Solution model and magnetism in first principle calculations

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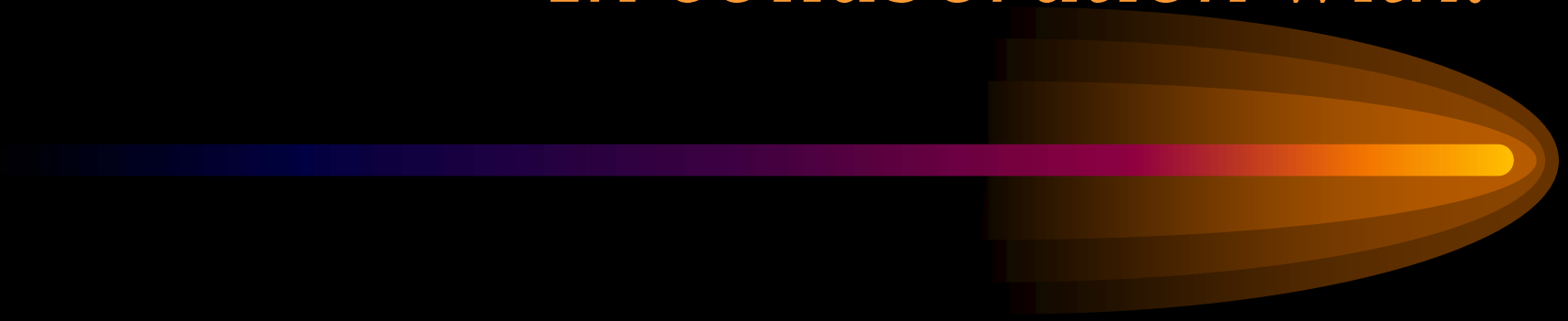
In collaboration with:



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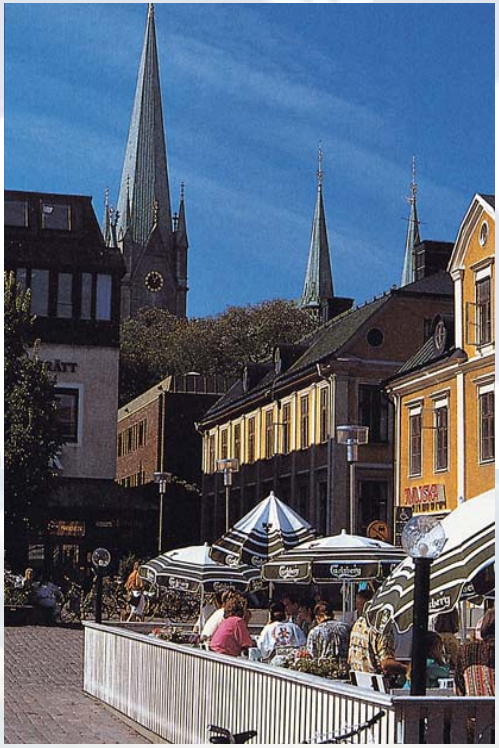
A. V. Ponomareva, MIS&A, Russia
O. Vekilova and S. I. Simak, LiU, Sweden

Linköping, Sweden



Theoretical Physics

Igor Abrikosov

Igor Abrikosov, Professor

- *Ab initio* electronic structure theory
- Materials simulations
- Mesoscopic physics, semiconductor structures in the quantum regime, transport and chaos
- Understanding of fundamental molecular interactions
- Dynamical simulations of metallic heterostructures
- Energy localization in descrete systems
- Non-linear dynamics of anharmonic lattices

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Bo Sernelius

Magnus Johansson

Leonid Pourovskii

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ALVA lector

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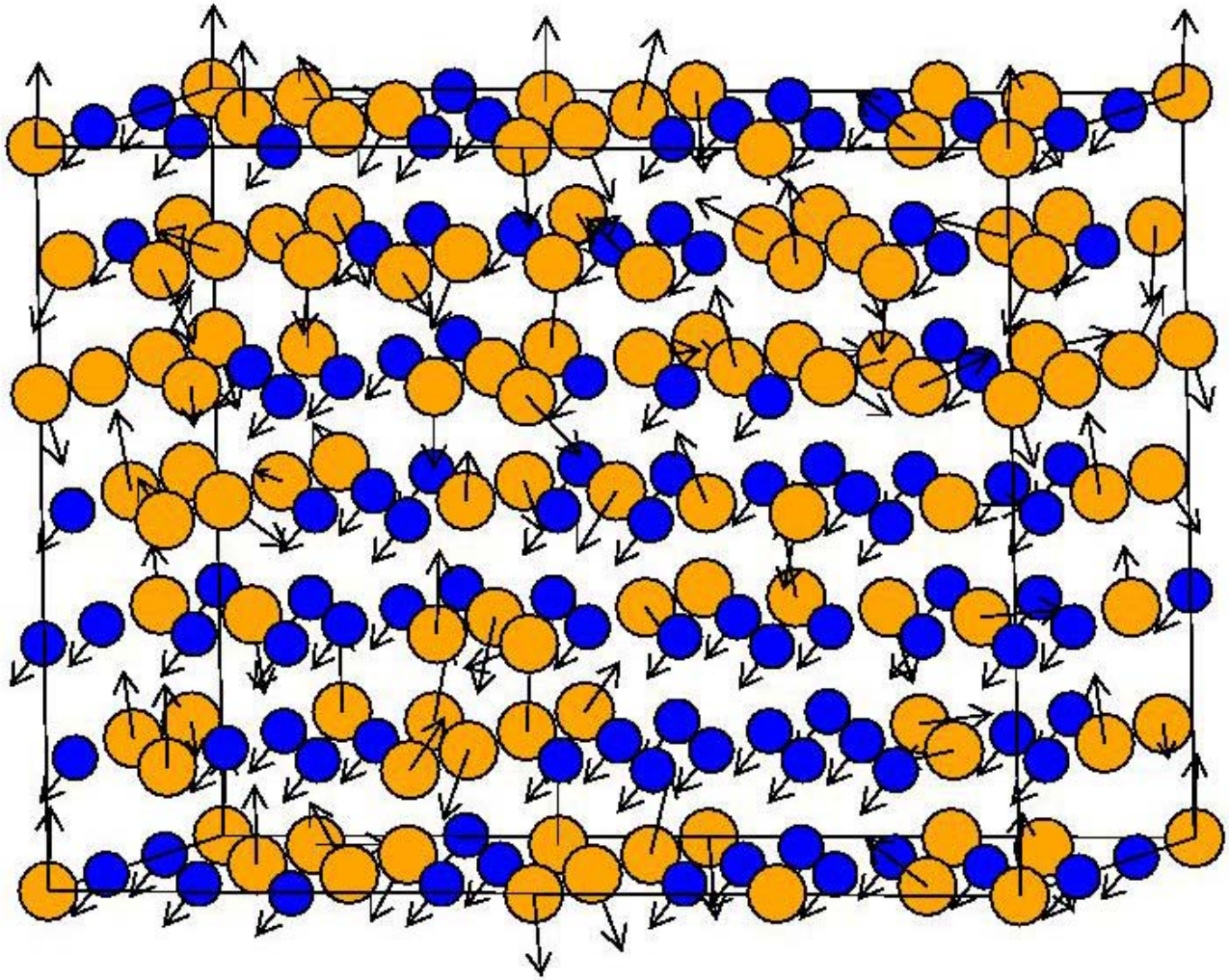
Assistant Professor

Olle Hellman

Dr. Weine Olovsson,
Bitr. Lektror&applicationexpert

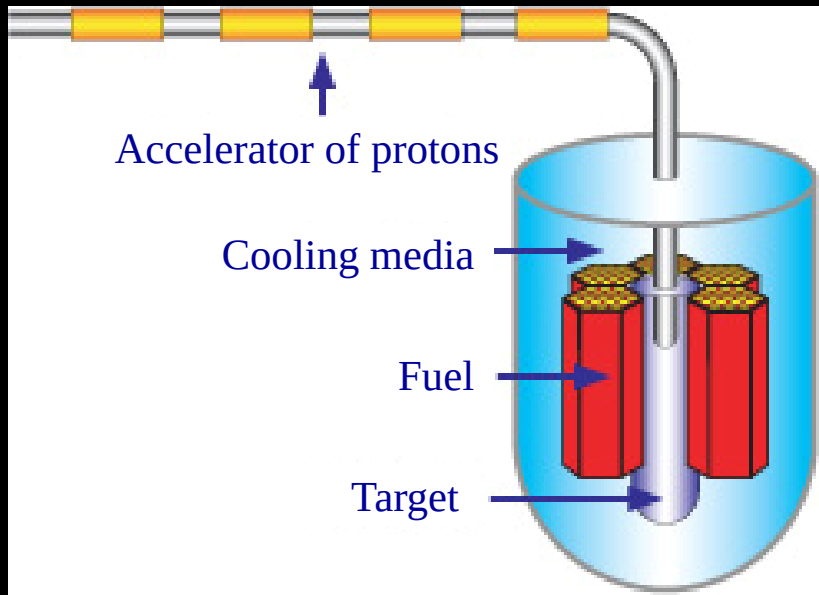
CONTENTS :

- First-principles simulations: basic idea
- First-principles simulations: treatment of solution phases
- Magnetic effects on the electronic structure
- Fe-Cr alloys: influence of magnetic state on thermodynamic properties and interatomic interactions
- Conclusions

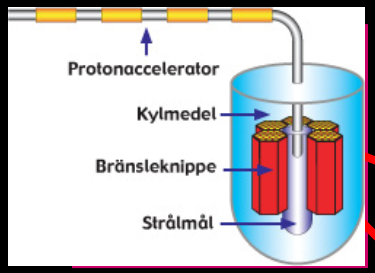


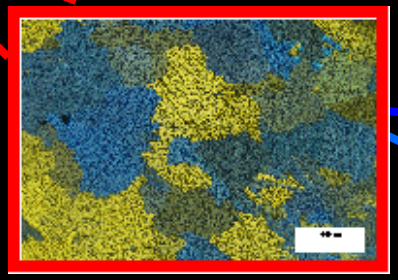
Fe-Cr alloys

- Are the base for many important industrial steels
- Used as cladding material in fast neutron reactors
- Low Cr steels, up to 10 % Cr, show:
  anomalous stability
  resistance to neutron radiation induced swelling
  corrosion resistance
  increased ductile to brittle transition temperature

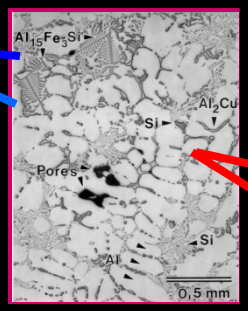


Microstructure – Property Relationships



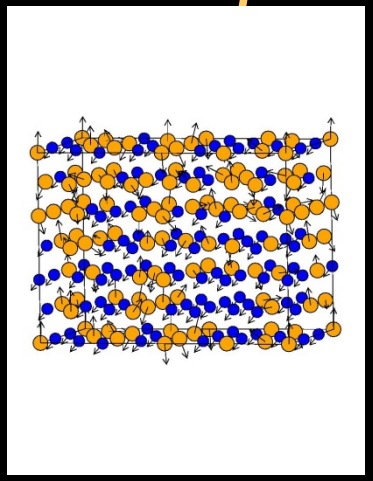


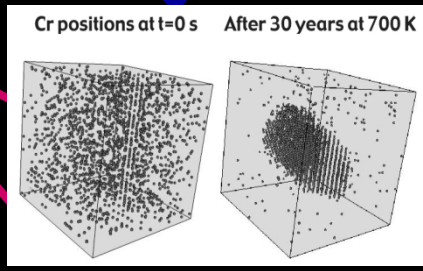
Microstructure
- Grains
≅ 1 – 10 mm
Properties
• High cycle fatigue
• Ductility



Microstructure
- Phases
≅ 100 – 500 microns
Properties
• Yield strength
• Ultimate tensile strength
• High cycle fatigue
• Low cycle fatigue
• **Thermal Growth**
• Ductility

Microstructure
- Phases
≅ 3-100 nanometers
Properties
• Yield strength
• Ultimate tensile strength
• Low cycle fatigue
• Ductility





