (1 + (n-1)\frac{4}{5}), \text{ calculated from } R^{\text{min}}$$

latt.	bcc, fcc, hcp orc tet mcl cub dia rhl
int.	● (1=MDP) ○ (2) ● (3) ◇ (4)



conclusions:

- The four strongest planar peaks K_{hkl} follow the K_n^{MIN} which are derived from radial diffraction rules.
- p-ranges: The K_1^{min} are well occupied.

Valence for dense packed crystals: Rough estimates

length scales: R^{\min} and the assigned large interplanar distance d_{hkl}

joined planar/radial interference: momentum transfers K at the interference peaks

$$K_1^{\min} = \frac{5}{4} \frac{2\pi}{R^{\min}}, \quad K_{\text{hkl}} = \frac{2\pi}{d_{\text{hkl}}} = \frac{2\pi}{\alpha_{\text{hkl}} R^{\min}} \approx K_1^{\min}, \quad \alpha_{\text{hkl}} < 1$$

structure: roughly characterized by the packing ratio β , atom number density \mathcal{N}_{at}

$$\beta \equiv \frac{4\pi}{3} \left(\frac{R^{\min}}{2} \right)^3 \mathcal{N}_{\text{at}}$$

true backscattering: over the degenerate Fermi body (\approx Fermi sphere, Z electrons contributed per atom), maximum momentum transfer

$$K = 2 \left(3\pi^2 \mathcal{N}_{\text{at}} Z \right)^{\frac{1}{3}} = 2 \left(\frac{9\beta Z}{4\pi^2} \right)^{\frac{1}{3}} \frac{2\pi}{R^{\min}}$$

support by constructive interference: $K_1^{\min} \approx K_{\text{hkl}} \approx K$

$$1.25 \approx \frac{1}{\alpha_{\text{hkl}}} \approx 1.22 (\beta Z)^{\frac{1}{3}}$$

conclusion: For hcp, ideal $\frac{c}{a} = 2\sqrt{\frac{2}{3}}$, $\frac{1}{\alpha_{101}} = \sqrt{\frac{41}{24}} \approx 1.31$, $\beta = 0.74$ the valence $Z \approx 1.45 \dots 1.67$ ensures that both the radial and the planar MDP can be excited in true backscattering. Generally, βZ slightly above unity may serve as a guide.

Trial valence

take arbitrary $Z_{\text{trial}} = 1, 2, \dots, 8$
obtain a sequence $\{K_{\text{trial}}\}$
compare with diffraction results

trial valence: Z_t arbitrarily set to values $1, 2, \dots, 8 \implies K_t = 2 \left(3\pi^2 \mathcal{N}_{at} Z_t \right)^{\frac{1}{3}}$

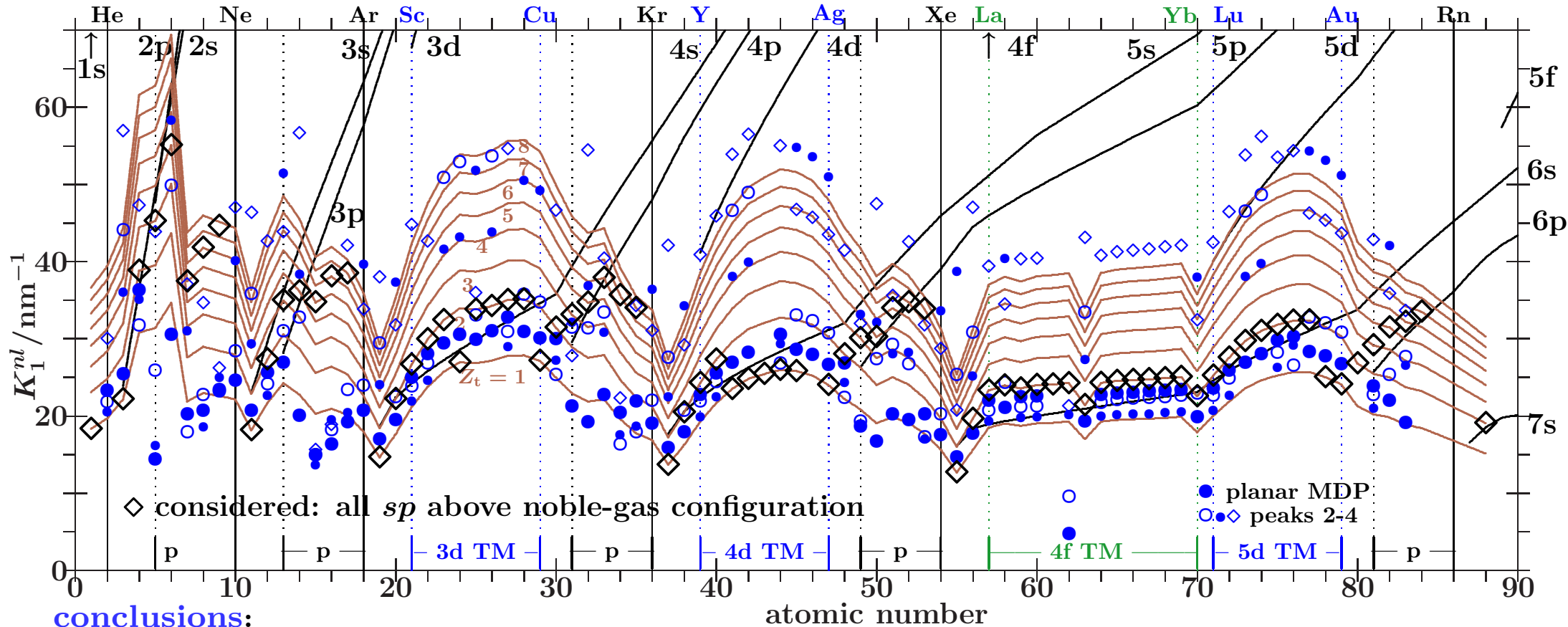
$$K_n^{\text{MIN}} = K_1^{\text{min}}(1 + (n - 1)\frac{4}{5}), \text{ the radial peak sequence derived from the MDP } K_1^{\text{min}} = \frac{5}{4} \frac{2\pi}{R_{\text{min}}}$$


- s-ranges: MDPs K_1^{\min} can be excited with Z_t between 1 and 2, i.e. no p -orbitals included, note: due to K_2^{\min} $R^{\min} = 2\pi(2 + \frac{1}{4})$ support for R^{\min} by 8-electron shells
- p-ranges: MDPs K_1^{\min} can be excited with $Z_t > 2$, i.e. p -orbitals included

Crystals: Excitation of the planar peak sequence

trial valence: Z_t arbitrarily set to values 1, 2, ..., 8 $\Rightarrow K_t = 2 (3\pi^2 \mathcal{N}_{at} Z_t)^{\frac{1}{3}}$

for comparison (\diamond): free atoms, Z_{sp} sp -electrons above noble-gas, $K_{sp} = 2 (3\pi^2 \mathcal{N}_{at} Z_{sp})^{\frac{1}{3}}$



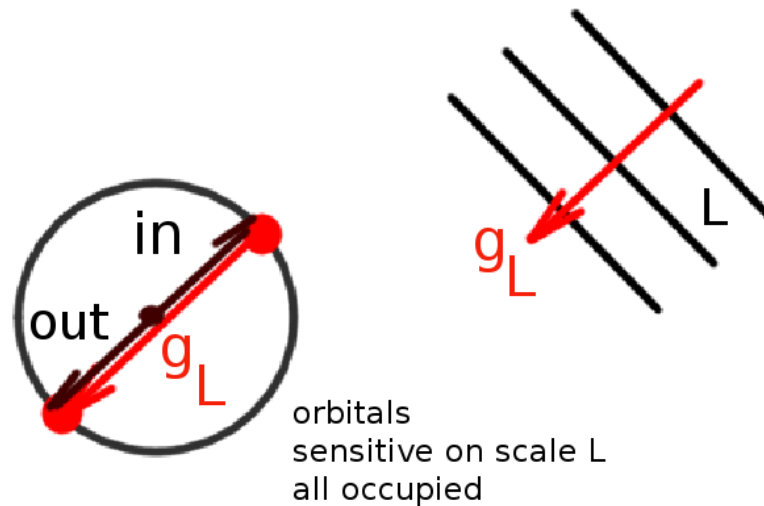
- s-ranges: The planar MDPs behave just like the K_1^{\min} .
- p-ranges: Less intensive planar peaks and K_{sp} follow the internal pp contacts in subsystems, cf. K_1^{\min} . Planar MDPs tend to drop down even below $Z_t = 1$.
The arrangement of subunits must thus be stabilized by true backscattering across a small part of the total sp content.

Virtual valence

take a lattice type (bcc, fcc, hcp, dia, ...)

take an interference peak (**planar** (hkl), **radial** R)

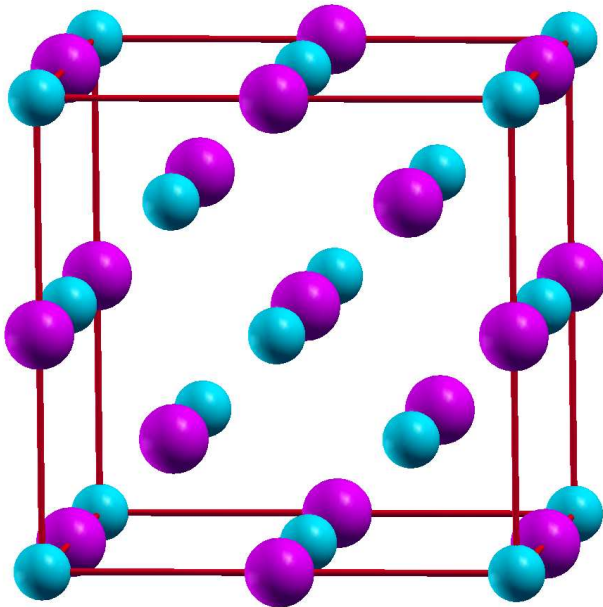
ensure true backscattering with excitation of this interference peak



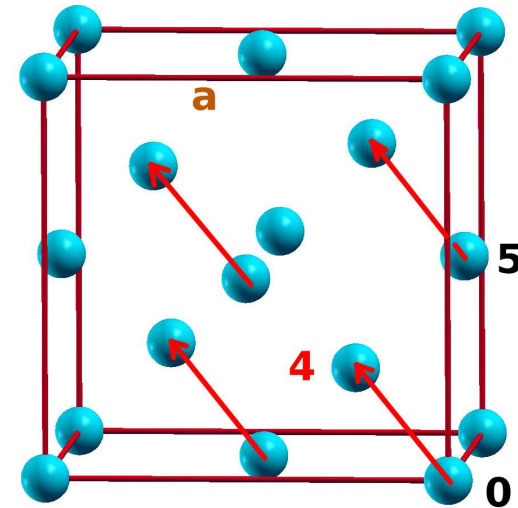
obtain a universal virtual valence $Z(\text{lattice type, interference peak})$