Atoms
≅ 10-100 Angstroms
Properties
• Thermal Growth

Original idea for this figure belongs to Chris Wolverton Ford Motor Company

$$G = E + PV - TS$$

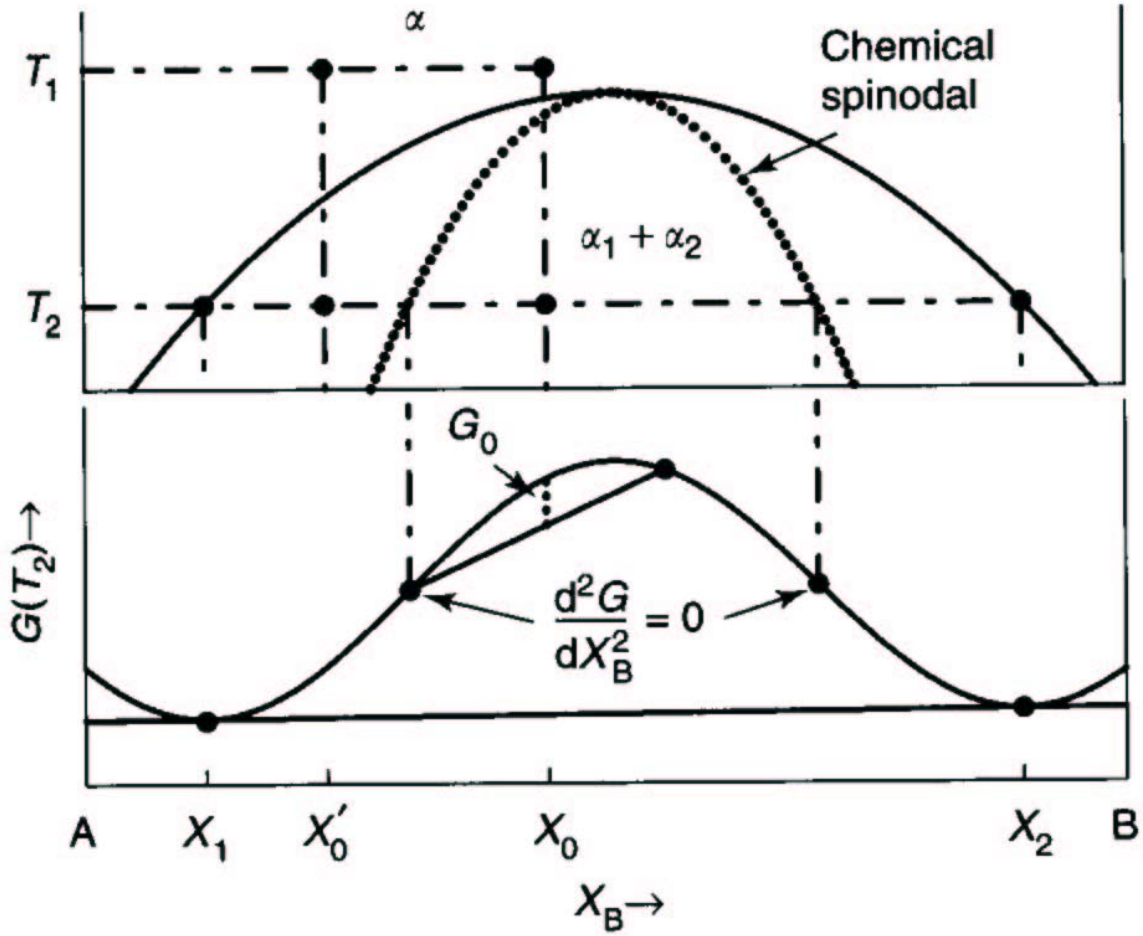
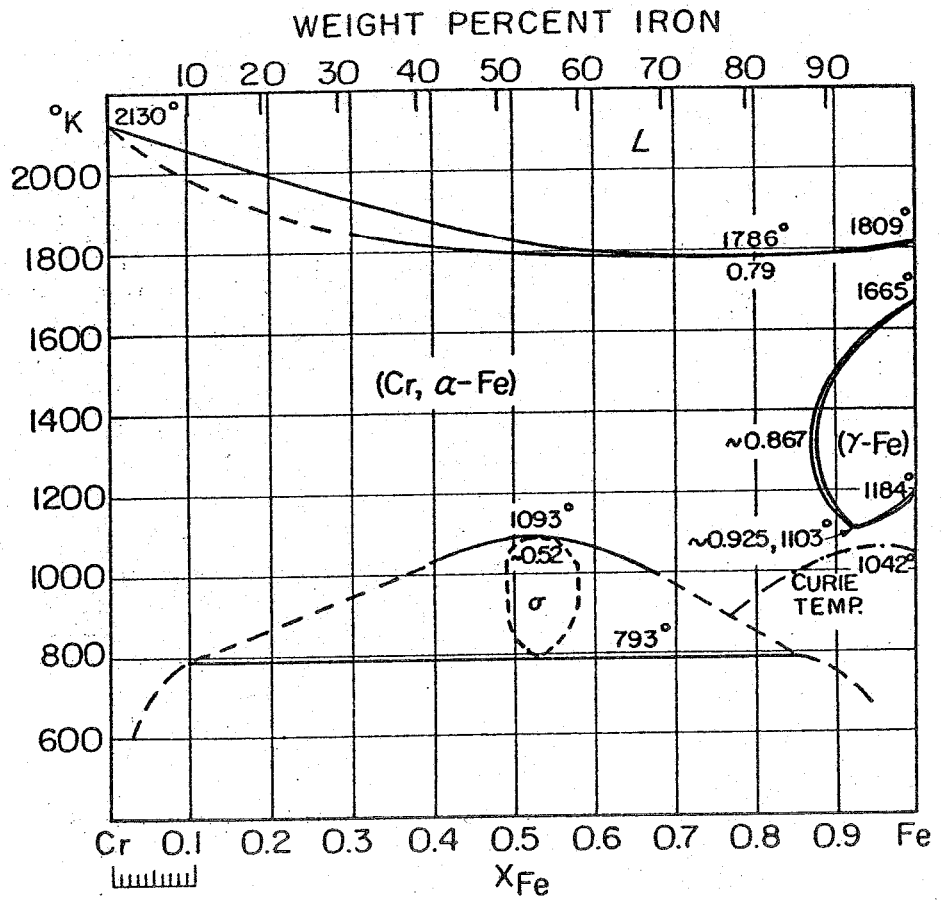
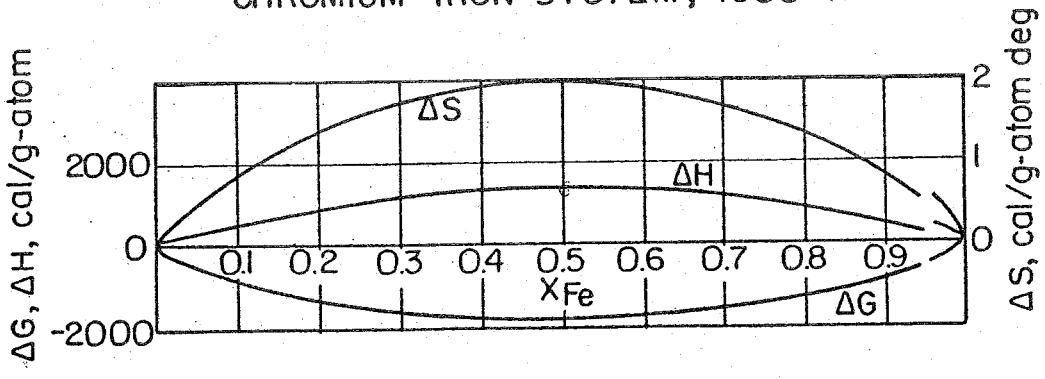


Figure 9 (a) Schematic phase diagram and (b) free energy vs. composition diagram for alloys between the spinodal points, which are unstable and can decompose into two coherent phases α_1 and α_2 without overcoming an activation energy barrier. Alloys between the miscibility gap and the spinodal are metastable and can decompose only after nucleation of the other phase.

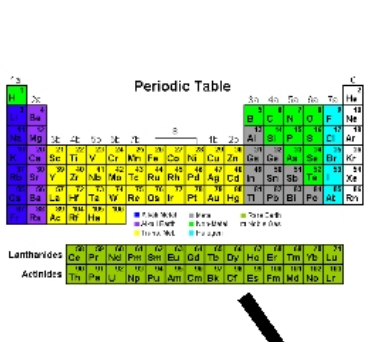


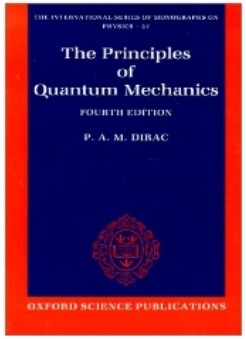
CHROMIUM - IRON SYSTEM, 1600 °K



First–principles calculations

Matter@NSC
Linköping
4128 cores
37 TFLOPS

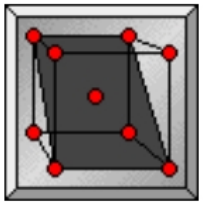




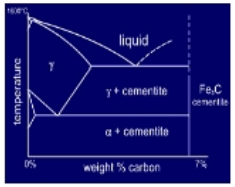
Approximations:
LDA, CPA ...
Methods:
LMTO, MD,
Monte Carlo ...

Experimental data

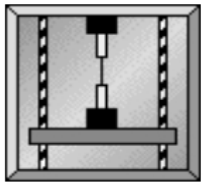
Adjustable parameters



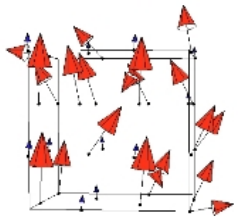
Structure



Phase equlilbria



Mechanical properties



Magnetism

Fundamental understanding

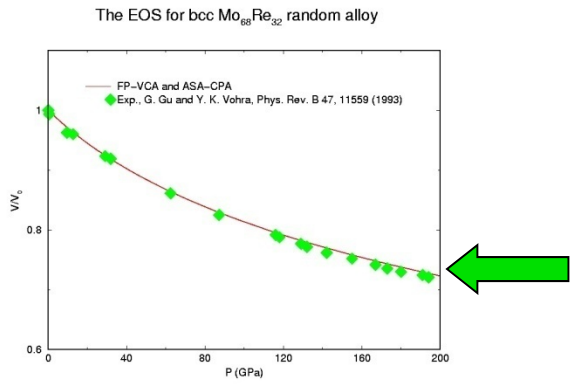
Lindgren@PDC
KTH
36384 cores
305 TFLOPS

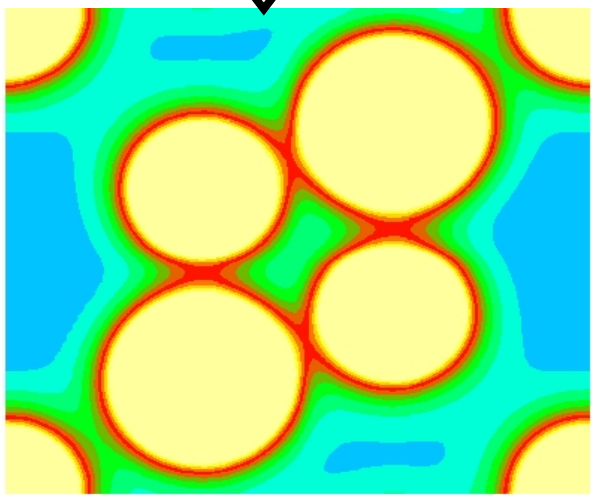
A atom

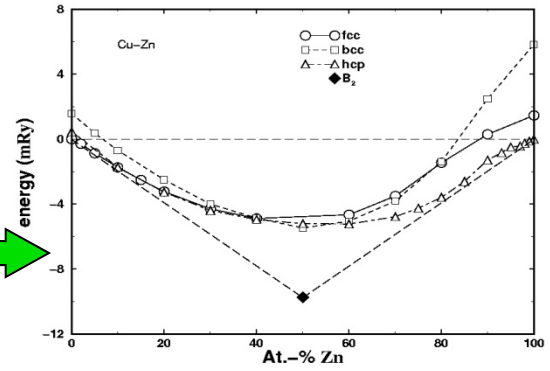
B atom

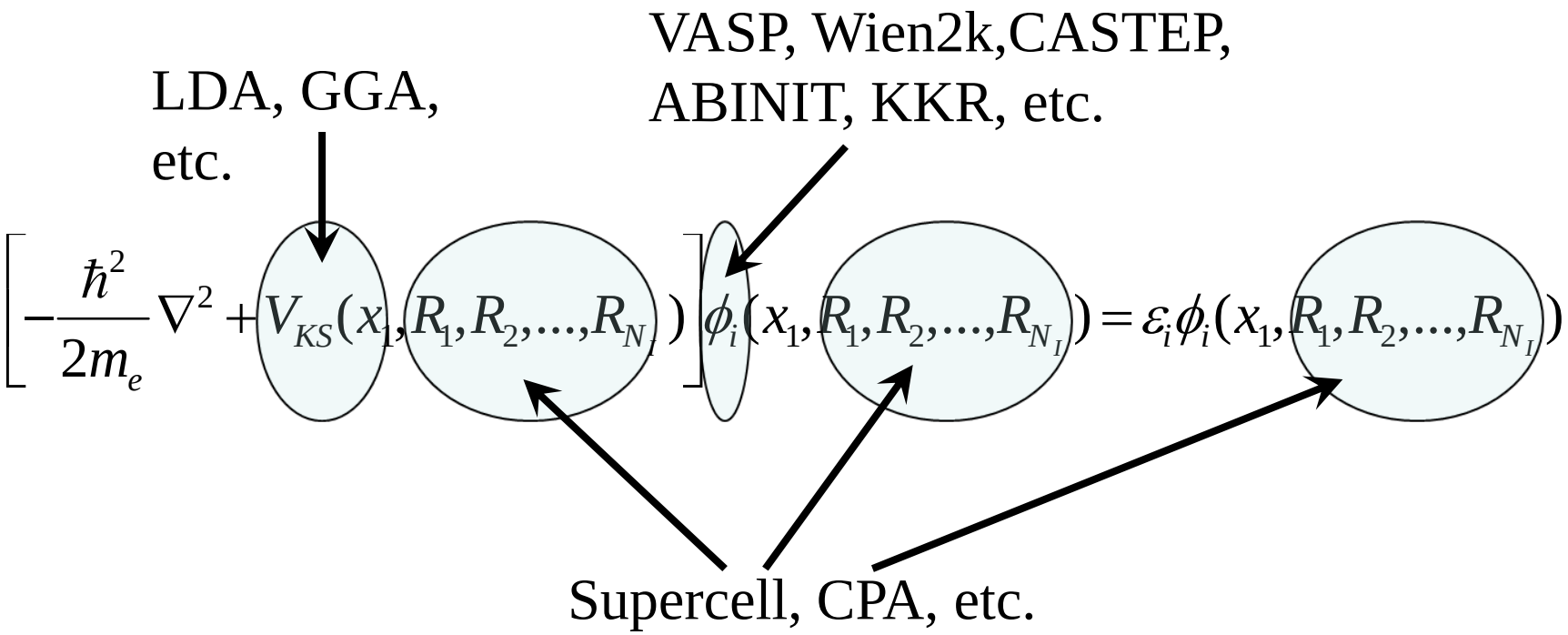
A_xB_{1-x} alloy

$n(\mathbf{r})$, the electron density





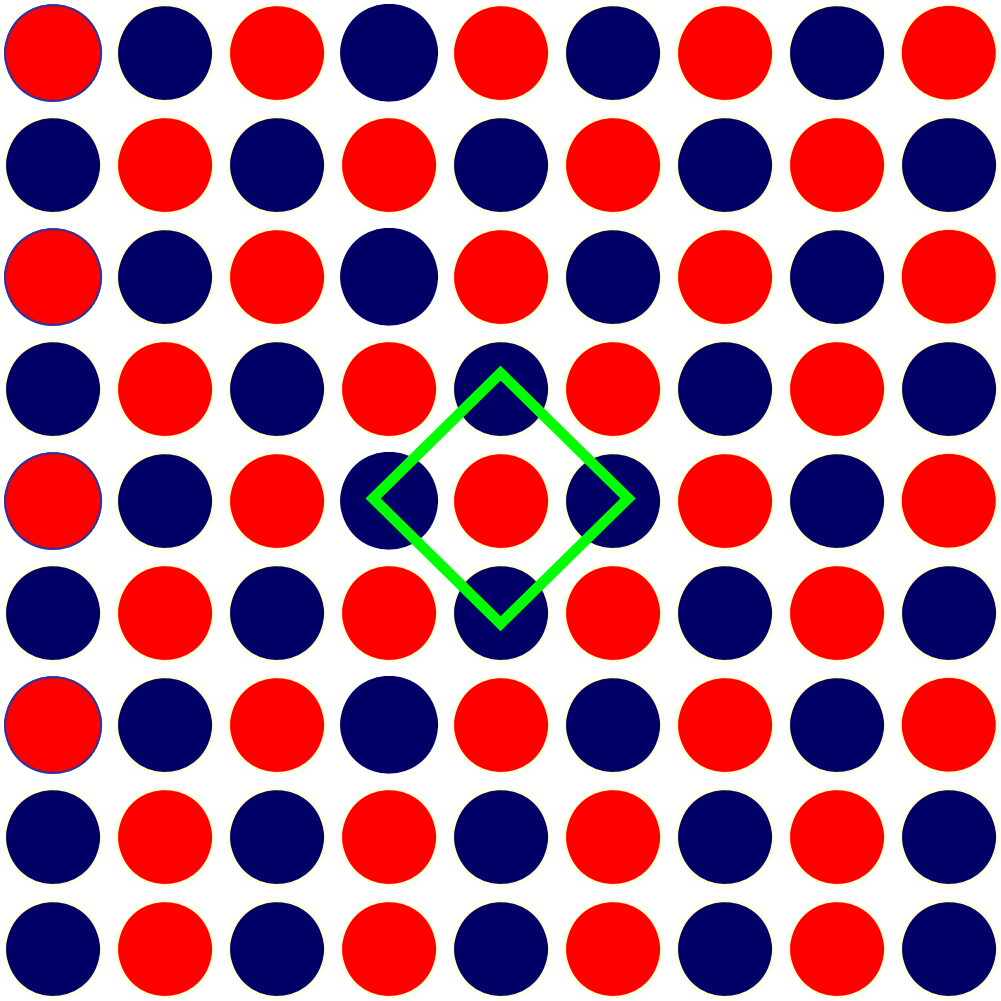


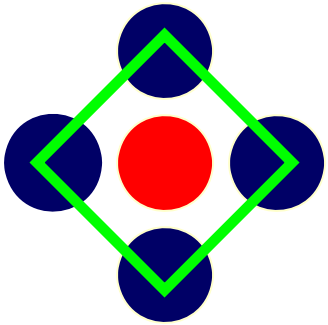


It is NOT a trivial task to run *ab initio* software!

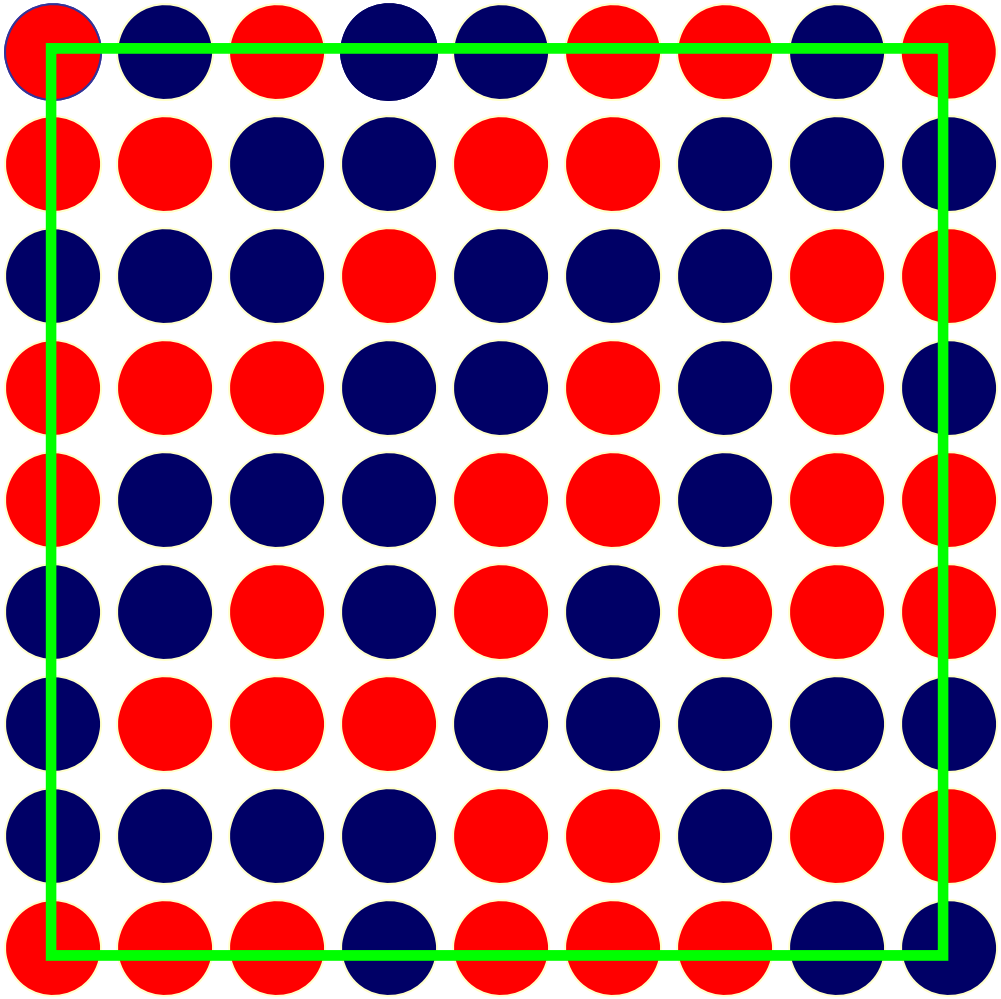
P. E. A. Turchi, I. A. Abrikosov, *et al.*, CALPHAD **31**, 4 (2007).

Ordered compounds

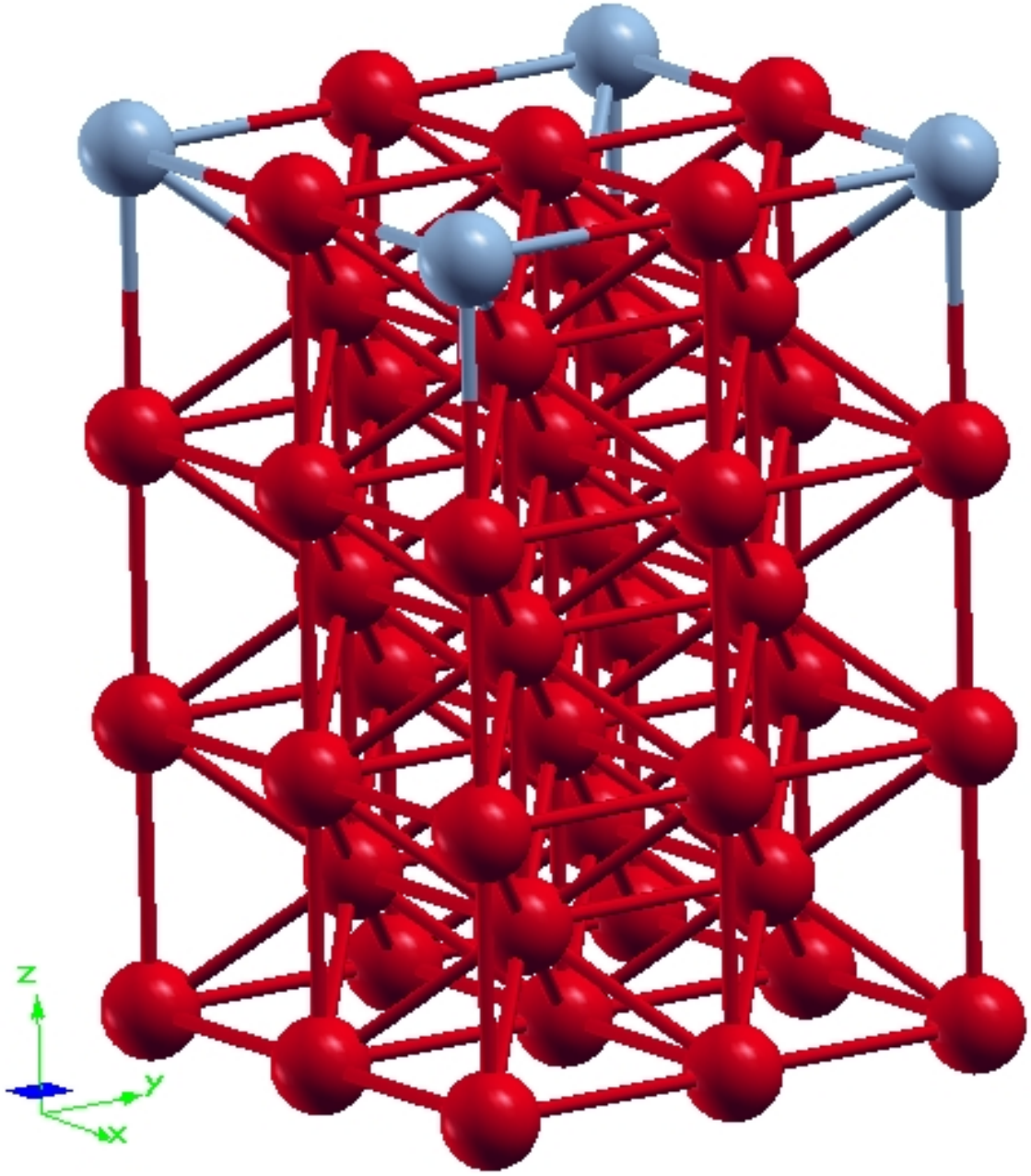




Solution phases: supercell method

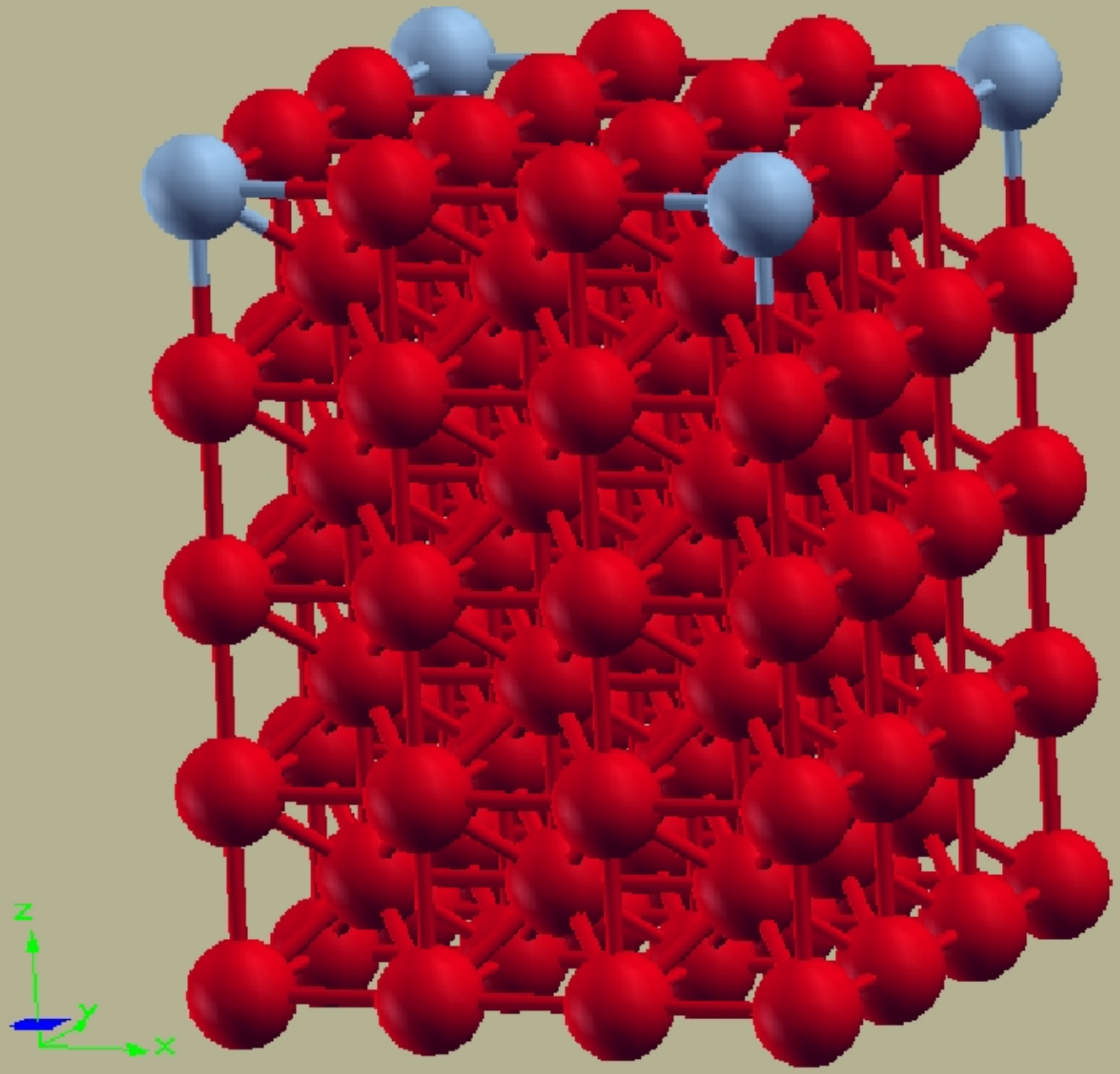


2X2X7, segregation energy -0.043 eV



A. V. Ponomareva *et al.*, Phys. Rev. B 75, 245406 (2007)

3X3X9, segregation energy 0.090 eV



A. V. Ponomareva *et al.*, Phys. Rev. B 75, 245406 (2007)

Model:

$$[-\frac{1}{2}\nabla^2 + U(\vec{r})]\psi = \varepsilon\psi$$

$$U(\vec{r}) = \sum_j U_j(\vec{r} - \vec{R}_j)$$

U_j are random

- Substitutional disorder: $< \vec{R}_j >= n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
- Topological disorder: $< \vec{R}_j >\neq n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$
- Random alloy is a system with equilibrium atomic configuration in the limit $V/T \to 0$, where V is the strongest effective interaction in the system
- Spatial homogenity: $< U(\vec{r}_1 + \vec{a})U(\vec{r}_2 + \vec{a})...U(\vec{r}_n + \vec{a}) >=< U(\vec{r}_1)U(\vec{r}_2)...U(\vec{r}_n) >$
- Disappearance of statistical correlations:

$$< U(\vec{r}_1 + \vec{a})U(\vec{r}_2 + \vec{a})...U(\vec{r}_n + \vec{a})U(\vec{r}_1')U(\vec{r}_2')...U(\vec{r}_n') >=< U(\vec{r}_1 + \vec{a})U(\vec{r}_2 + \vec{a})...U(\vec{r}_n + \vec{a}) >< U(\vec{r}_1')U(\vec{r}_2')...U(\vec{r}_n') >$$

where $|\vec{a}| \to \infty$

Self-averaging

- Extensive quantities: $A(V_1 + V_2) = A(V_1) + A(V_2)$
- Examples: total energy, density of states, volume, etc.
- Quantity *A* is self-averaging if it has well-defined, non-random value in a random alloy with volume $V \to \infty$
- Theorem: In a random alloy molar values of extensive quantities are self-averaging.
- Crystal potential or wave function **are not** self-averaging quantities

Cluster expansion of the total energy

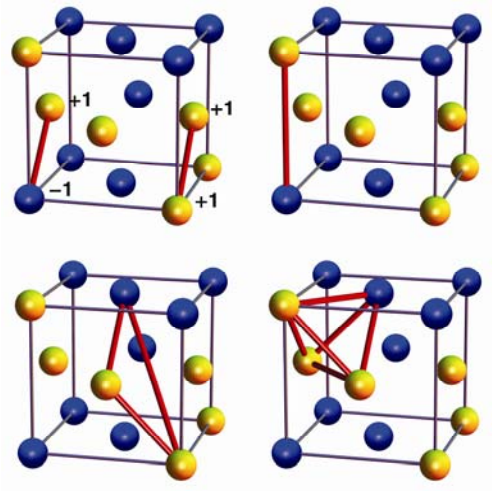
$$\Phi_f^{(n)}(\sigma) = \prod_{i \in f} \sigma_i$$

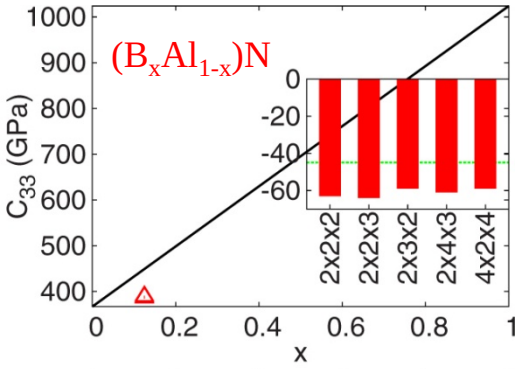
$$F(\sigma) = \sum_f F_f^{(n)} \Phi_f^{(n)}(\sigma)$$

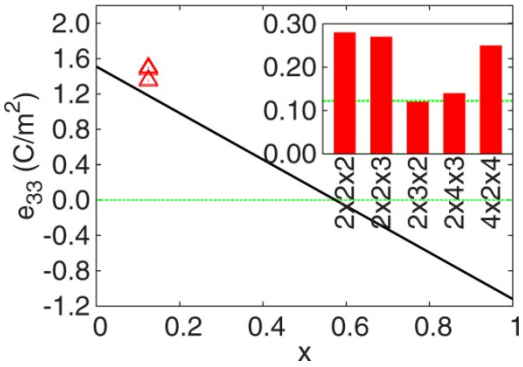
$$F_f^{(n)} = \left\langle F(\sigma) \Phi_f^{(n)}(\sigma) \right\rangle$$

$$V_f^{(n)} = \left\langle E_{tot}(\sigma) \Phi_f^{(n)}(\sigma) \right\rangle$$

$$E_{tot} = \sum_f V_f^{(n)} \left\langle \Phi_f^{(n)}(\sigma) \right\rangle$$







Special quasirandom structure method

[A. Zunger *et al.*, Phys. Rev. Lett. **65**, 353 (1990)]