Related lattices: $\text{BCC} = 2 \times \text{DIA} = 4 \times \text{FCC}$

$\text{BCC} = 2 \times \text{DIA}$

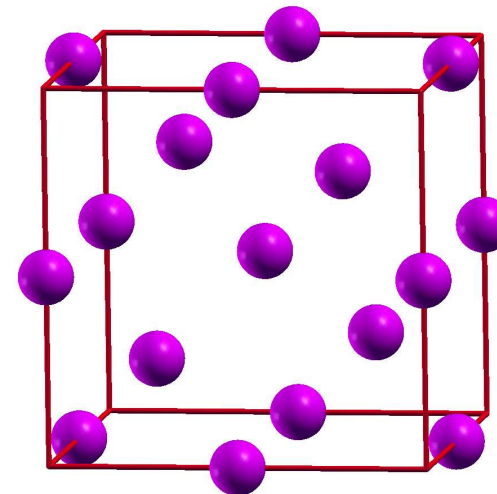


=



atoms
= $2 \times \text{FCC}$

+



holes
= $2 \times \text{FCC}$

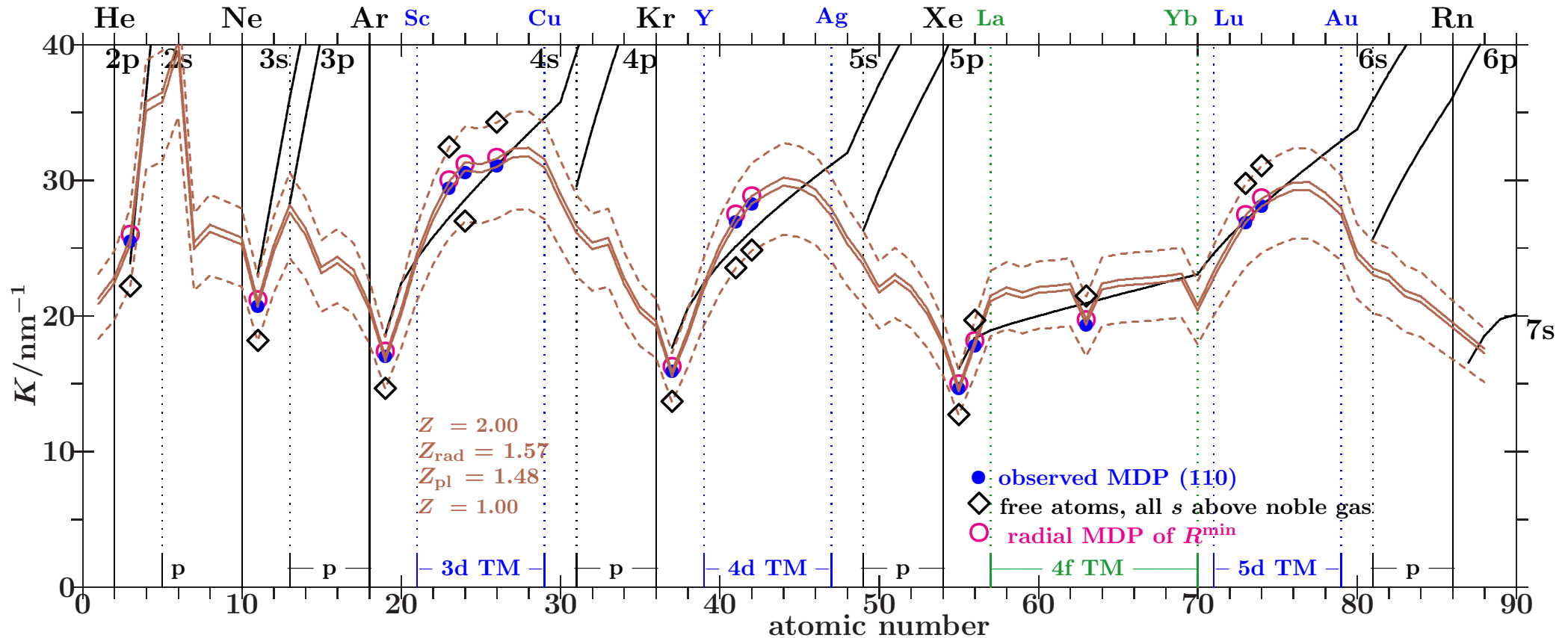
conclusions:

- decomposition of $2 \times 2 \times 2$ BCC: DIA(holes) obtained on shifting DIA(atoms) by $a/2$ along an arbitrary side of the cube
- decomposition of DIA: FCC-2 obtained on shifting FCC-1 by $a\sqrt{3}/4$ along a space diagonal of the cube

Virtual valence: BCC lattice (cube side length a)

$$K = 2 \left(3\pi^2 \mathcal{N}_{\text{at}} Z \right)^{\frac{1}{3}} = 2 \left(3\pi^2 \frac{2}{a^3} Z \right)^{\frac{1}{3}}$$

$$\begin{aligned} R^{\min} \text{ radial} &\equiv \frac{5}{4} \frac{2\pi}{a\sqrt{3}/2} \Rightarrow Z_{\text{rad}} = \frac{125\pi}{144\sqrt{3}} \approx 1.57 \\ (110) \text{ planar} &\equiv \frac{2\pi}{a\sqrt{2}/2} \Rightarrow Z_{\text{pl}} = \frac{\pi\sqrt{2}}{3} \approx 1.48 \end{aligned}$$



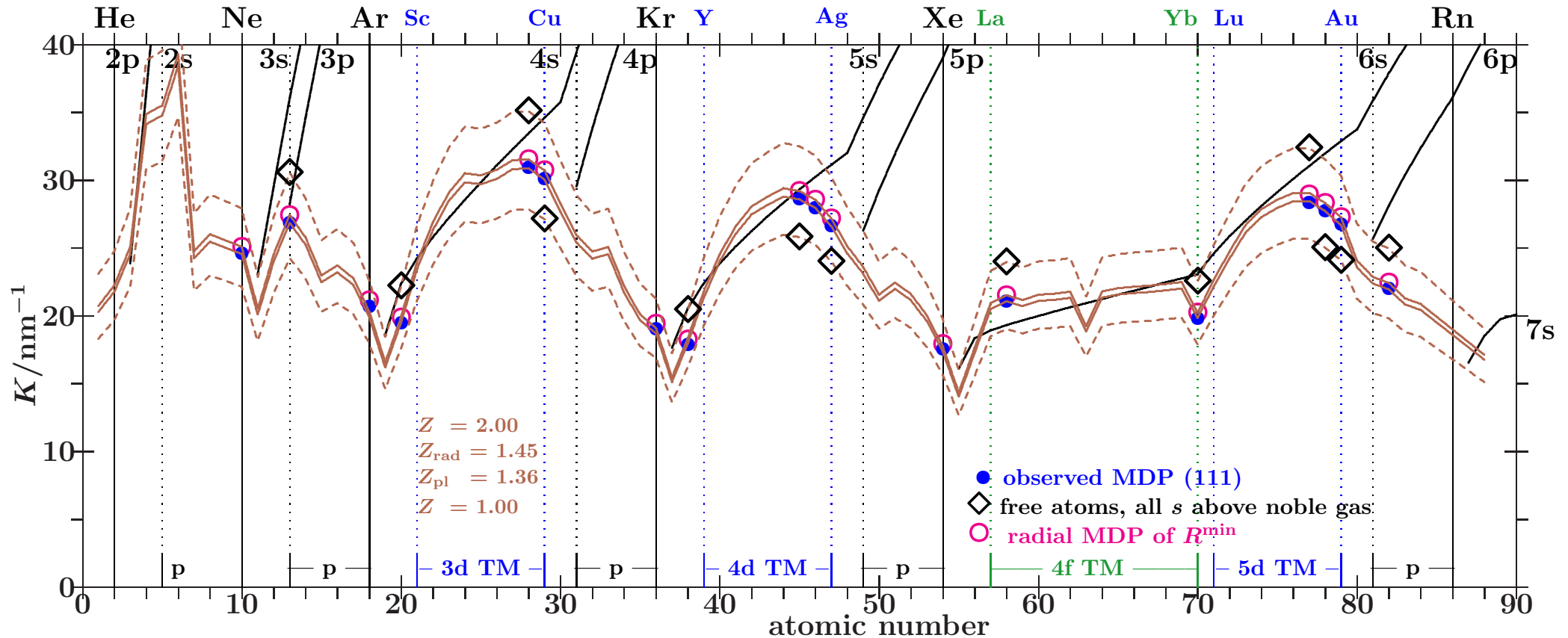
conclusion:

- universal for bcc: $Z_{\text{pl}} = 1.48$ for best planar MDP (110), $Z_{\text{rad}} = 1.57$ for best radial MDP R^{\min}

Virtual valence: FCC lattice (cube side length a)

$$K = 2 \left(3\pi^2 \mathcal{N}_{\text{at}} Z \right)^{\frac{1}{3}} = 2 \left(3\pi^2 \frac{4}{a^3} Z \right)^{\frac{1}{3}}$$

$$\begin{aligned} R^{\min} \text{ radial} &\equiv \frac{5}{4} \frac{2\pi}{a\sqrt{2}/2} \Rightarrow Z_{\text{rad}} = \frac{125\pi}{192\sqrt{2}} \approx 1.45 \\ (111) \text{ planar} &\equiv \frac{2\pi}{a\sqrt{3}/3} \Rightarrow Z_{\text{pl}} = \frac{\pi\sqrt{3}}{4} \approx 1.36 \end{aligned}$$



conclusions:

- universal for fcc: $Z_{\text{pl}} = 1.36$ for best planar MDP (111), $Z_{\text{rad}} = 1.45$ for best radial MDP R^{\min}

Virtual valence: BCC, FCC, DIA (cube side length a)

The following applies to the radial MDP of the interatomic distance R

$$K = 2 \left(3\pi^2 \frac{NZ(R)}{a^3} \right)^{\frac{1}{3}} = \frac{5}{4} \frac{2\pi}{R} \implies NZ(R) = \frac{125\pi}{192} \left(\frac{a}{R} \right)^3,$$

respectively to the planar peak (hkl) of the interplanar distance $d_{(hkl)} = a/\sqrt{h^2 + k^2 + l^2}$

$$K = 2 \left(3\pi^2 \frac{NZ(hkl)}{a^3} \right)^{\frac{1}{3}} = \frac{2\pi}{d_{(hkl)}} \implies NZ(hkl) = \frac{\pi}{3} \left(\frac{a}{d_{(hkl)}} \right)^3.$$

N is the number of contributing sites per cube a^3 . $Z(R)$ and $Z(hkl)$ designate the required virtual valences per site.

universal virtual valences:

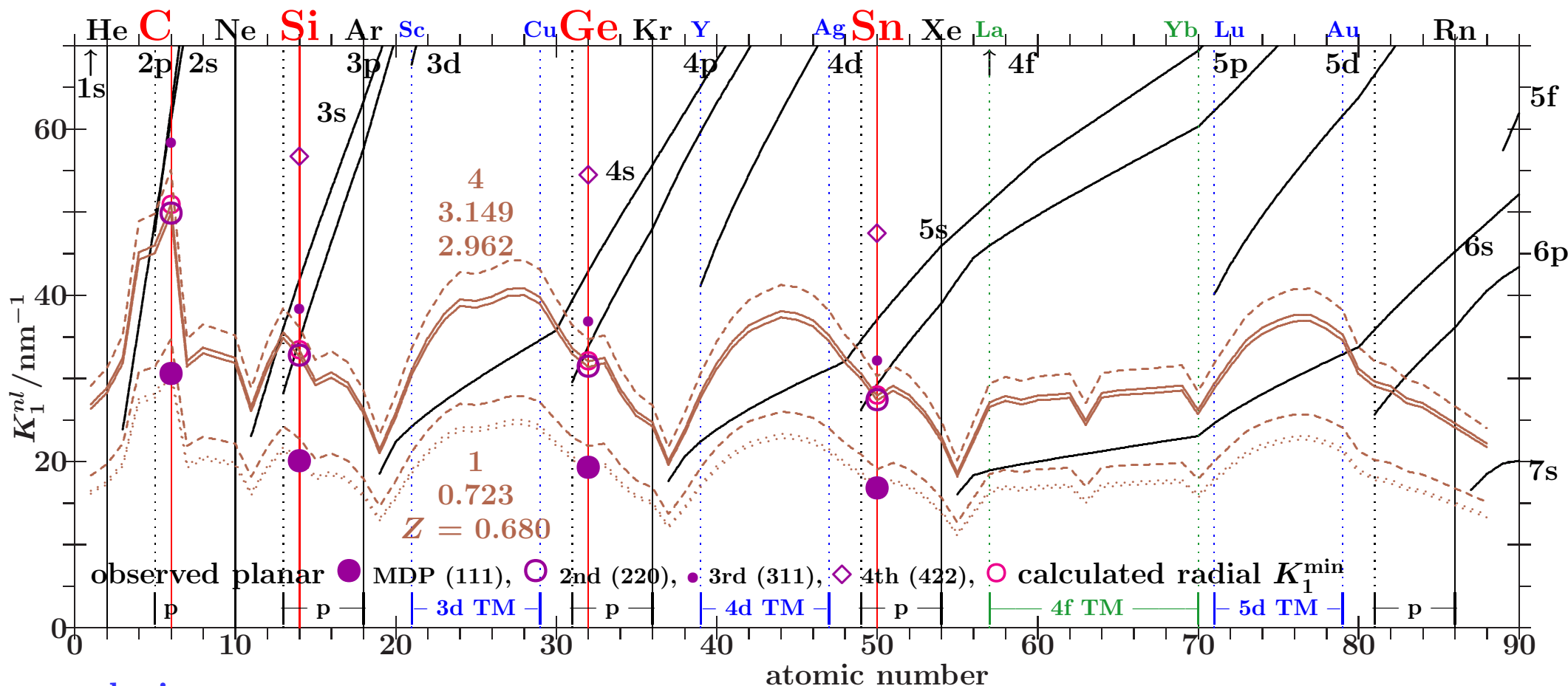
stabilized distance	bcc ($N = 2$)	fcc ($N = 4$)	dia ($N = 8$)
$R(0 \rightarrow 4)$	$R(0 \rightarrow 4)/a = \sqrt{3}/2$ $Z(0 \rightarrow 4) = 1.574$		$R(0 \rightarrow 4)/a = \sqrt{3}/4$ $Z(0 \rightarrow 4) = 3.149$
$R(0 \rightarrow 5)$		$R(0 \rightarrow 5)/a = \sqrt{2}/2$ $Z(0 \rightarrow 5) = 1.446$	$R(0 \rightarrow 5)/a = \sqrt{2}/2$ $Z(0 \rightarrow 5) = 0.723$
$d_{(110)}, d_{(220)}$	$d_{(110)}/a = \sqrt{2}/2$ $Z(110) = 1.481$	$d_{(220)}/a = \sqrt{2}/4$ $Z(220) = 5.924$	$d_{(220)}/a = \sqrt{2}/4$ $Z(220) = 2.962$
$d_{(111)}$		$d_{(111)}/a = \sqrt{3}/3$ $Z(111) = 1.360$	$d_{(111)}/a = \sqrt{3}/3$ $Z(111) = 0.680$
$d_{(200)}$	$d_{(200)}/a = 1/2$ $Z(200) = 4.189$	$d_{(200)}/a = 1/2$ $Z(200) = 2.094$	

Virtual valence: Diamond lattices of C, Si, Ge, and Sn

solid/dashed curves: K calculated with the indicated valence and the actual \mathcal{N}_{at} (cf. Table).

added: the observed planar peaks (111),(220) and K_1^{min}

omitted: the radial MDP due to $R(0 \rightarrow 5)$



conclusion:

- universal for dia: intra-tetrahedral scale (2.962, 3.149), inter-tetrahedral scale (0.680, 0.723), each case - (planar/radial)

Interference features in the density of states

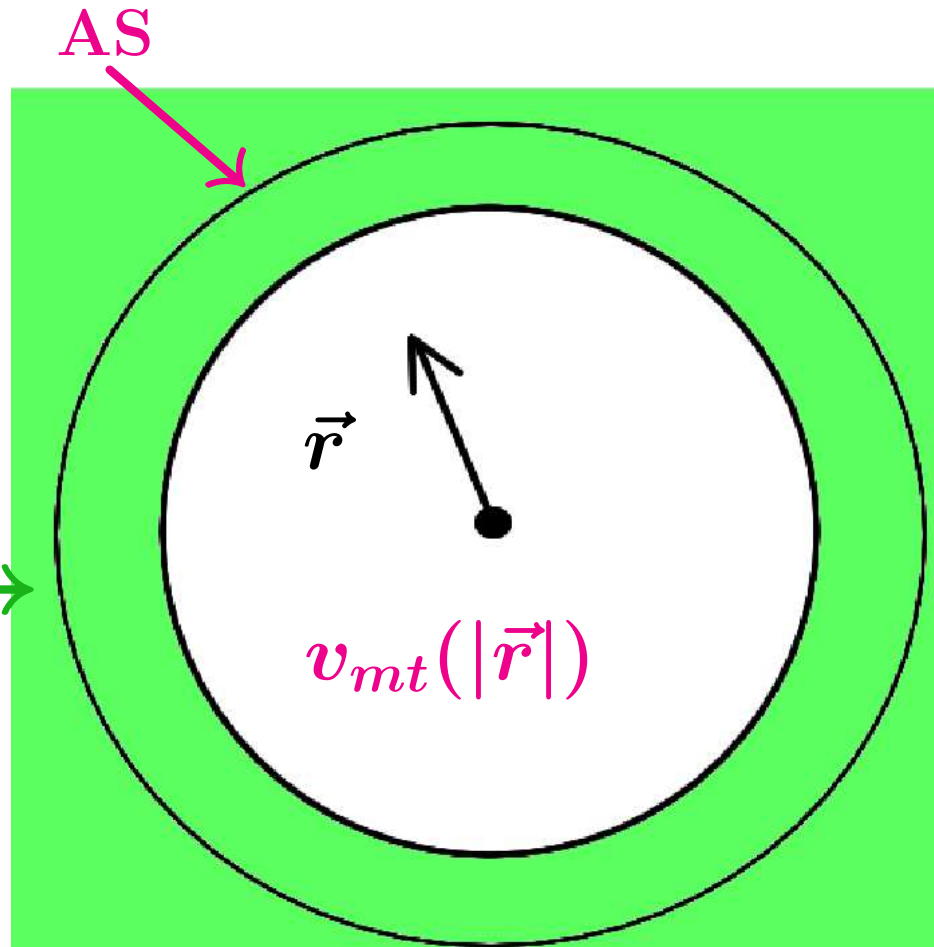
How to proceed?

Search for possible entry point of free-electron descriptions of band electrons.

Atomic sphere with a muffin-tin potential inside

atomic spheres (**AS**),
space-filling
 \Rightarrow slightly overlapping

constant potential
"muffin-tin zero"
MT0



v_{mt} ,
spherically symmetric,
no overlap with
adjacent v_{mt}

conclusion:

- effective atoms: modelled as spherical potentials immersed into a constant potential

Multiple-scattering approach to the AS-DOS⁵

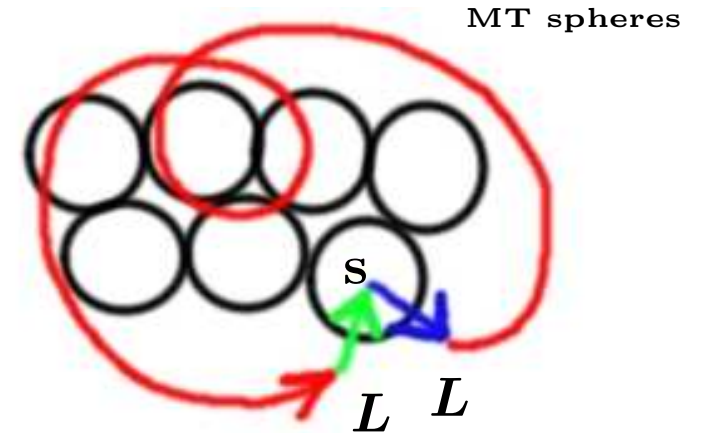
Suppose, we know the self-consistent atomic spheres (identifier s , partial DOS $D_{sl}^o(\epsilon)$, phase shifts η_{sl}). Then, the DOS of the atomic spheres (AS) with environment will be

$$D_s(\epsilon) = -\frac{2}{\pi} \int_{AS_s} d^3\vec{r} \Im G(\vec{r}, \vec{r}, \epsilon) = \sum_l D_{sl}^o(\epsilon) \left(1 + \Re \frac{1}{2l+1} \sum_{m=-l}^l T_{sL,sL}(\epsilon) \right)$$