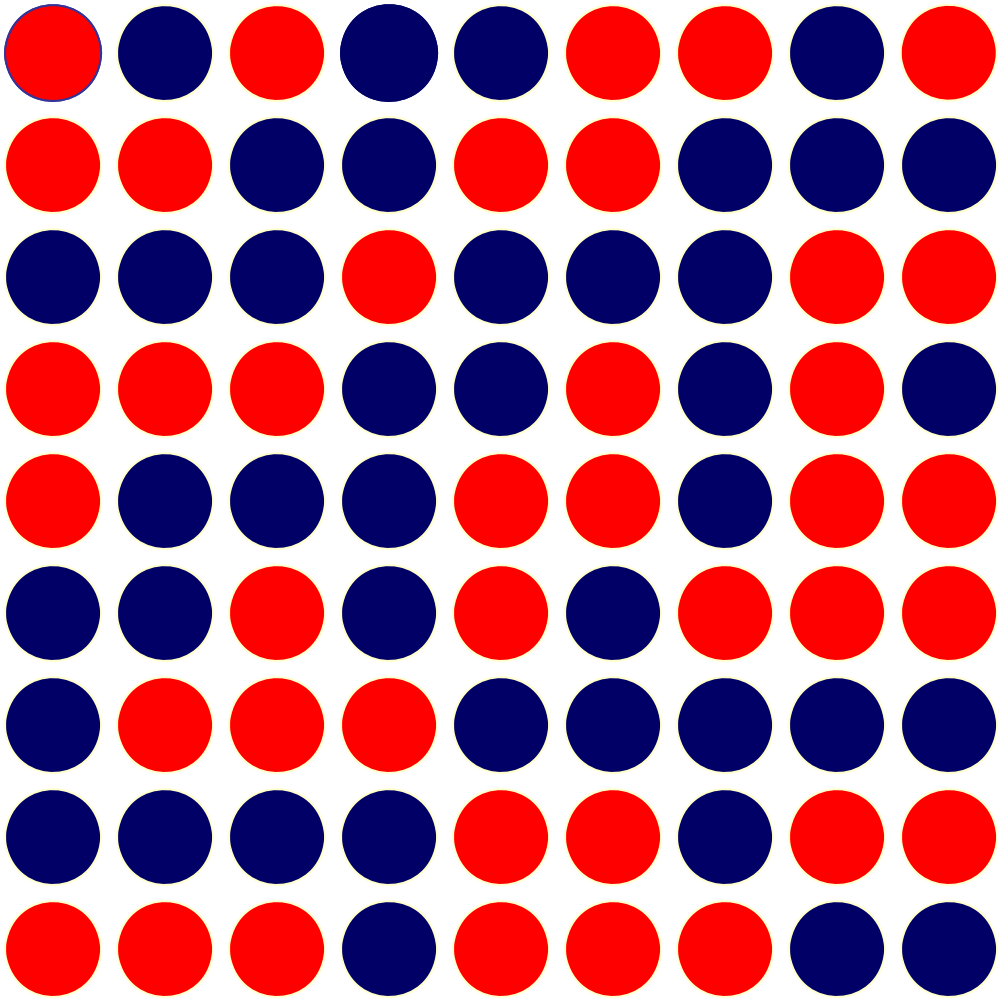
$$V_f^{(n)} \neq 0 \Leftrightarrow \left\langle \Phi_f^{(n)}(\sigma) \right\rangle = 0$$

$$V_f^{(n)} = 0 \Leftrightarrow \left\langle \Phi_f^{(n)}(\sigma) \right\rangle \neq 0$$

A. V. Ruban and I. A. Abrikosov, Rep. Prog. Phys. 71, 046501 (2008).

F. Tasnadi, IAA, and I. Katardjiev, Appl. Phys. Lett. 94, 151911 (2009).

Solution phases: coherent potential



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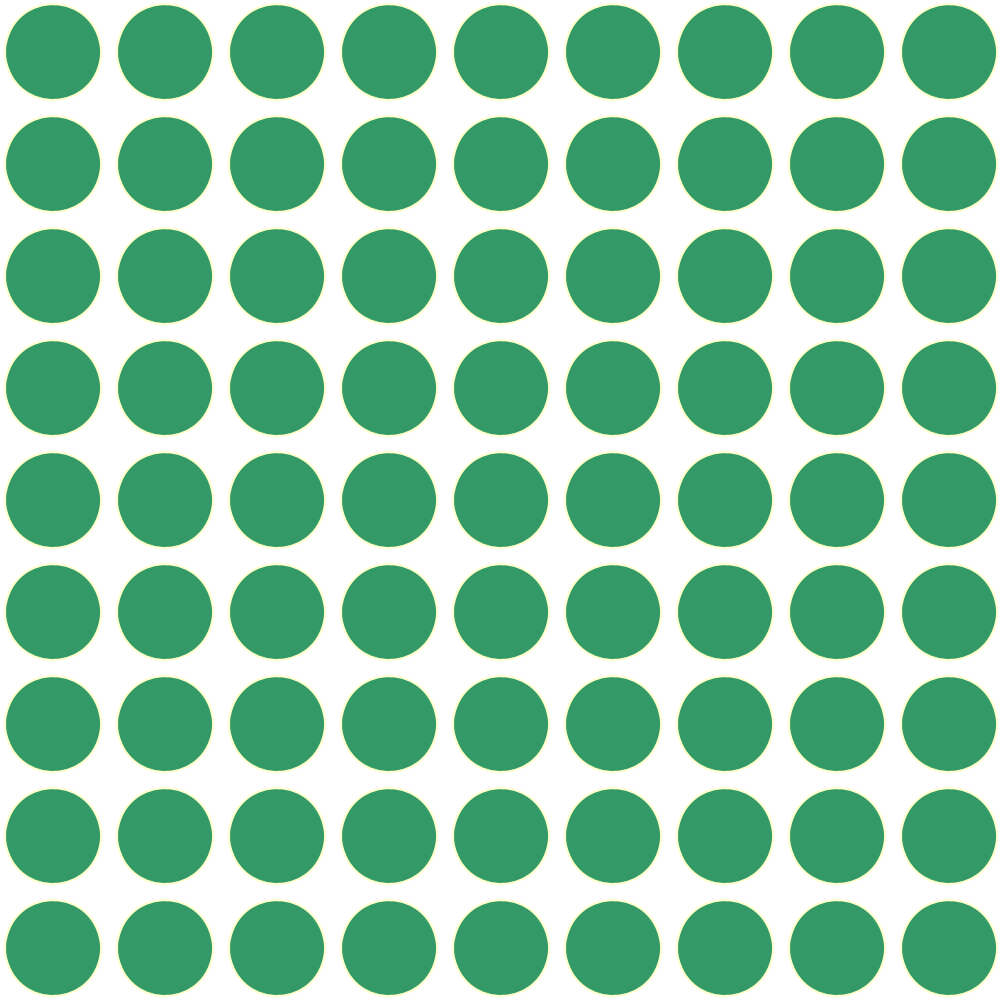
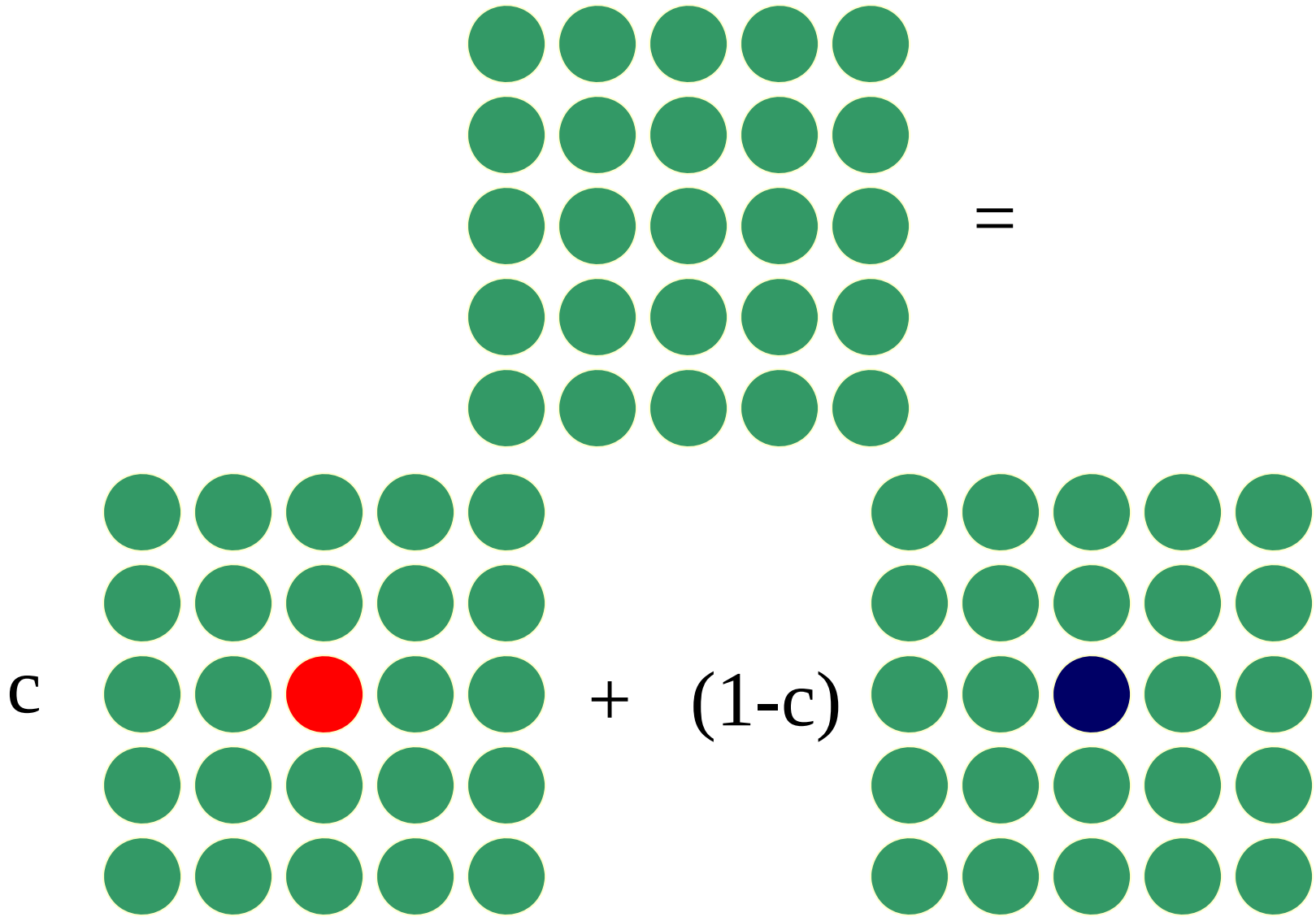


A. V. Ruban and I. A. Abrikosov, Rep. Prog. Phys. 71, 046501 (2008).



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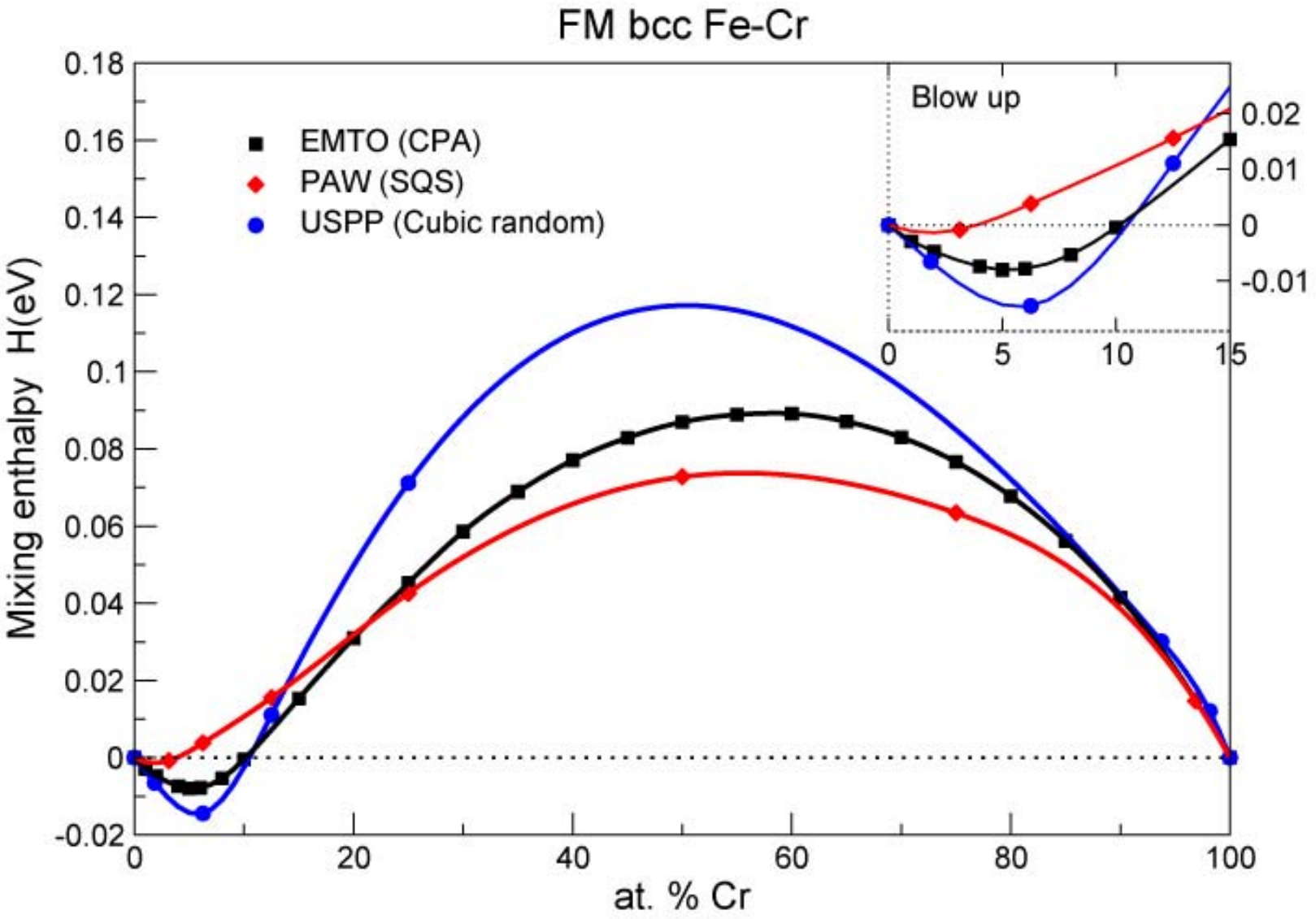
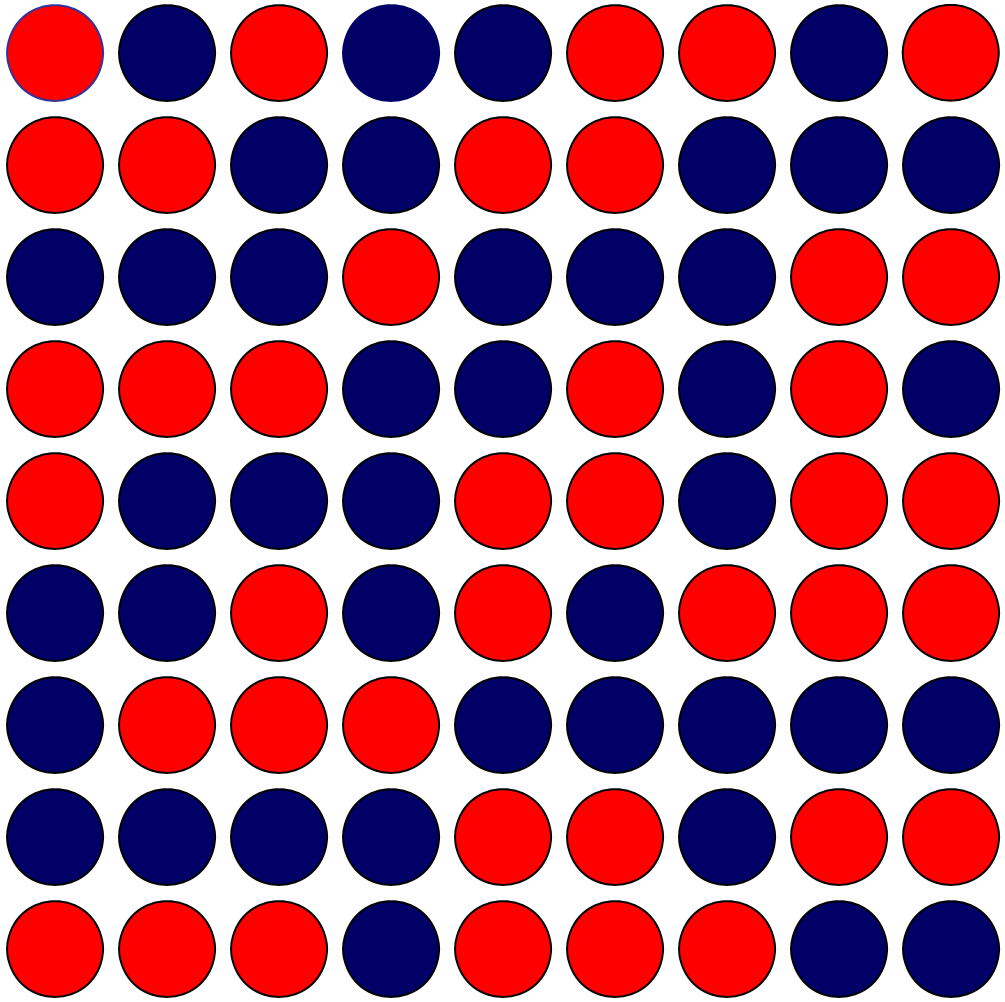
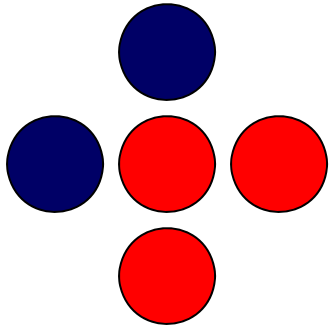


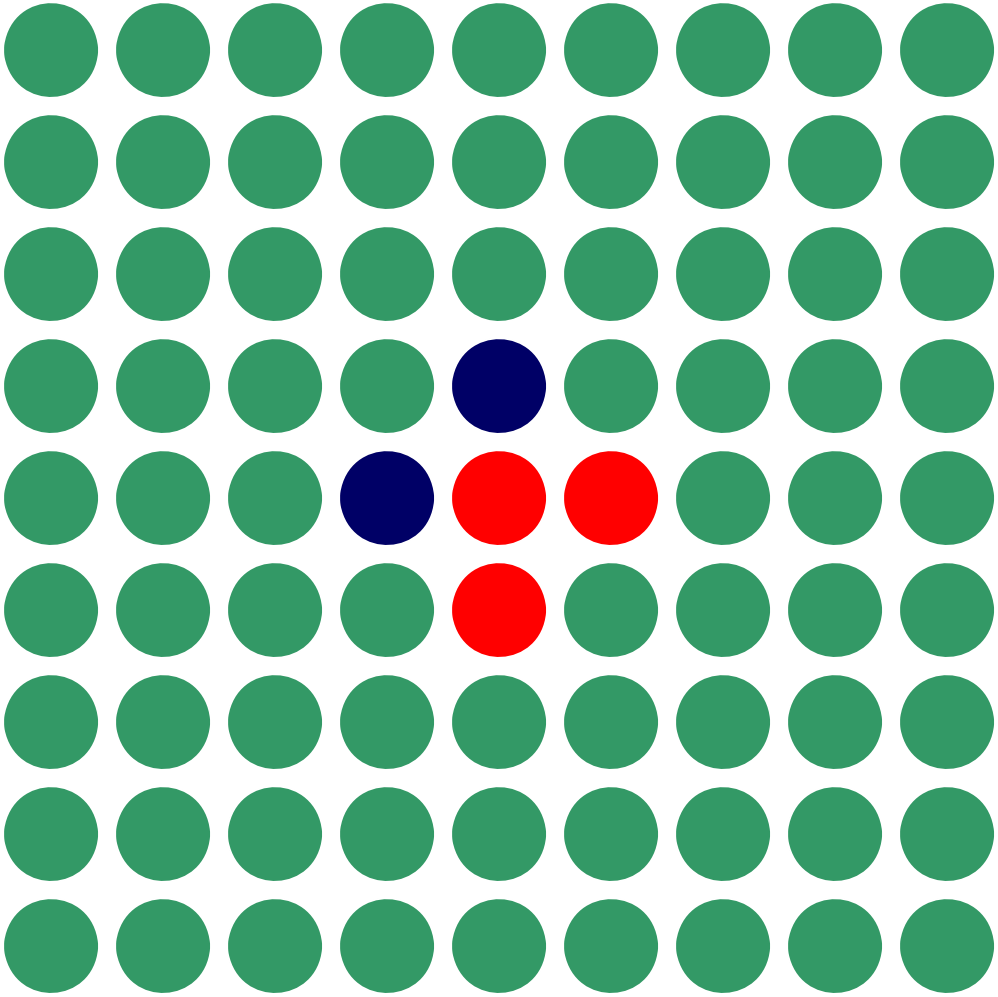
P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B 73, 104416 (2006)

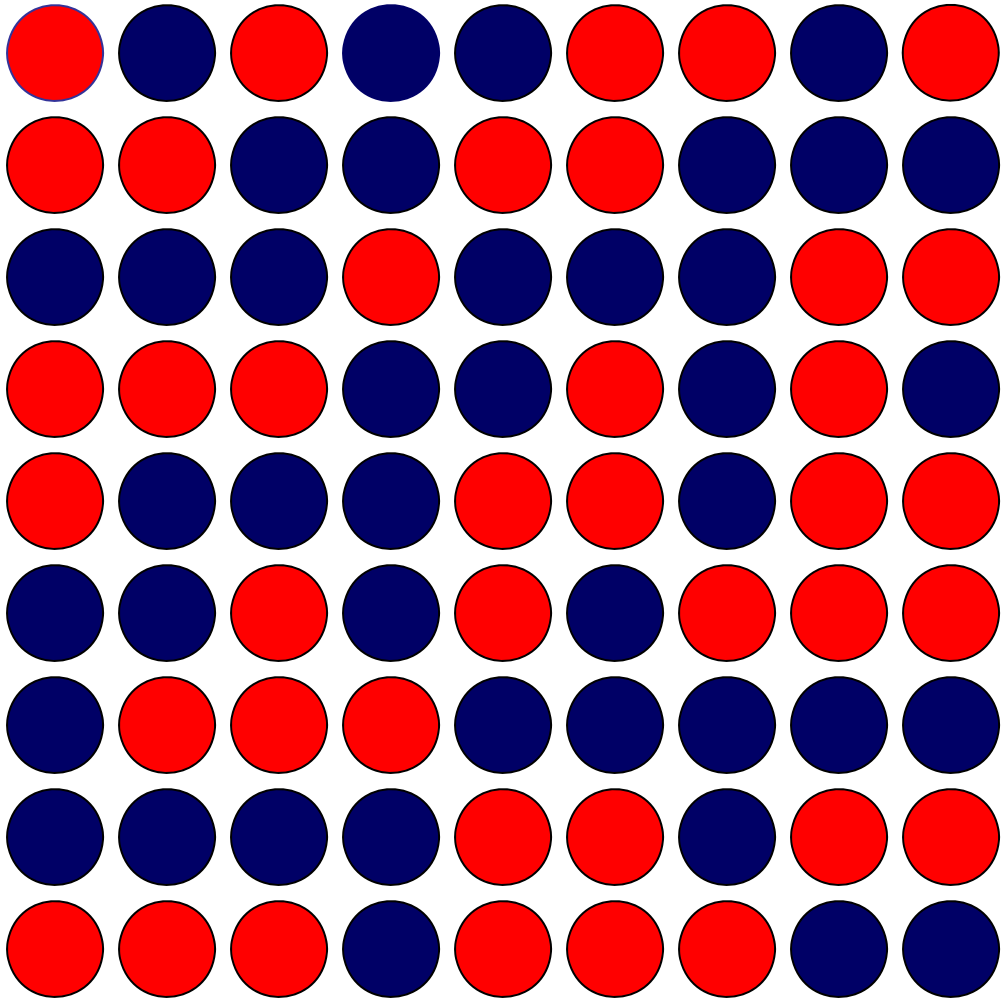
Locally Self-consistent Green's Functon method (LSGF)

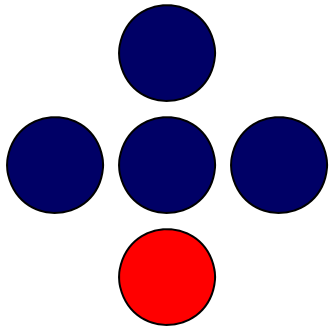


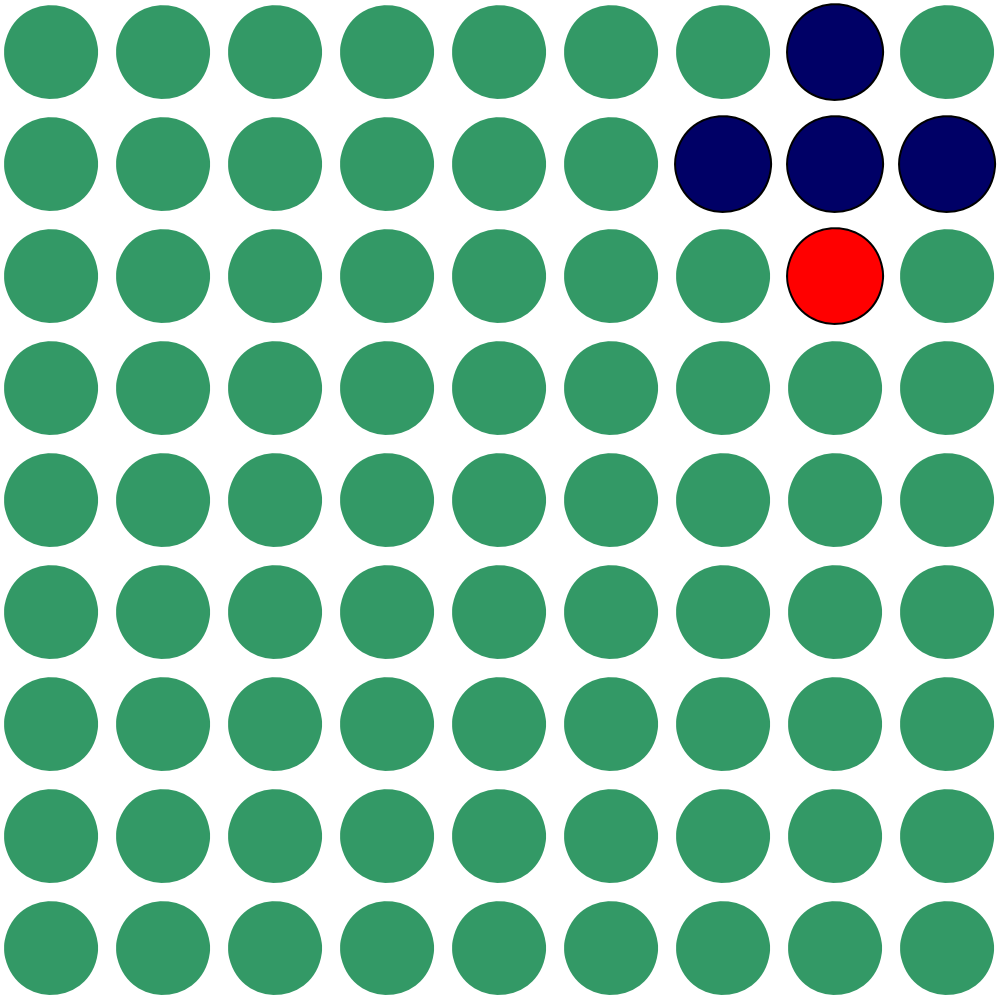
I. A. Abrikosov *et al.*, Phys. Rev. Lett. **76**, 4203 (1996)