$\{T_{sL,s'L'}\}$, the scattering-path matrix ($L = l, m$)

$$T_{sL,sL} = e^{i\eta_{sl}} \overbrace{\langle sL | (I - PF)^{-1} P | sL \rangle}^{\text{multiple scattering of vacuum waves}} e^{i\eta_{sl}}$$

$\uparrow \uparrow$
 propagation scattering



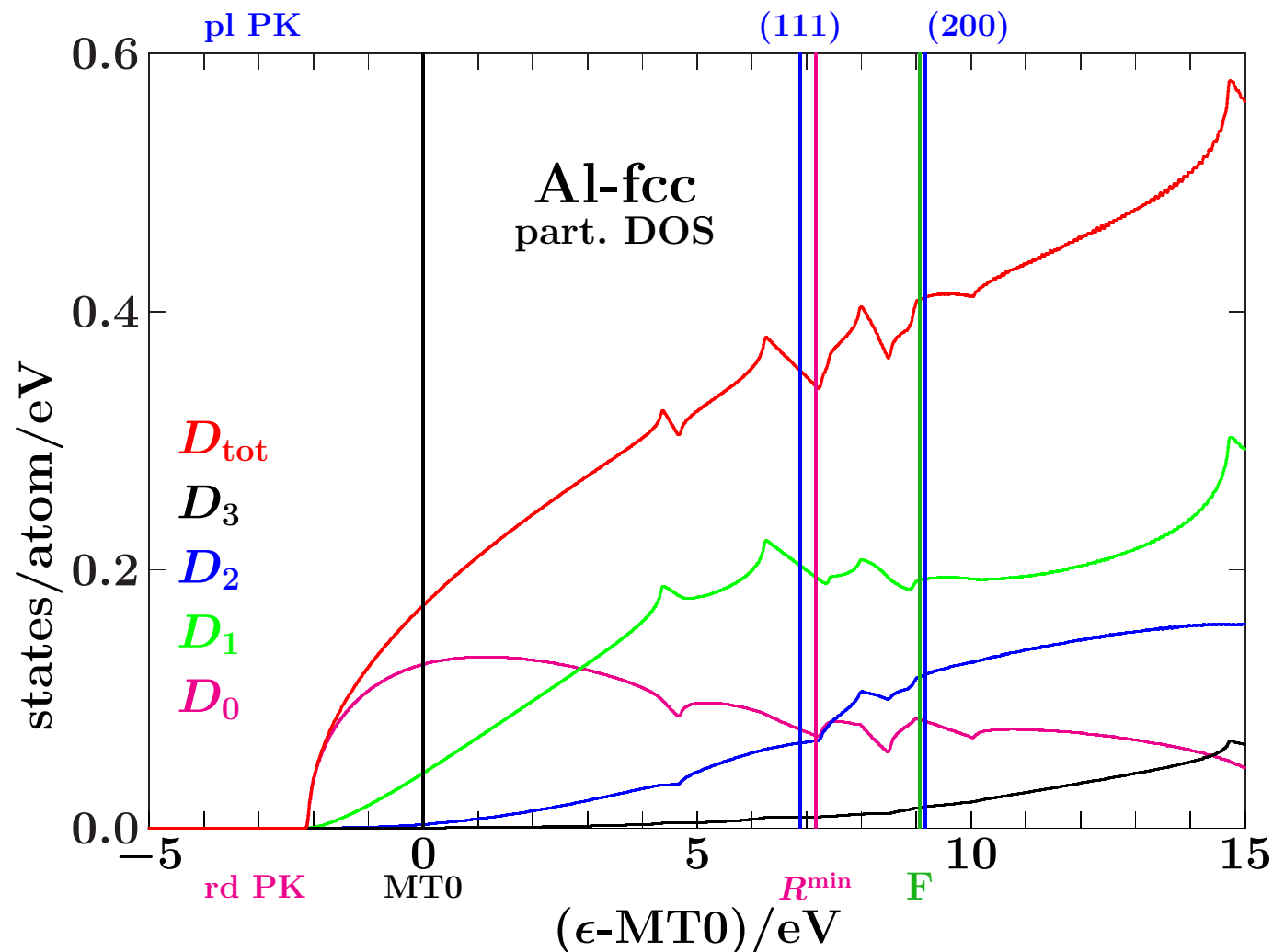
conclusions:

energies ϵ and MT0 both with reference to the Fermi level

- interatomic free propagation: effective energy = $(\epsilon - \text{MT0})$, momentum = $\sqrt{\epsilon - \text{MT0}}$
- single-scattering DOS: approximate DOS with only one scattering in the environment, spectral features, e.g. due to the planar peaks (hkl) at $\epsilon = \text{MT0} + \left(\frac{1}{2} \frac{2\pi}{d_{\text{hkl}}} \right)^2$
- task: Find the corresponding spectral features of the self-consistent DOS.

⁵ for this view cf. H Solbrig phys. stat. sol. (b) 139,223(1987)

Al-fcc: Partial AS-DOS and peak assignment



plotted: the partial DOS of Al-fcc as obtained from the LMTO-AS/MT code

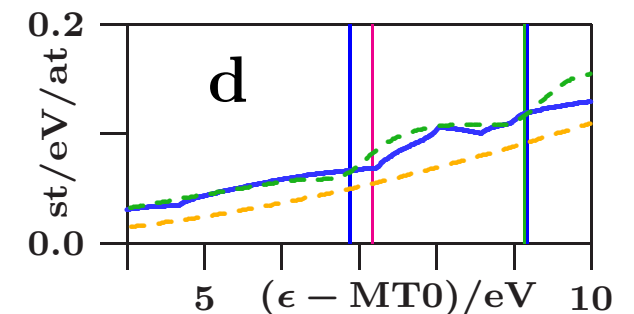
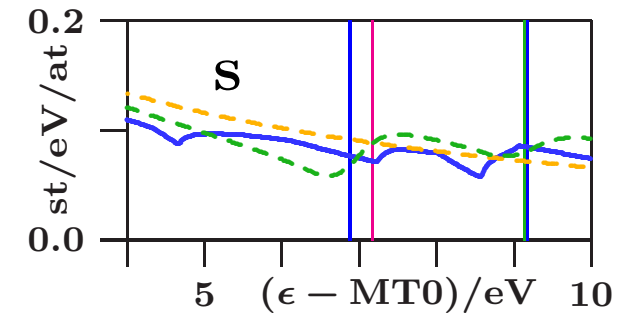
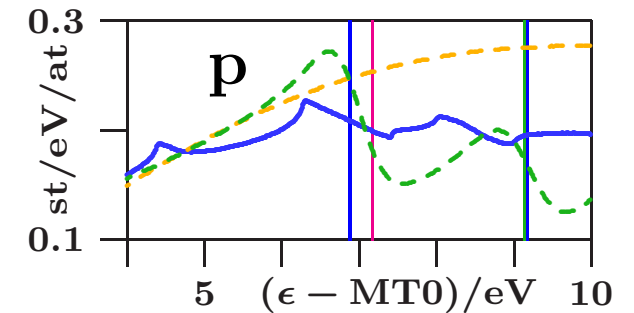
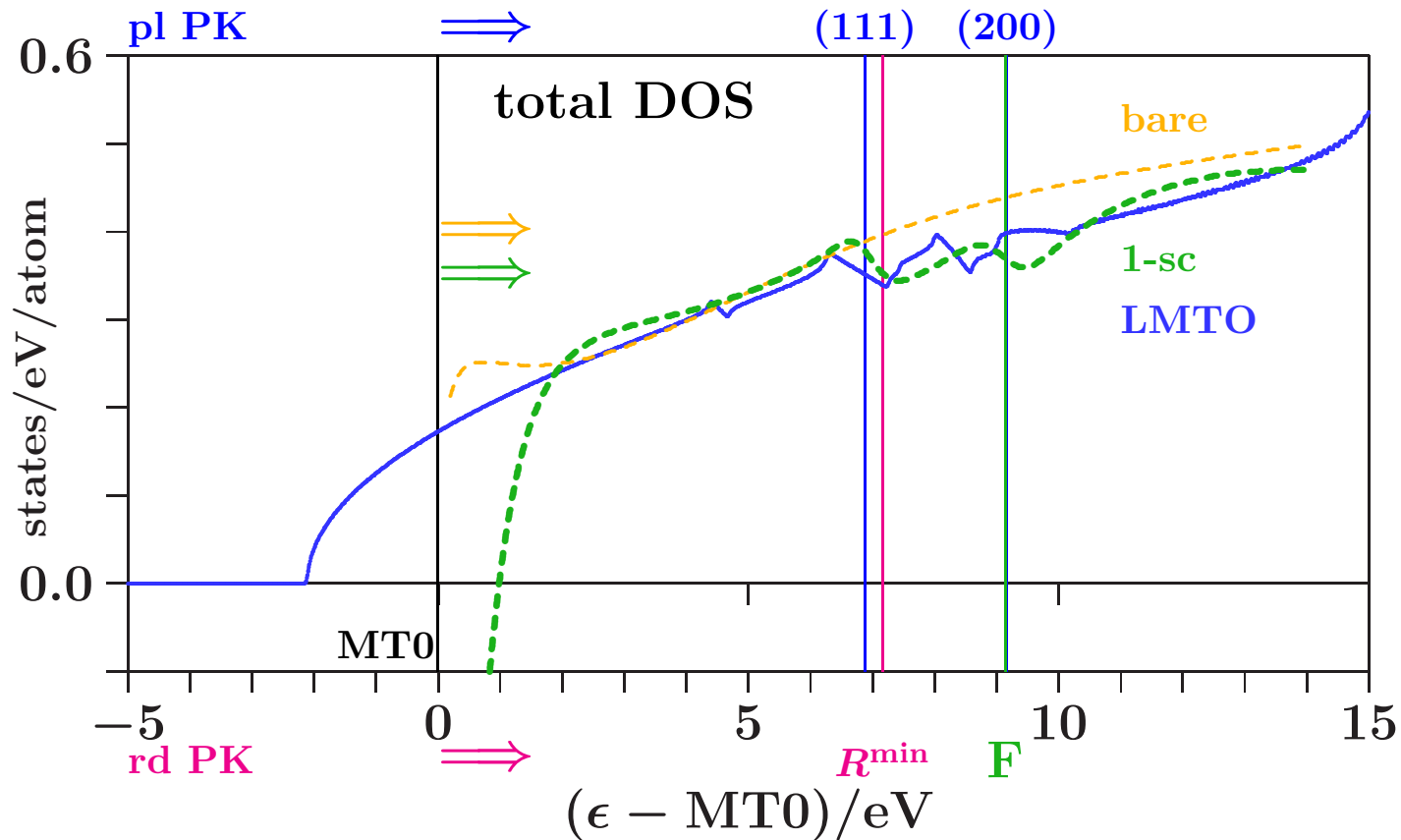
bars: with reference to MT0, the diffraction peaks (i) planar ((111),(200)) and (ii) radial (R^{min}), the Fermi energy F

competition: at F - d -DOS over s -DOS, below F - f -DOS not significant

conclusions:

- occupied orbitals: notable d -occupation towards the Fermi energy
- peak assignment: There are DOS features centered at (4.5 eV, 7 eV, 9.1 eV $\approx F$). Assigned planar peaks with ref. to MT0 (interatomic propagation) are (none, (111), (200))

Al-fcc: Single-scattering approximation to the AS-DOS

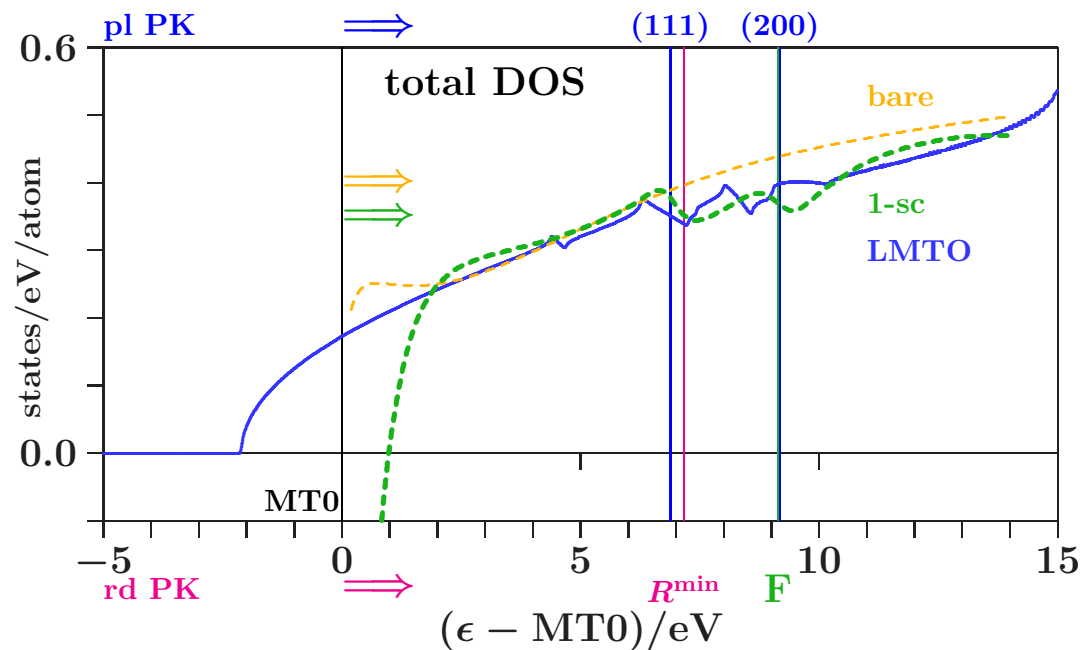


self-consistent calculation: LMTO-AS/MT with *spd*-orbitals

interference peaks: (111), R^{\min} , and (200) at the specific free-electron energies above MT0, note the nearly perfect coincidence of (200) and F (Fermi level).

for comparison: **bare-AS** - spd-DOS without environment, **1-sc** - spd-DOS with only one scattering event in the environment

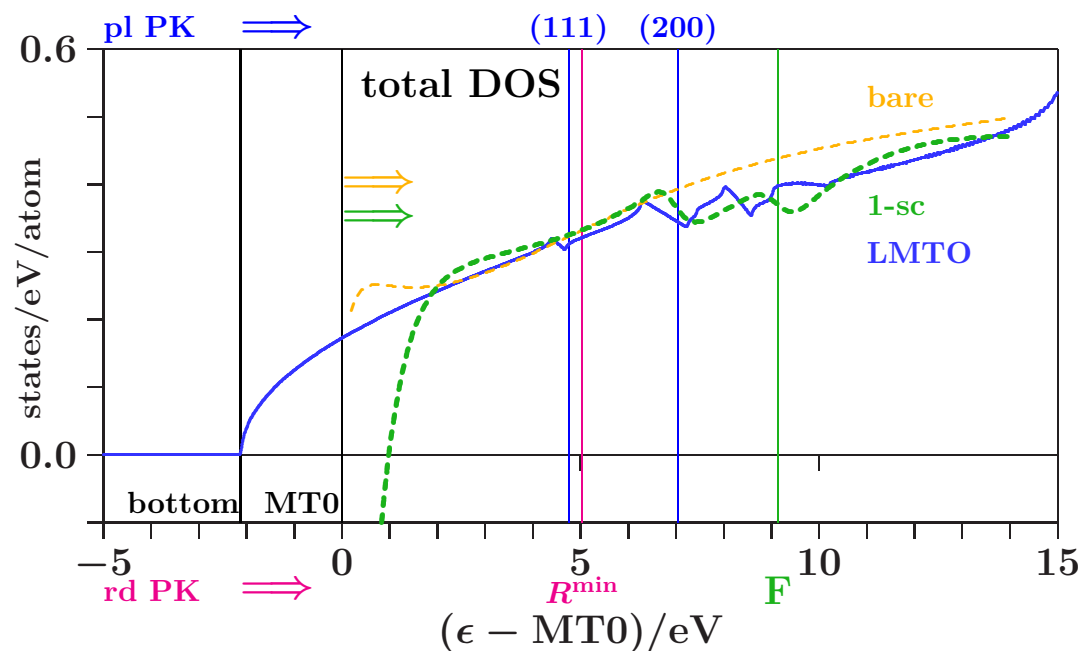
Al-fcc: On the reference energy of the diffraction peaks



peak energies with reference to MT0:

This choice reveals the origins of interference features in the single-scattering DOS.

Generally, after each scattering-propagation step of the multiple-scattering series, the scattered waves are subject to the indicated interferences at the indicated energies.



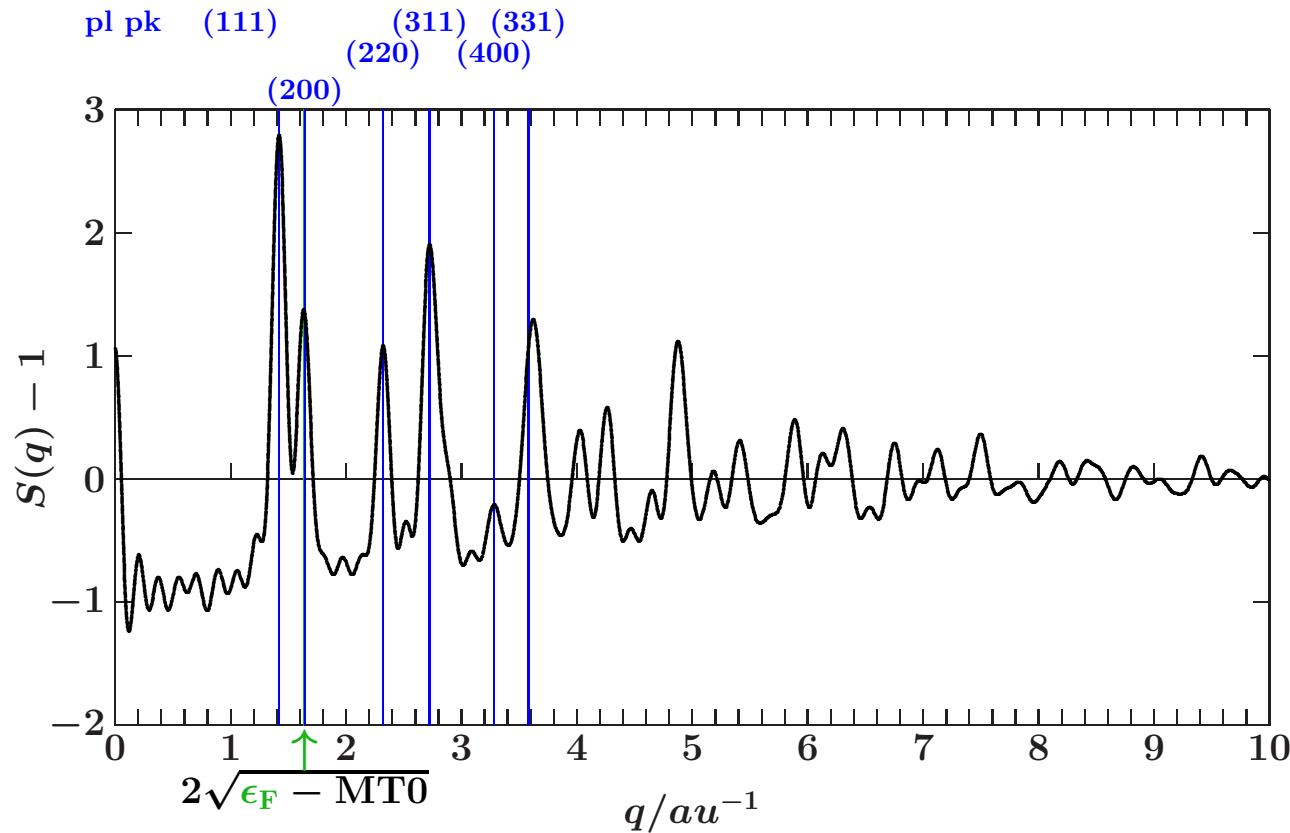
peak energies with ref. to the bottom:

The energy of a planar peak with reference to the bottom shows where a Brillouin-zone boundary is reached in the empty-lattice model.

The electronic band states decompose into free-electron components which are affected by diffraction at the zone boundaries. This gives rise to DOS features.

Note that there is twofold diffraction support for the spectral feature around 7 eV - with reference to MT0 due to (111) and with reference to the bottom due to (200).

Al-fcc: Interatomic free propagation enhanced at ϵ_F



plotted: the structure factor of Al-fcc, powder diffraction, attenuation length 10 Å

top labels: the observed planar peaks (hkl)

interatomic free propagation: electron energy with reference to MT0,

(↑), the momentum transfer in the true backscattering at the Fermi level allows for the excitation of the planar peak (200)

conclusion:

- "second-class" interference support at ϵ_F :

Due to

$$|\epsilon_F - \text{MT0}| \approx \epsilon_{200} = \left(\frac{1}{2} \frac{2\pi}{d_{200}} \right)^2$$

the planar interference (200) acts on the interatomic free propagation.