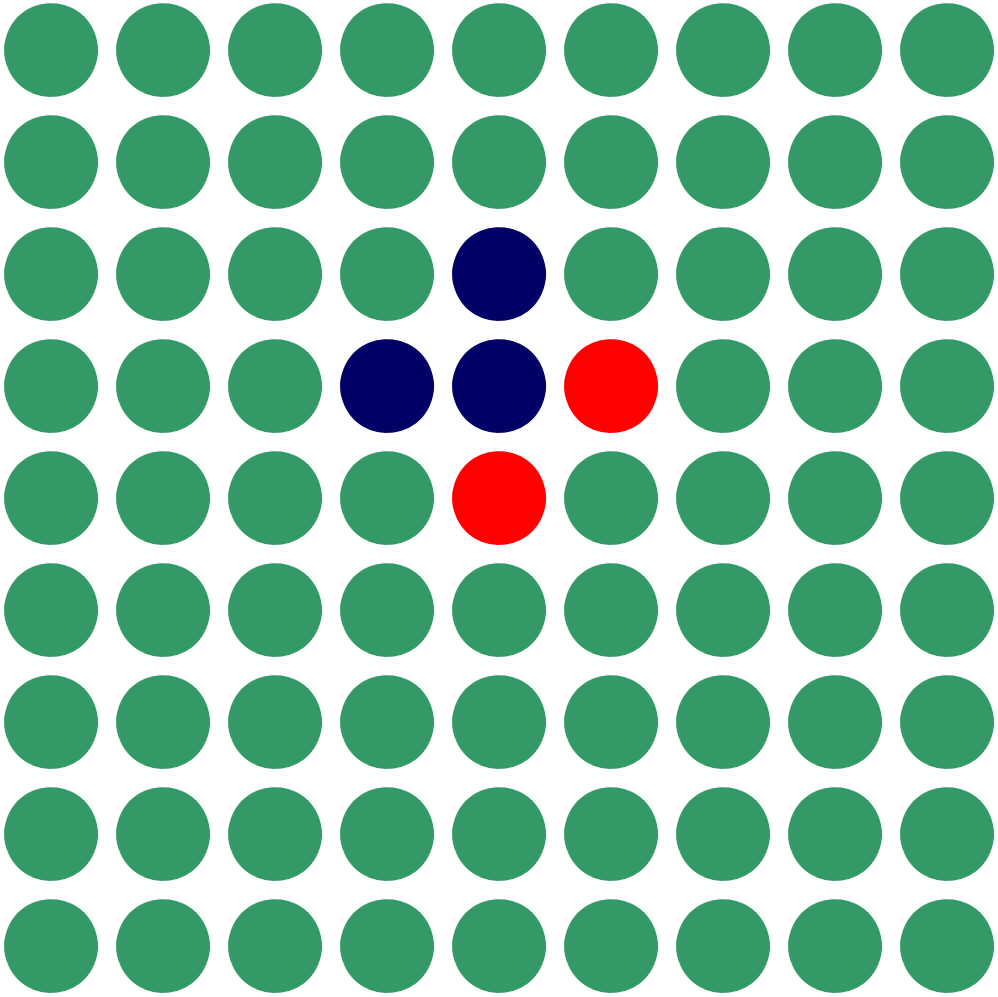


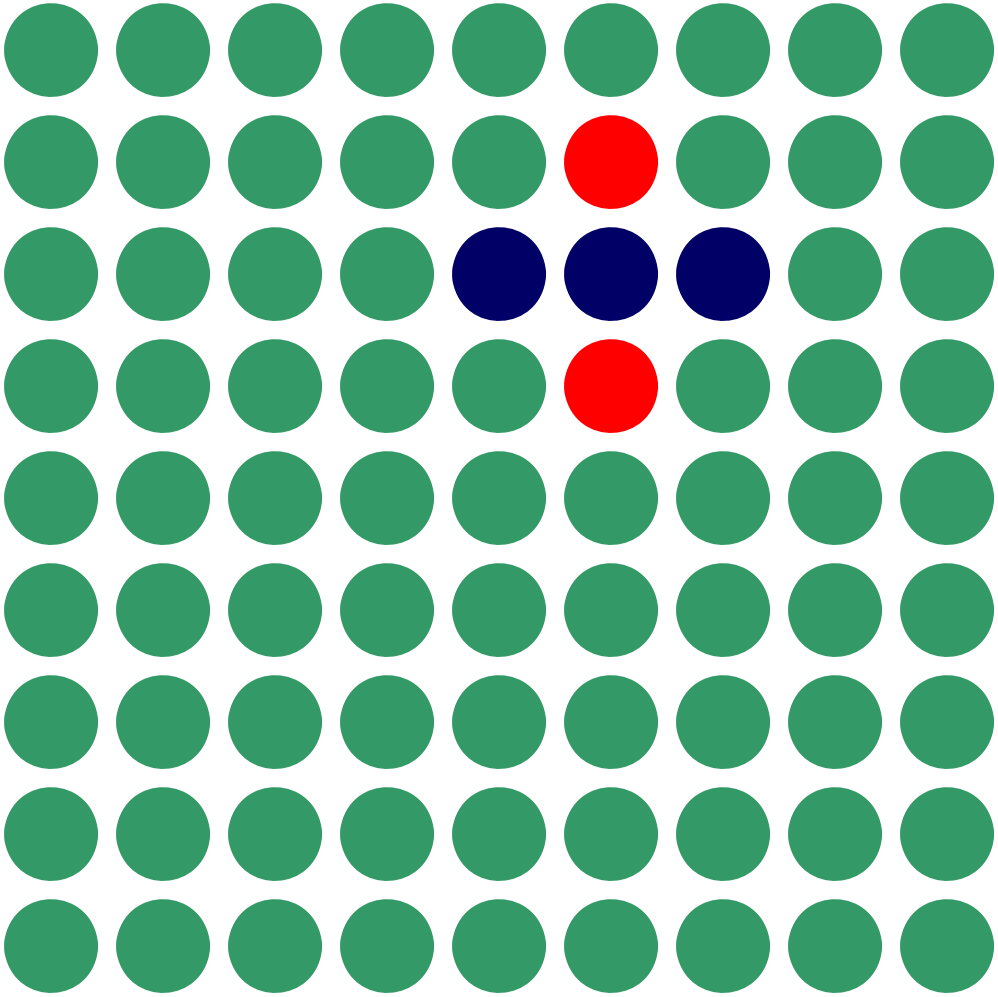


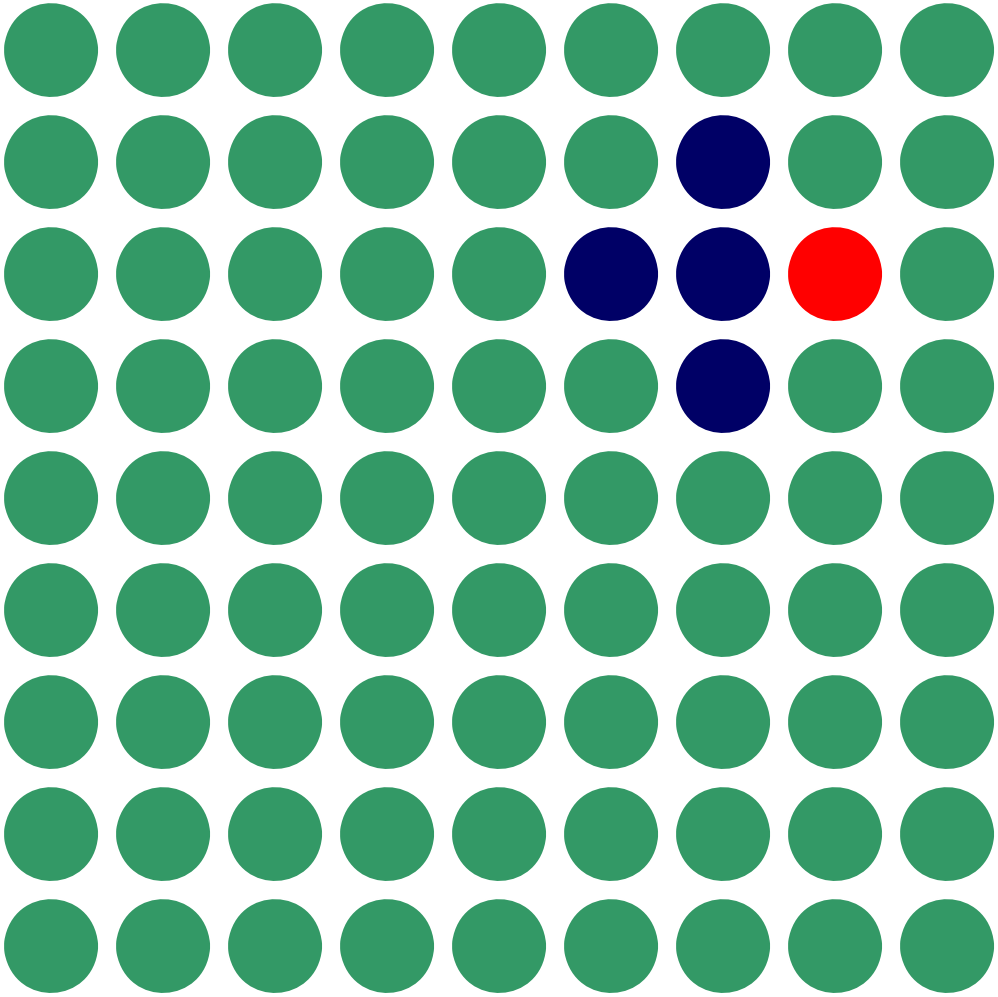


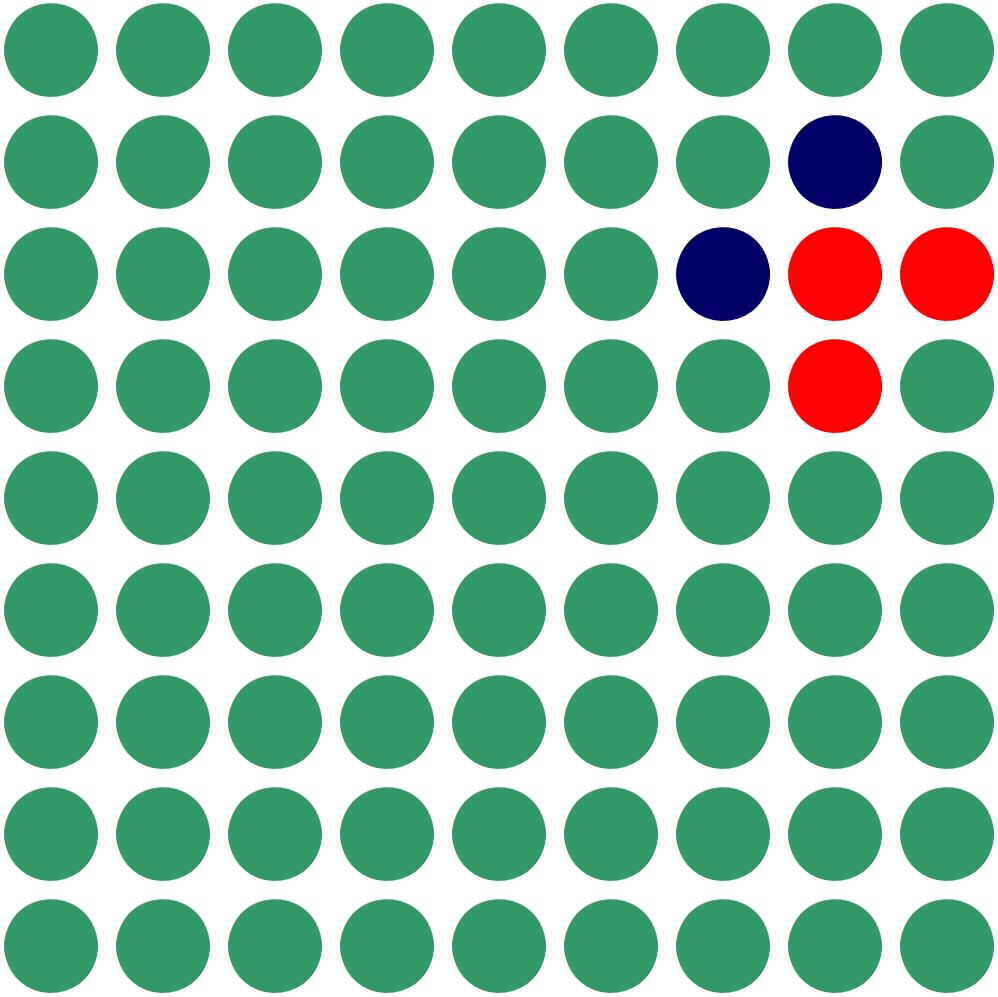


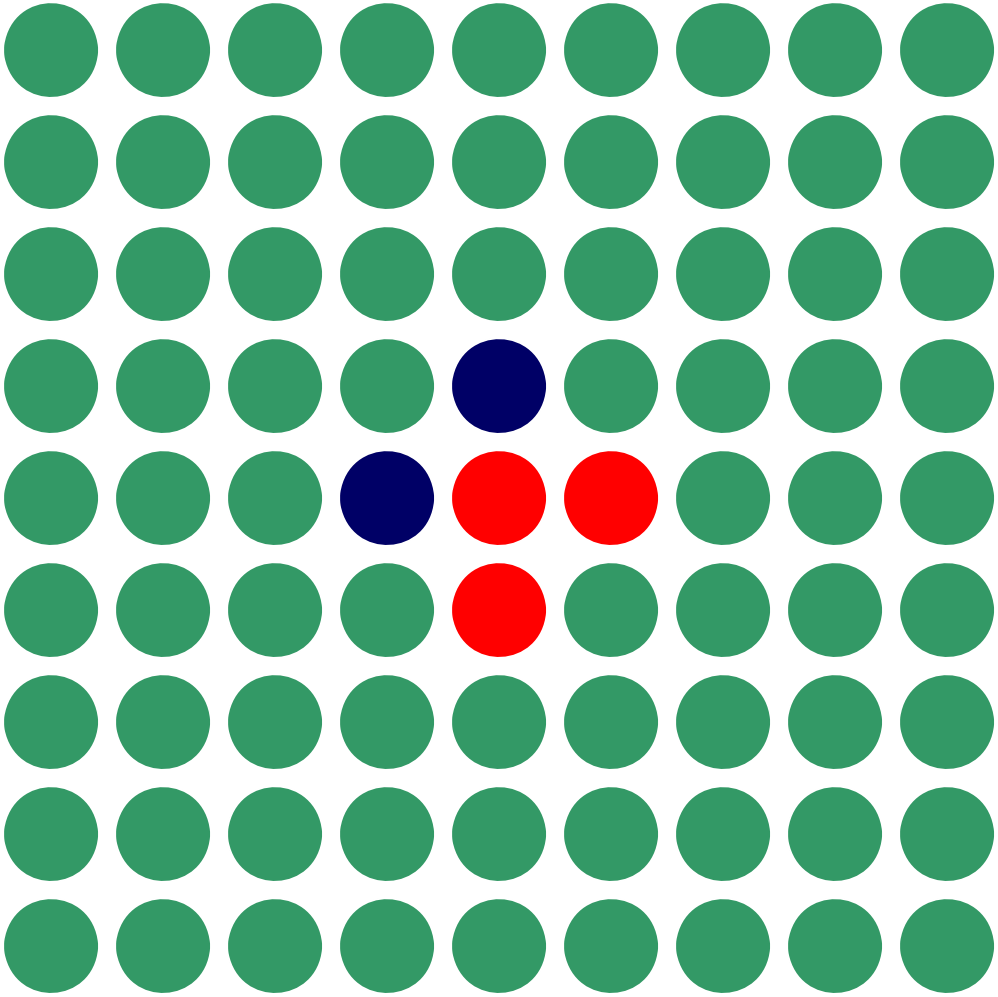


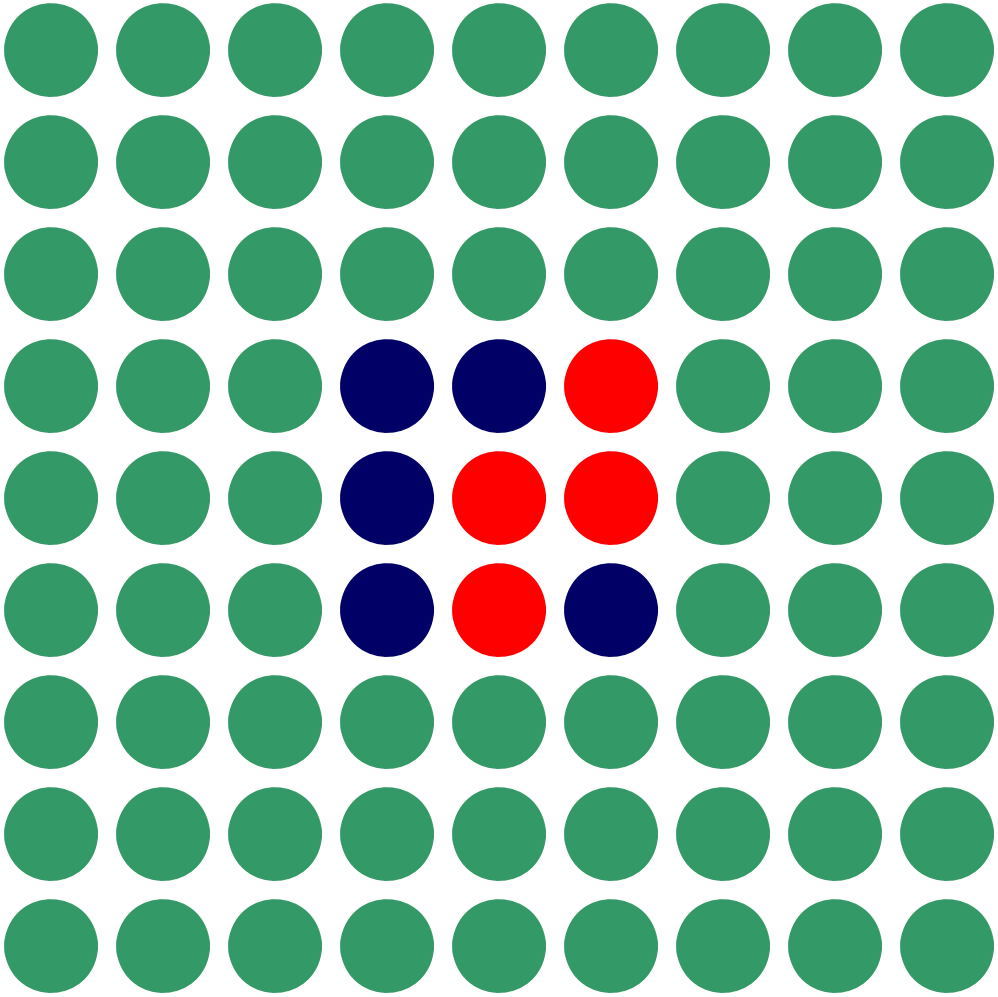


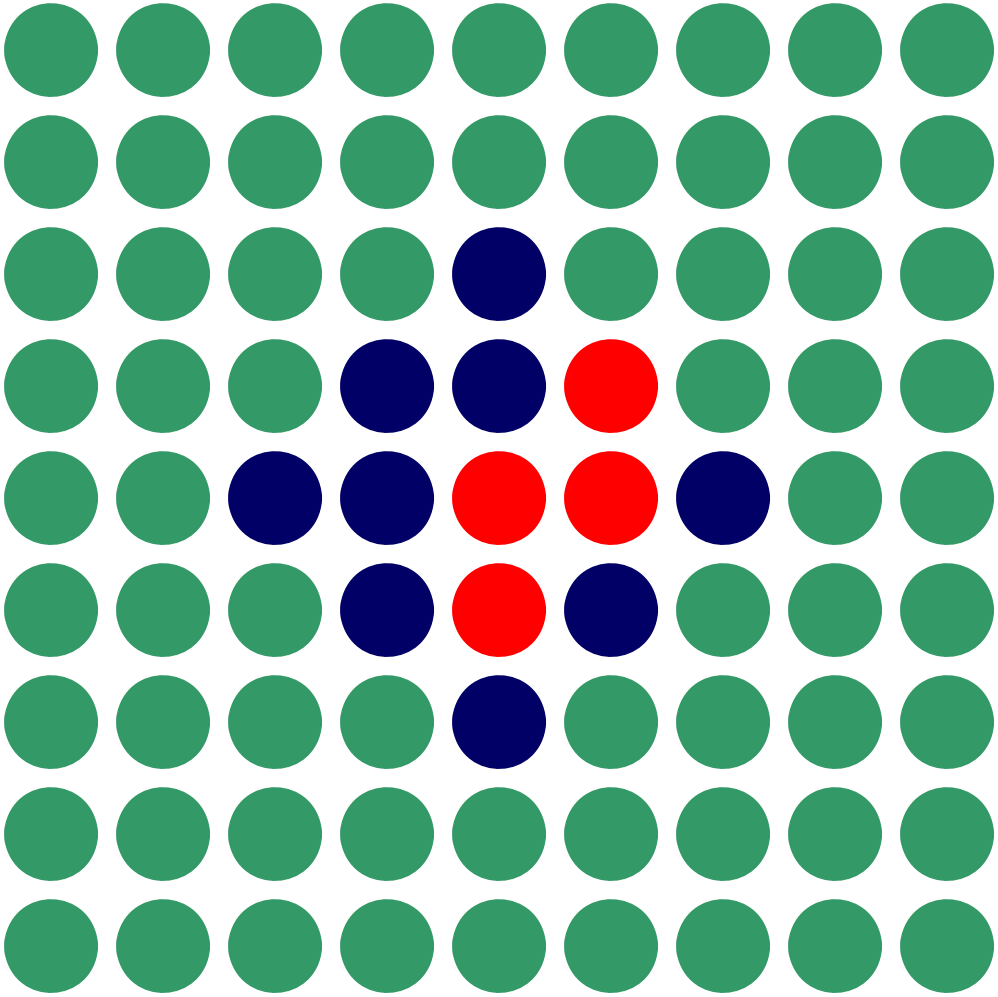