DOS feature and interference

muffin-tin scattered-wave approach:

free electron propagation between successive scatterings, energy refers to MT0

single-scattering approximation to the DOS includes only one scattering in the environment, spectral features due to planar/radial interference emerge at the free-electron peak energies above MT0

gaps, ... of the self-consistent DOS have counterparts in the single-scattering DOS

allows labelling

diffraction peaks with reference to the bottom of the valence band:

compares the self-consistent DOS with the empty-lattice band structure

free-particle decompositions of band states around the peak energies are subject to strong diffraction effects

allows labelling

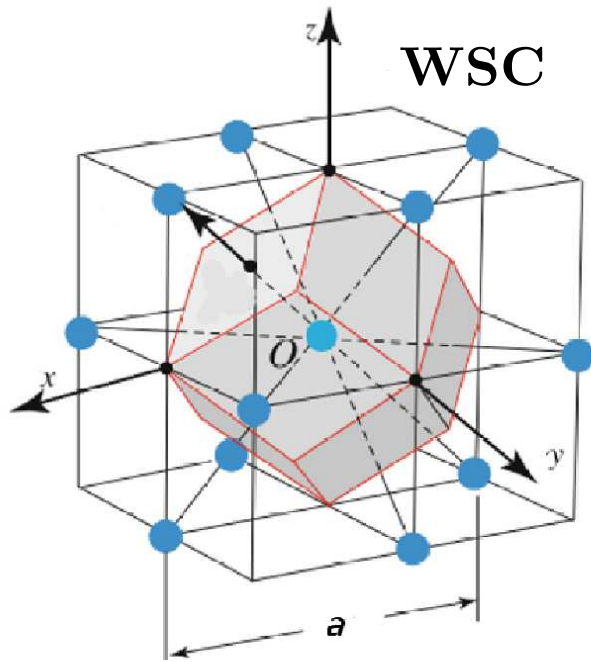
both mechanisms can cumulate:

the offset of MT0 above the bottom must equal the distance between the cumulated peak energies

Virtual valence and band structure

try to connect virtual valences with integrated partial state densities

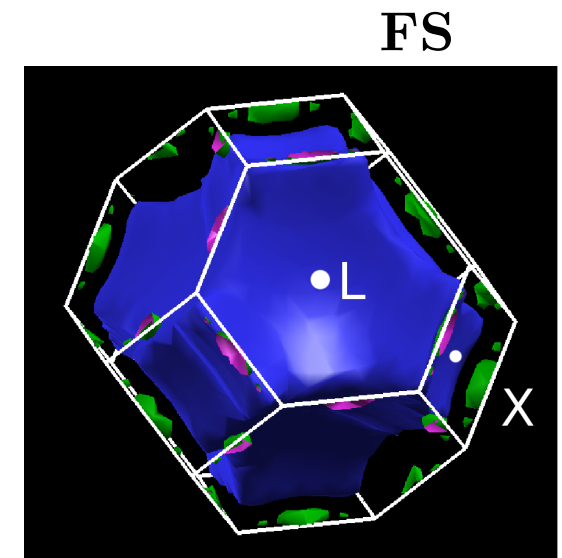
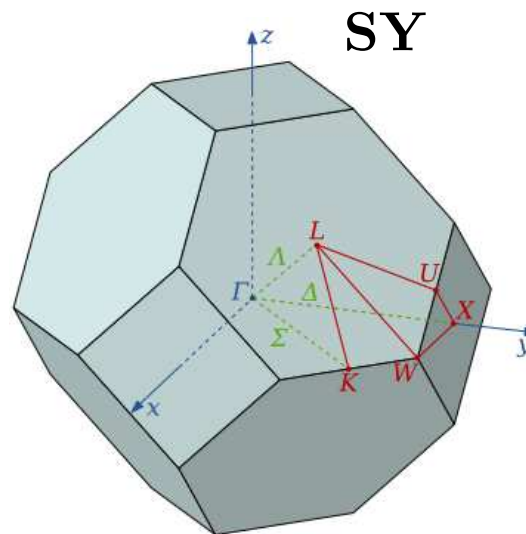
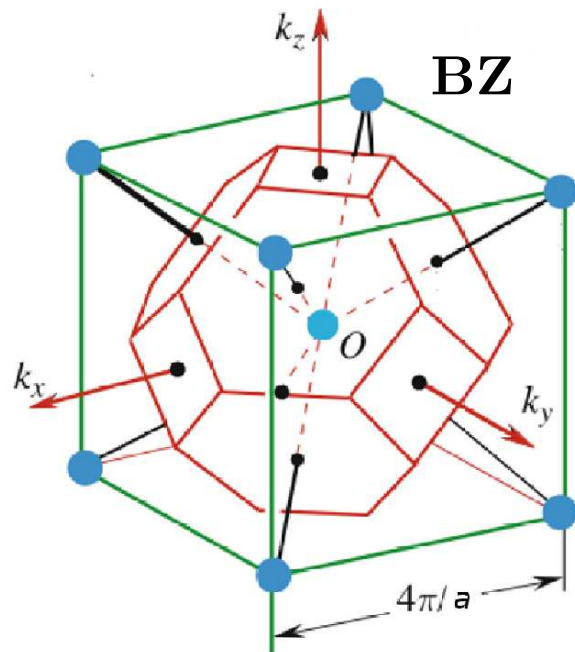
Al-fcc: Unit cells, symmetry directions, Fermi surface



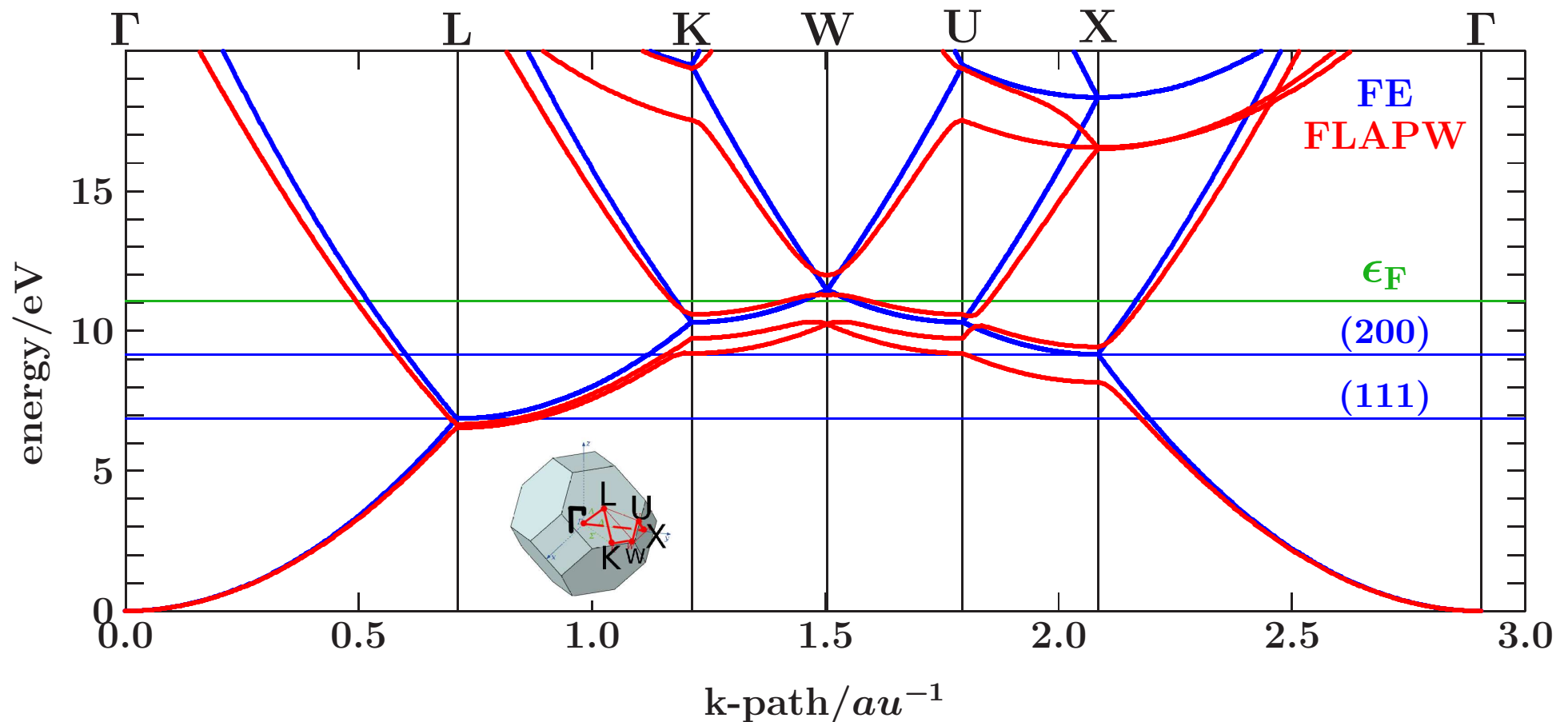
With reference to the cubic cell ($a = 4.0496 \text{ \AA}$): Wigner-Seitz cell (WSC), 1st Brillouin zone (BZ), symmetry points (SY), Fermi surface (FS)

conclusions:

- L point: momentum $k_L = \frac{1}{4} \frac{4\pi}{a} \sqrt{3} = \frac{1}{2} \frac{2\pi}{a\sqrt{3}/3} \Rightarrow$ fulfilled Bragg condition for backscattering by (111) planes (planar spacing $a\sqrt{3}/3$) due to $2k_L a\sqrt{3}/3 = 2\pi$
- X point: momentum $k_X = \frac{1}{2} \frac{4\pi}{a} > k_L \Rightarrow$ fulfilled Bragg condition for backscattering by (200) planes (planar spacing $a/2$) due to $2k_X a/2 = 2\pi$