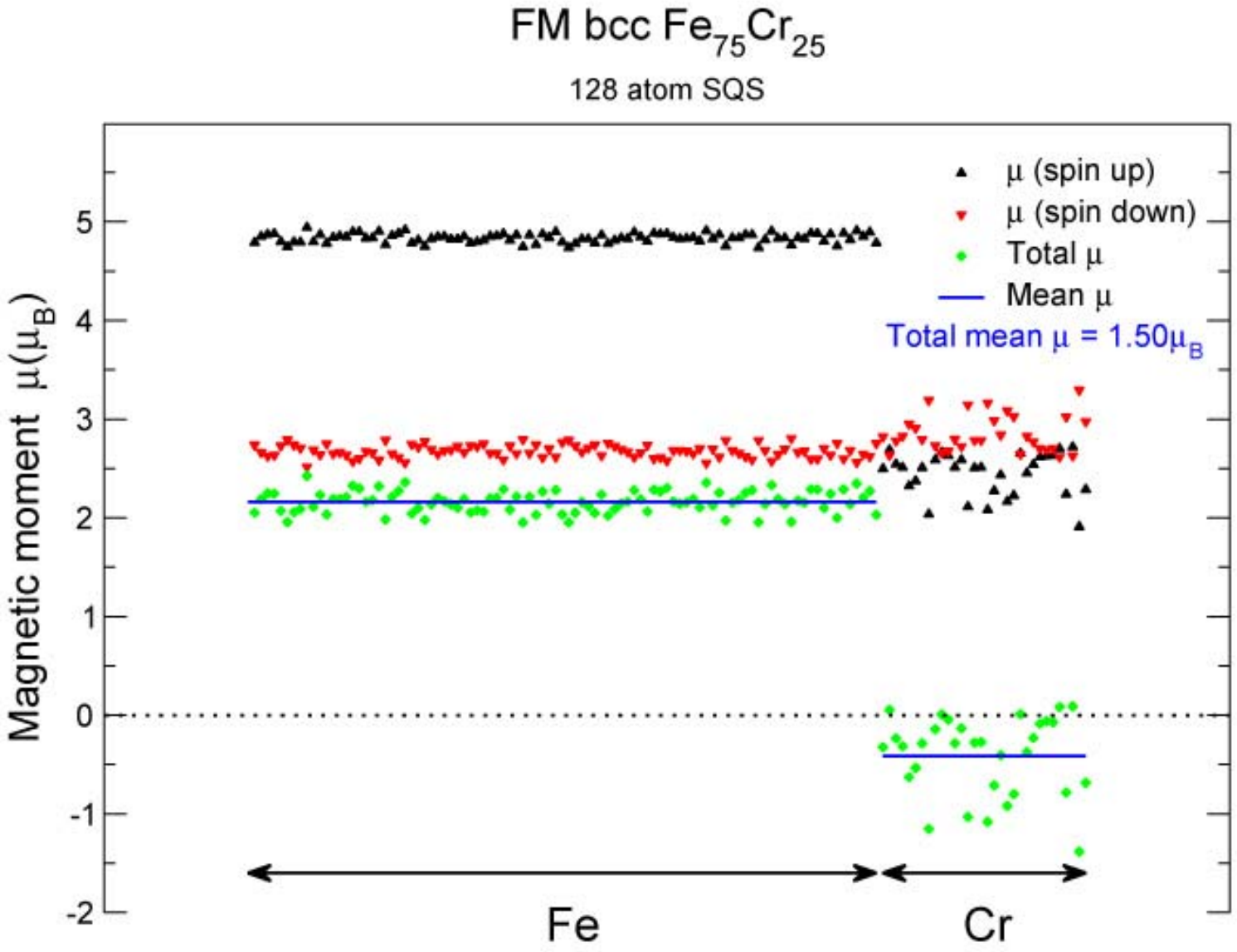


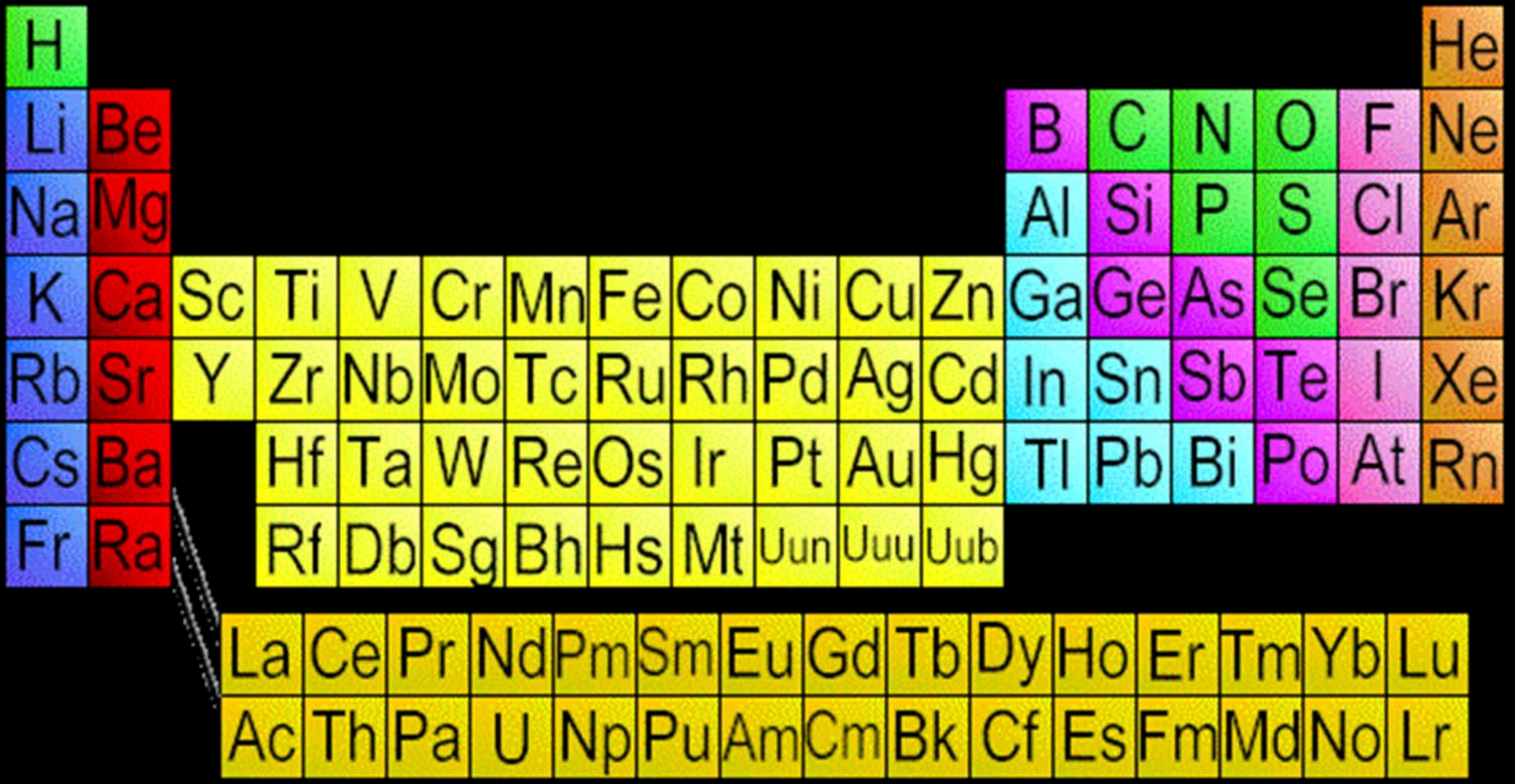


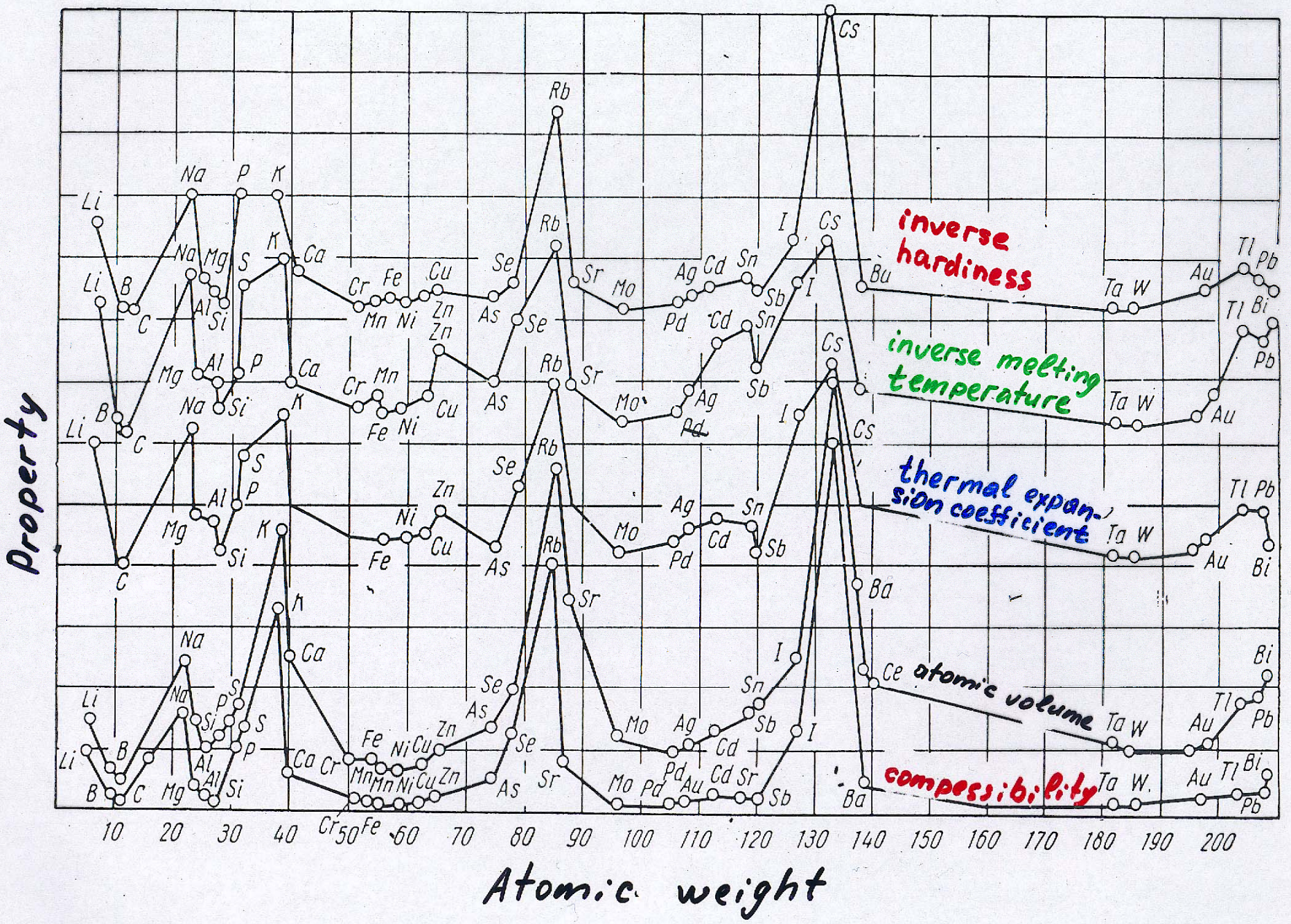




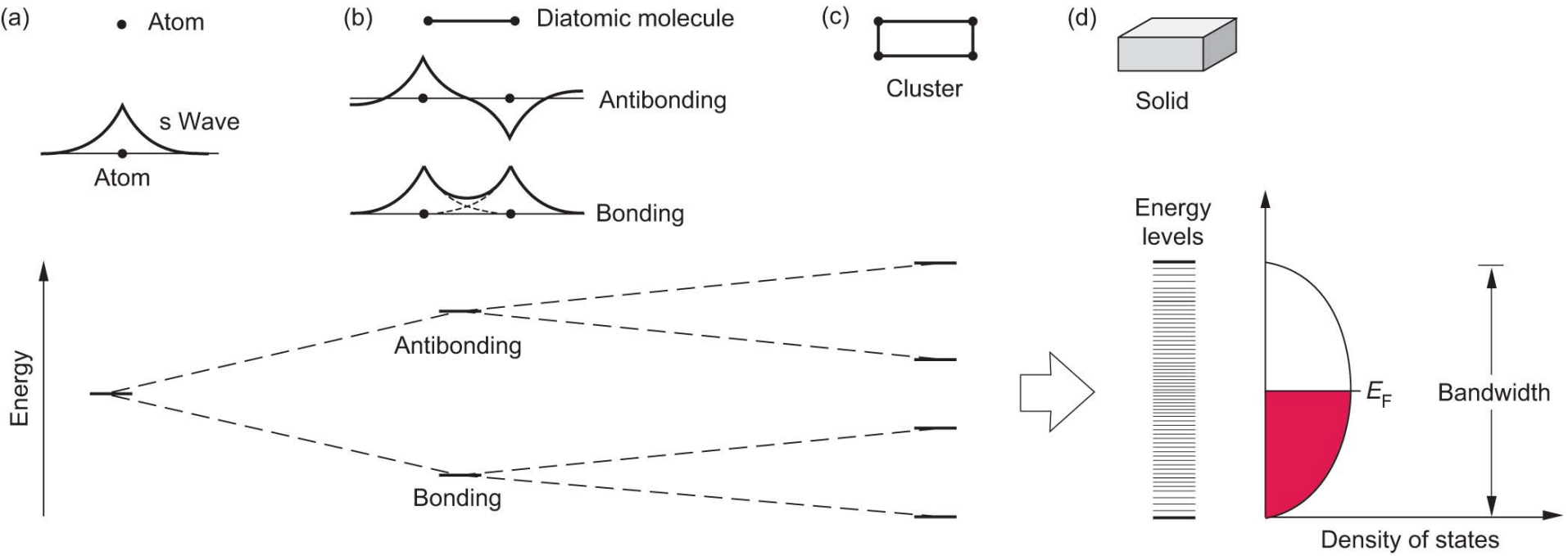



FM bcc $Fe_{75}Cr_{25}$
128 atom SQS
μ (spin up)
μ (spin down)
Total μ
Mean μ
Total mean μ = 1.50μ_B
Magnetic moment μ(μ_B)
5
4
3
2
1
0
-1
-2
Fe
Cr