Al-fcc: Band structure - FLAPW⁶ versus free electrons



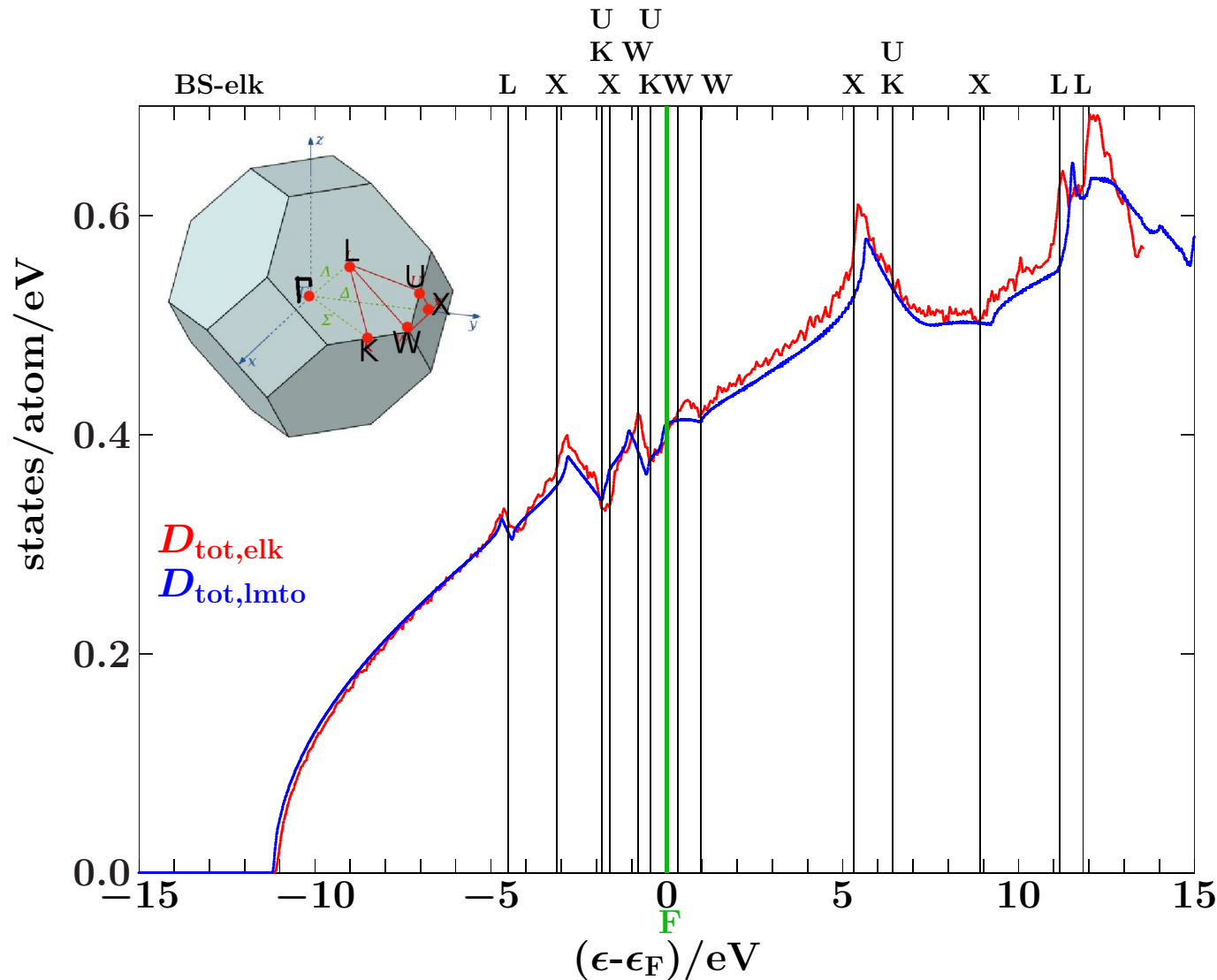
Energies refer to the bottom of the valence band.

conclusions:

- L point: (111) peak at 6.8786 eV, nearby DOS feature ascribed to the stabilization of the (111) planar spacing
- X point: (200) peak at 9.1714 eV, DOS feature clearly split and downshifted, ascribed to the stabilization of the (200) planar spacing

⁶ full-potential linearized augmented plane-wave code ELK developed at the Univ. of Graz

Al-fcc: DOS features and the symmetry points



applied codes: subscript "elk" for FLAPW⁶, subscript "lmt0" for LMTO-AS/MT¹

bars: the Fermi energy (F) and the energies where the FLAPW bands approach the specified symmetry points

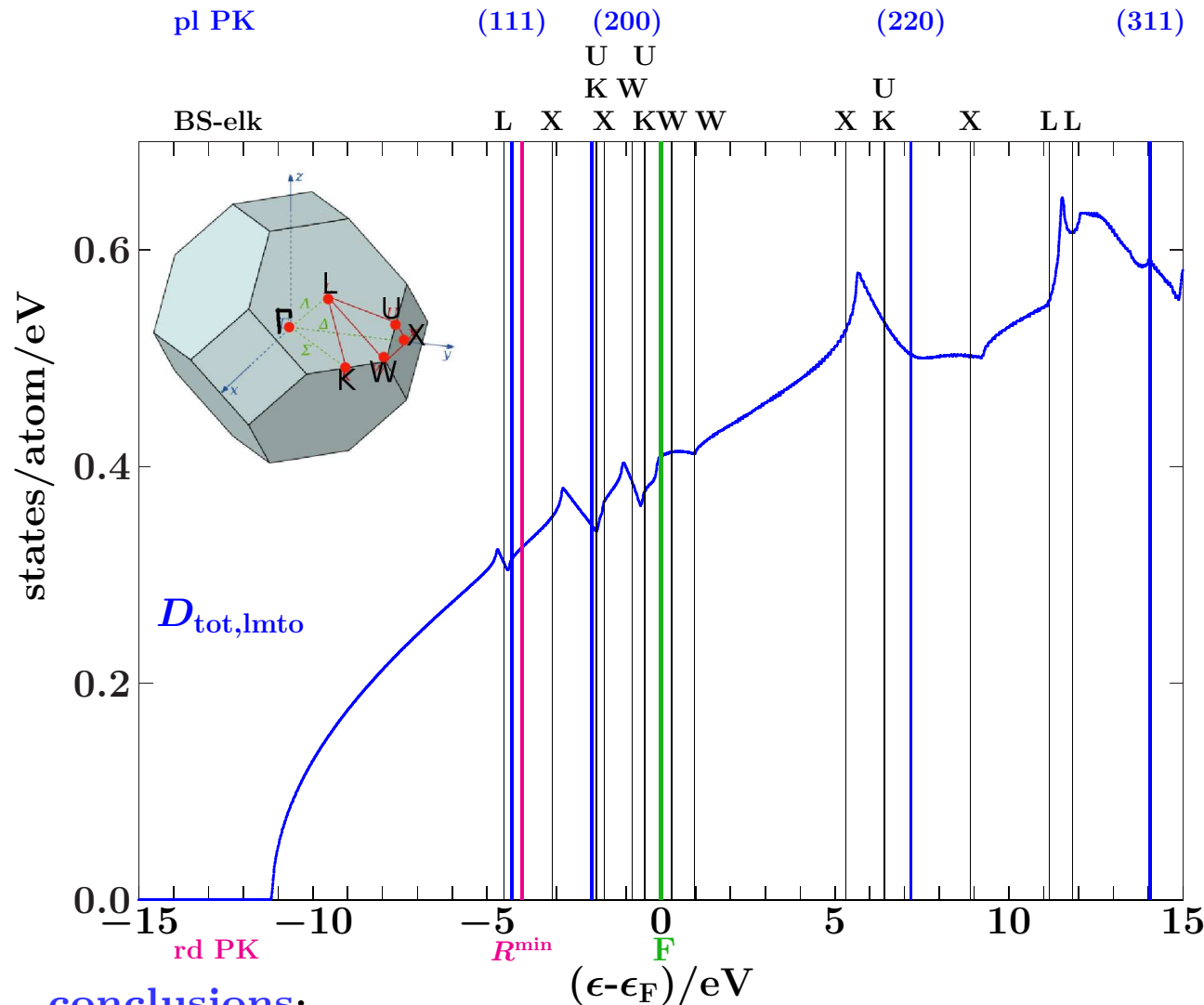
conclusions:

- The lowest-energy feature is assigned to L.
- The X-derived feature dominates below the Fermi level.
- The lowest (K,U) effect appears close to the X-derived dip.
- The Fermi level is surrounded by (W,K,U) effects.

⁶ full-potential linearized augmented plane-wave code ELK developed at the University of Graz

¹ LMTO-ASA extended to the muffin-tin model, R. Arnold, thesis, TU Chemnitz, 1998

Al-fcc: Diffraction peaks added



plotted: Al-fcc, total AS-DOS, LMTO-AS/MT

black bars: the energies where the FLAPW bands approach the indicated symmetry points

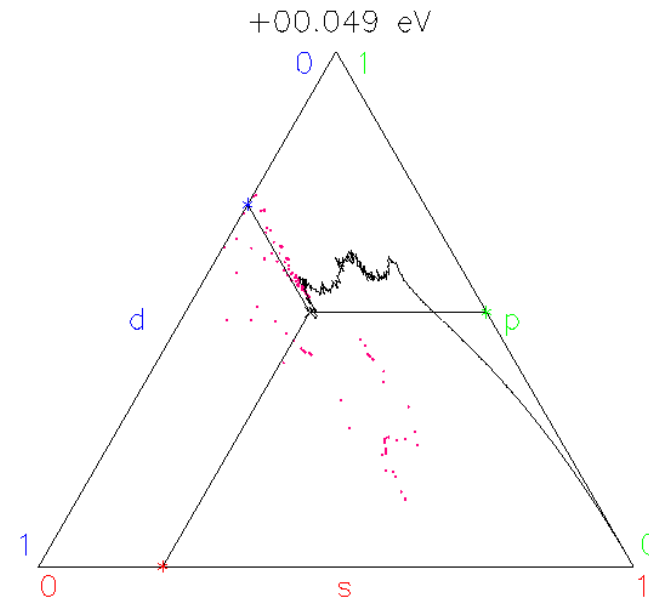
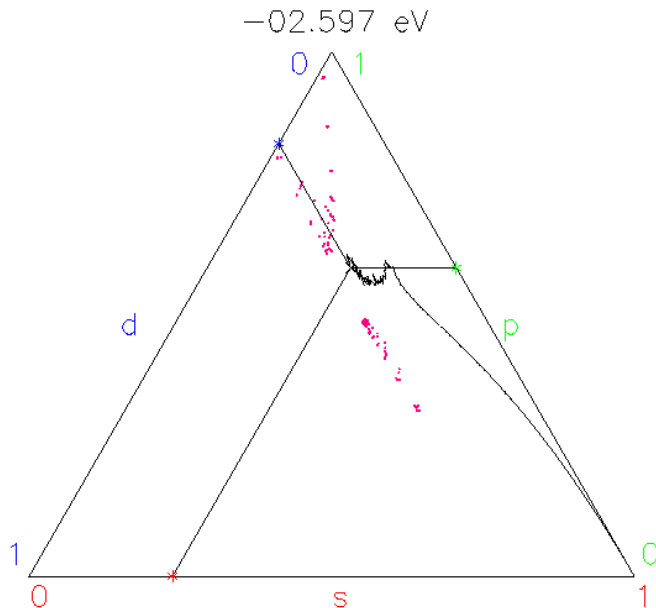
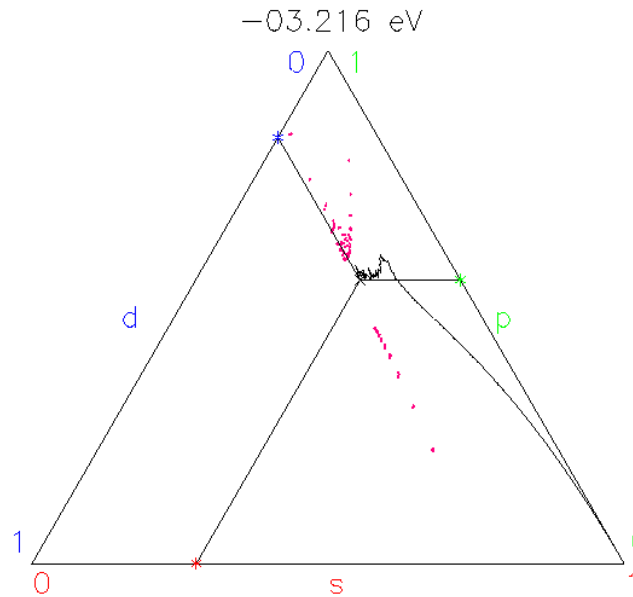
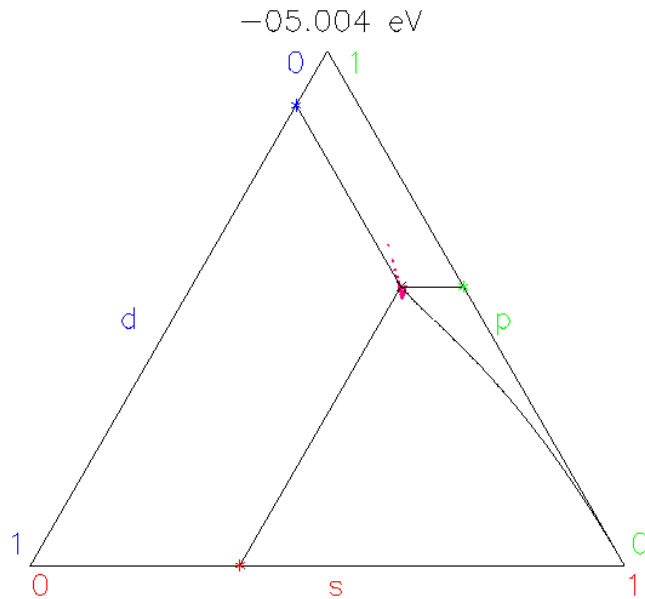
colored bars: (i) Fermi energy (**F**), (ii) **planar**/**radial** interference peaks with reference to the bottom of the valence band

With **this choice** of the reference energy, the blue bars **(111)**, **(200)** are to the free-electron fcc-bands what are the black bars L, X to the real fcc bands.

conclusions:

- The lowest DOS features can be assigned to symmetry point **and** diffraction peaks: (i) around -4.5 eV/L/**(111)** and (ii) around -2 eV/X/**(200)**.
- The virtual valences must be linked to the composition of the band states.

Al-fcc: spd content of LMTO band states



black curve: the trace of the average partial weights of band states in intervals (width 0.034 eV) around the indicated energies ($s+p+d=1$, $\epsilon_F=0.0$ eV).

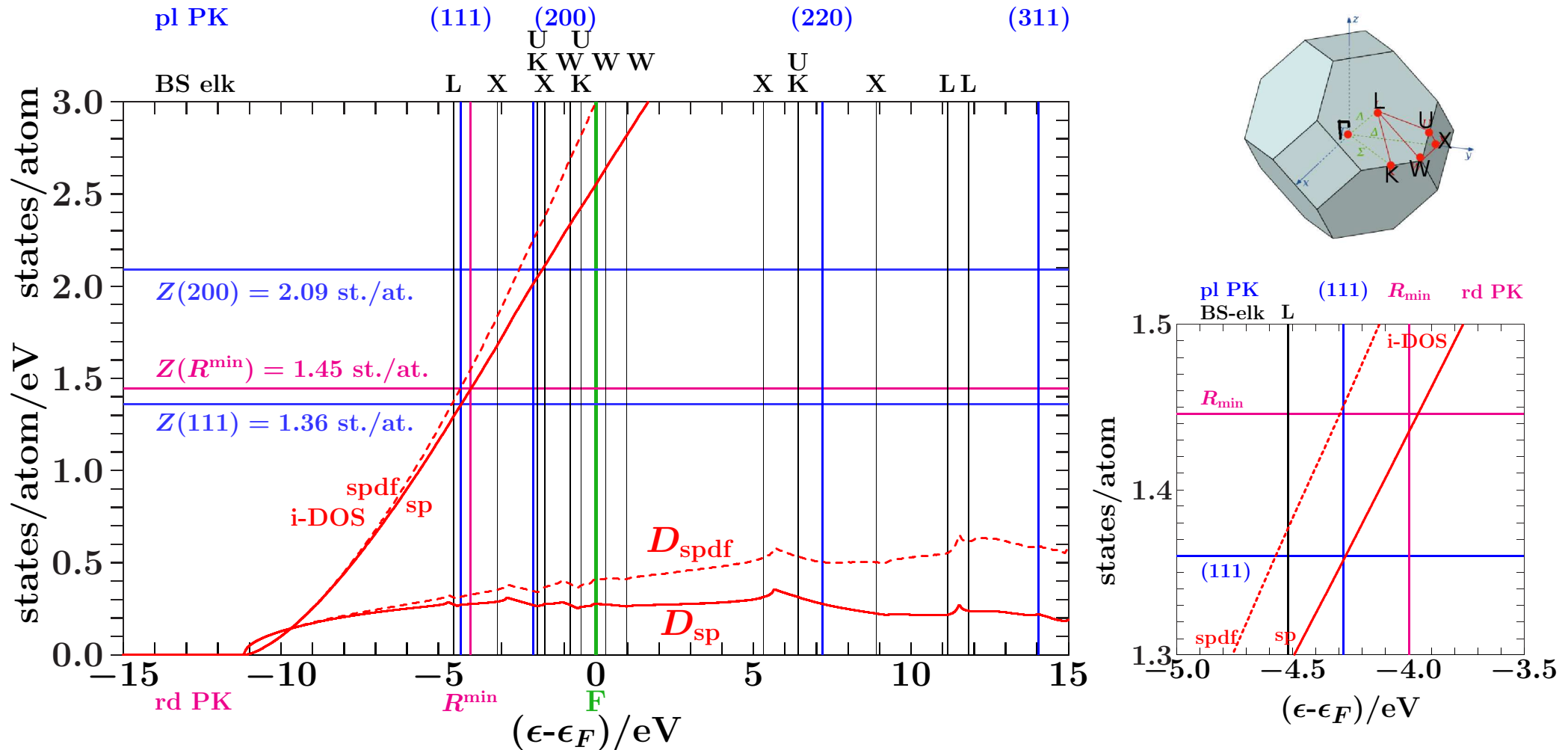
dots: represent each band state in the actual interval

discussion: Approaching the planar peak (111) (-4.32 eV) from below the **dots** start fluctuating mainly along the line of constant **d** (constant $s+p$).

In the energy range of the interference peaks the distribution of the **dots** forms a pronounced gap which indicates the markedly different **sp**-occupations of the participating band states.

Above ϵ_F the fluctuations get less restricted.

Al-fcc: Superfluous *sp*-weight is moved to *d*-orbitals



density of states D_{spdf} , D_{sp} , integrated density of states $i\text{-DOS}$

vertical lines: (BS elk) one-electron energies at symmetry points, (pl PK) planar (hkl) peaks, (rd PK) radial MDP R^{min} , peak energies with reference to the bottom of the band, (F) the Fermi level

horizontal lines: virtual valences on the scales $d_{111} = a/\sqrt{3}$, $R^{\text{min}} = a/\sqrt{2}$, $d_{200} = a/2$

Sensitive orbitals and virtual valence

- In the total DOS, D_{spdf} , the partial state densities are weighted with (1,1,1,1) whereas D_{sp} is obtained with (1,1,0,0). Integrating from the bottom of the band yields the corresponding **i-DOS**.
- The intersection of a horizontal line (virtual valence) with the equally labelled vertical line (interference peak) defines the point which should be passed by the integrated DOS if the weighting scheme is adapted to the sensitivity of the orbitals with regard to the length scale of interference.

This applies to the **integrated *sp*-DOS** especially with the planar (111) peak whereas small deviations occur with the other interference peaks.

Hence, the virtual valences at the three interference peaks are *sp*-like. In each case a notable superfluous weight is transferred to *df*-orbitals which are too short-ranged for participation on the length scales $d_{(111)}$, R^{min} , and $d_{(200)}$.

- These arguments resemble the concept proposed by Raynor⁷ for application to alloys of simple metals with transition metals. In that case, the transition atoms get substantially polar which pushes the Madelung energy to unrealistic high values.

This does not apply to the present one-component system where short-ranged orbitals are occupied on the expense of more long-ranged orbitals at the same atom.

conclusion:

- Generalizing we conclude that the estimated virtual valence can be reproduced within the self-consistent electronic structure as an integrated DOS where the partial contributions are weighted according to the range of the orbitals in comparison with the length scale of interference.

⁷ GV Raynor, Prog Met Phys 1,1(1949)

Summary

- nearest-neighbor distances: topmost charge shells of the effective atoms overlap, initial conditions of the diffraction-caused continuation of structure to the medium-order range
- stabilization of a length scale L achieved by sensitive orbitals: range at least $L/2$, are sp -type throughout the periodic table for the widest interplanar resp. the shortest interatomic distances
- p -ranges of the atomic number: there are subunits, two length scales to be stabilized, p -type stabilization of the shorter internal scale, s -type stabilization of the arrangement of subunits
- virtual valence Z_L : assigned to a given length scale L on demanding that the required momentum transfer equals the diameter of a sphere occupied with Z_L sensitive orbitals per atom
- proved for Al-fcc: virtual valences for the wide planar spacings are obtained as the integrated densities of sp -states, Superfluous sp -weight is deposited to insensitive orbitals (too short-ranged)
- spectral features of the self-consistent DOS: labelled with respect to the generation of interferences in twofold respect, (i) in view of the interatomic free propagation in the muffin-tin scattered-wave approach (reference energy MT0), (ii) in view of the decomposition of band states into free-particle components which are subject to diffraction at the peak energies (reference to the bottom of the valence band)