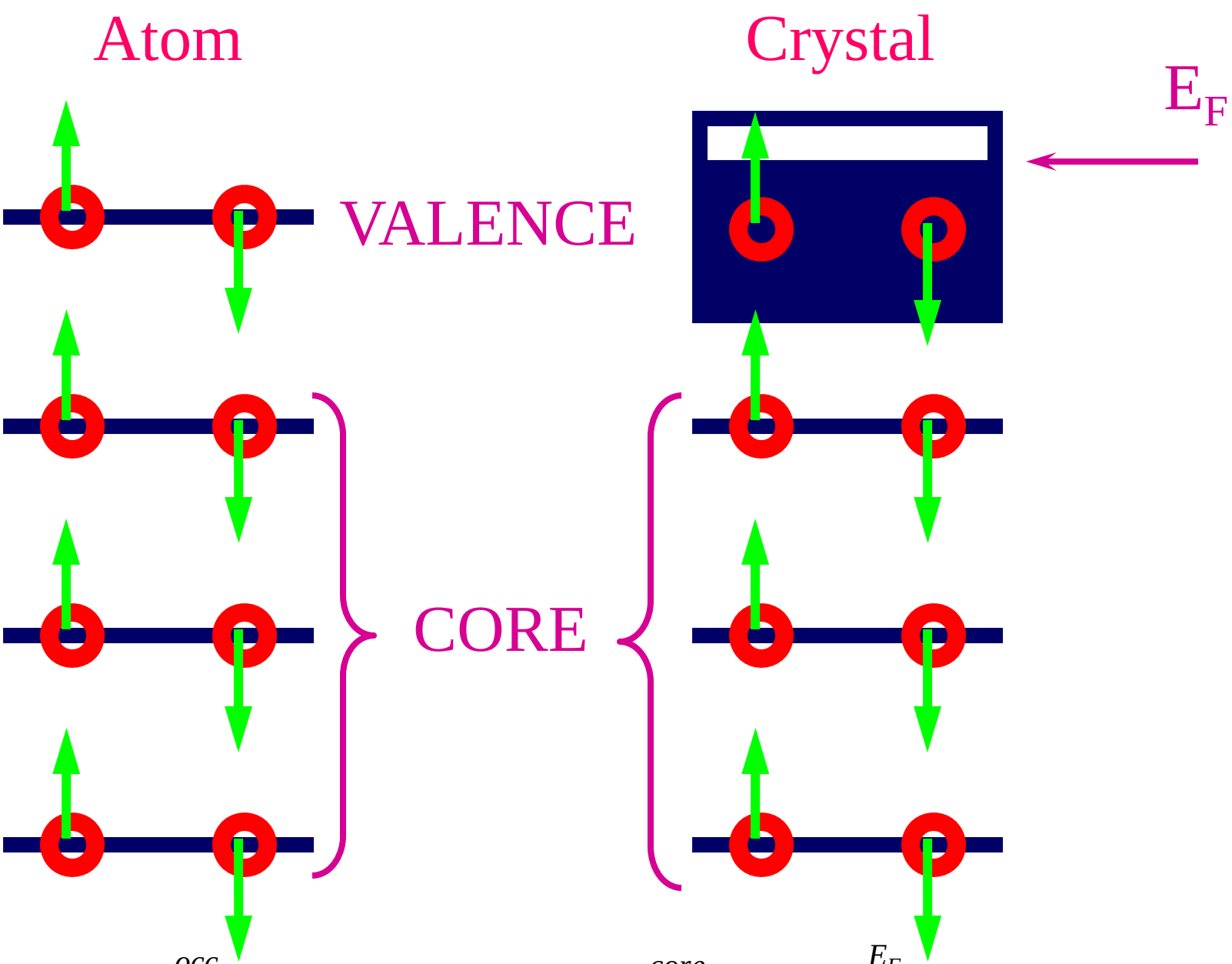

H
He
Li Be
B C N O F Ne
Na Mg
Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Rf Db Sg Bh Hs Mt Uun Uuu Uub
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

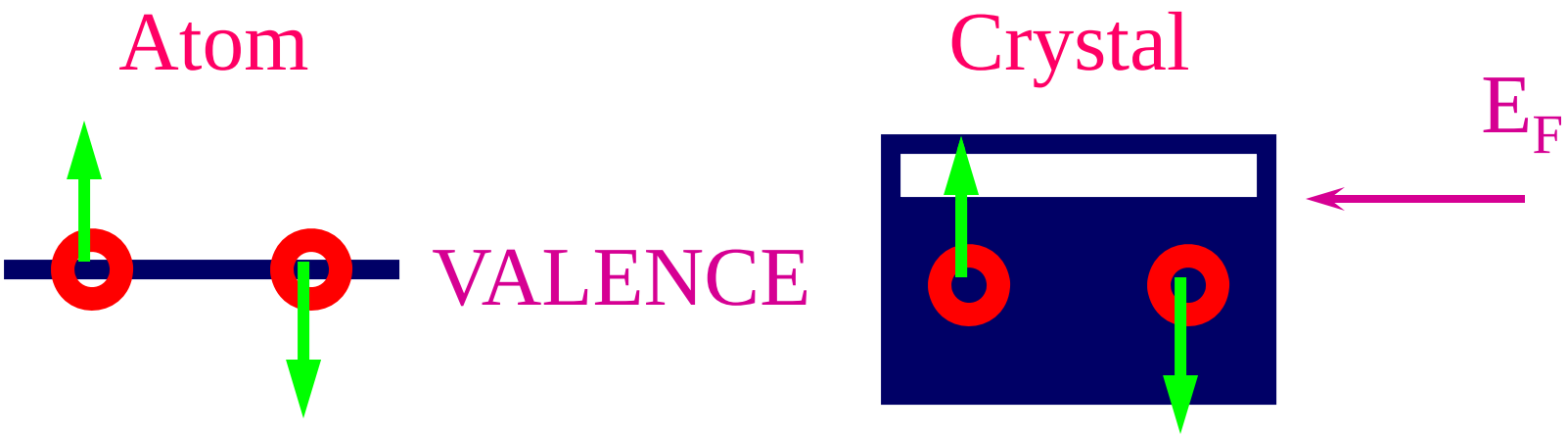

Property
inverse hardiness
inverse melting temperature
thermal expansion coefficient
atomic volume
compressibility
Atomic weight
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

Band formation



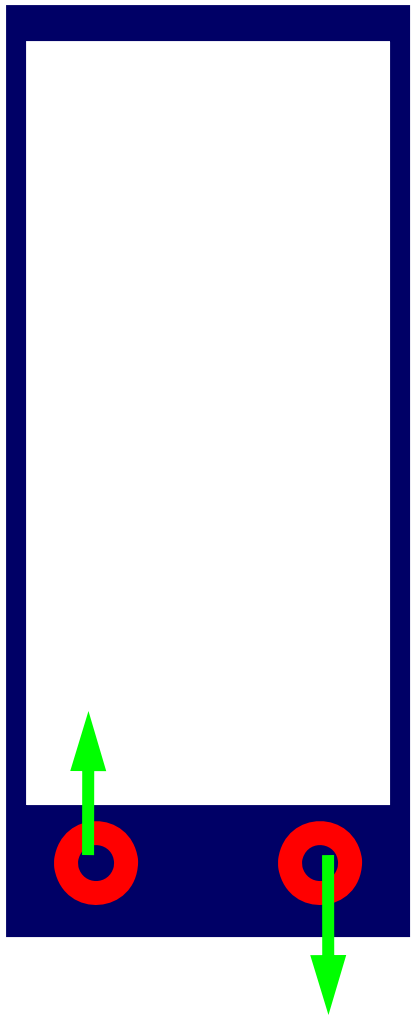
From J. M. Wills and O. Eriksson, *Los Alamos Science* Number 26, 128 (2000).


Atom
Crystal
E_F
VALENCE
CORE
$E_{tot} = \sum^{occ} E_i^{atom} n_i$
$E_{tot} = \sum^{core} E_i n_i + \int_{valence}^{E_F} E n(E) dE$



$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal

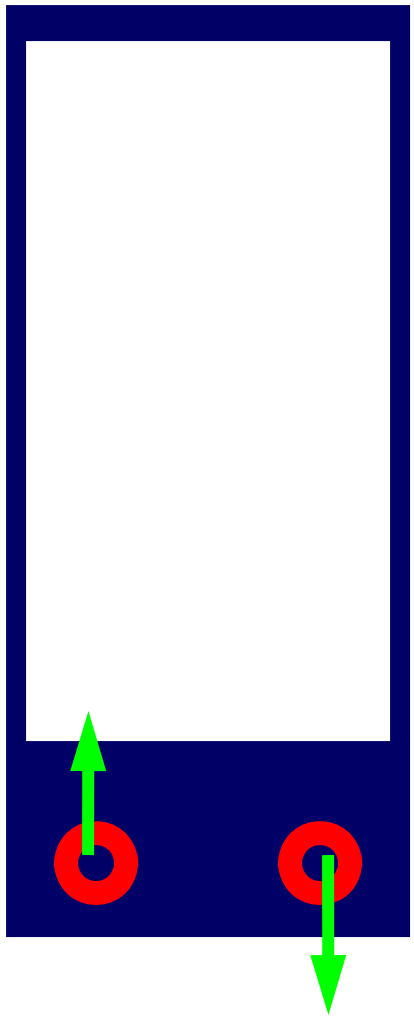


Zr

E_F

$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal

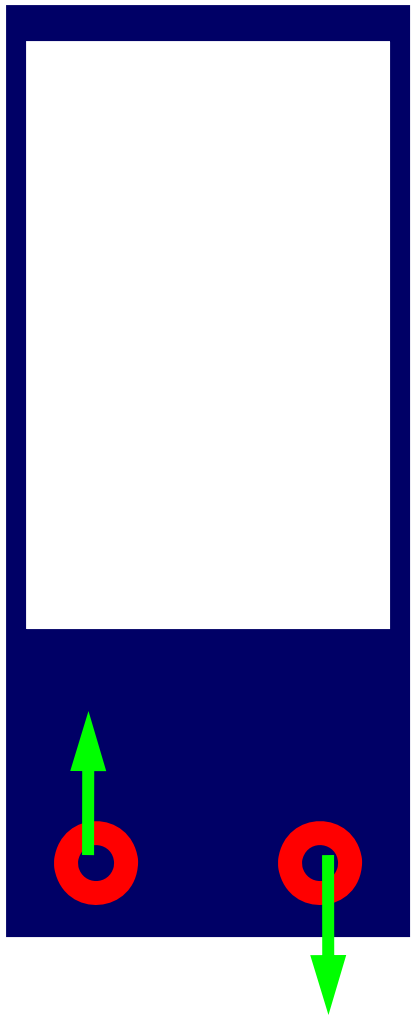


Nb

E_F

$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal

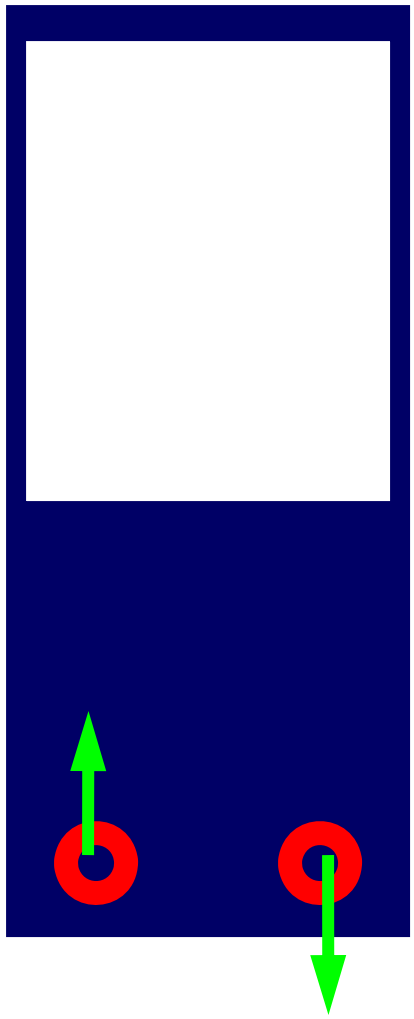


Mo

E_F

$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal



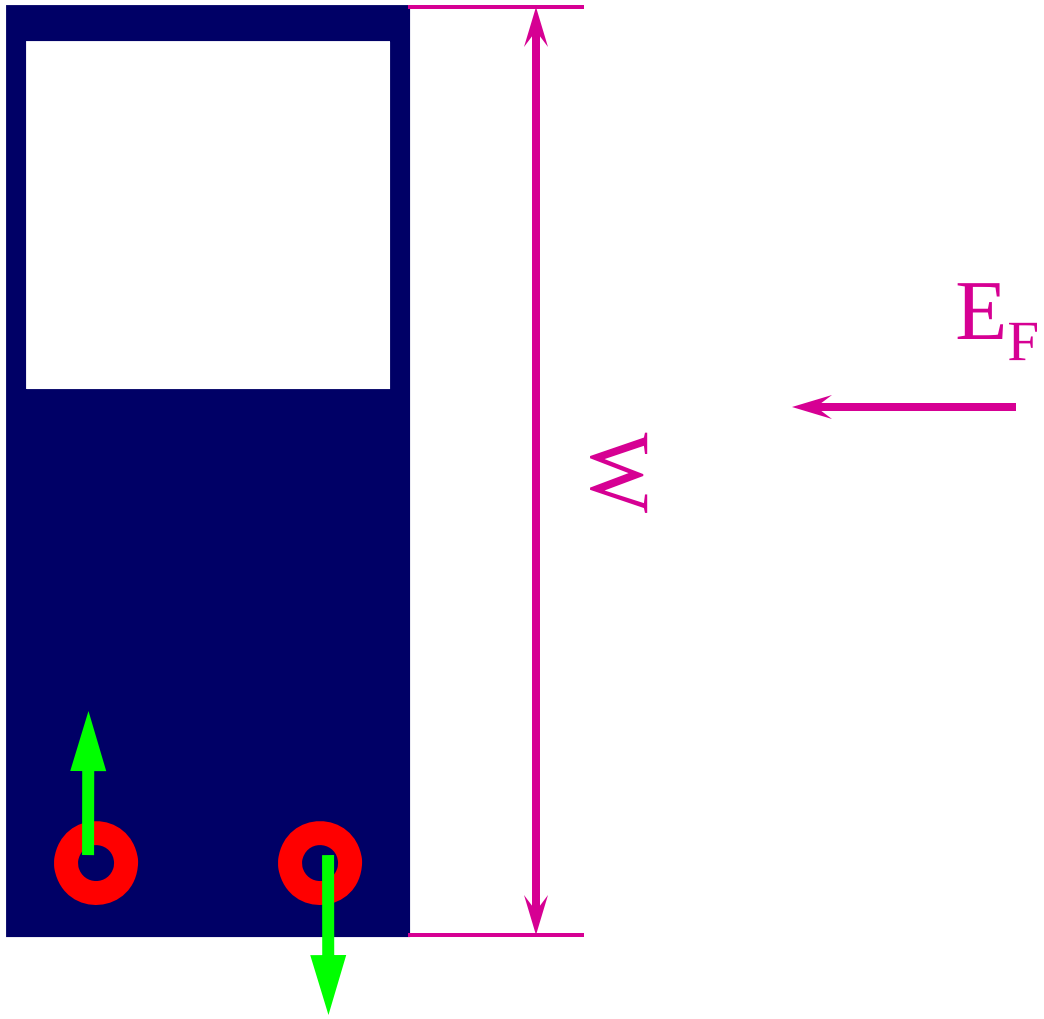
Tc

E_F

$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal

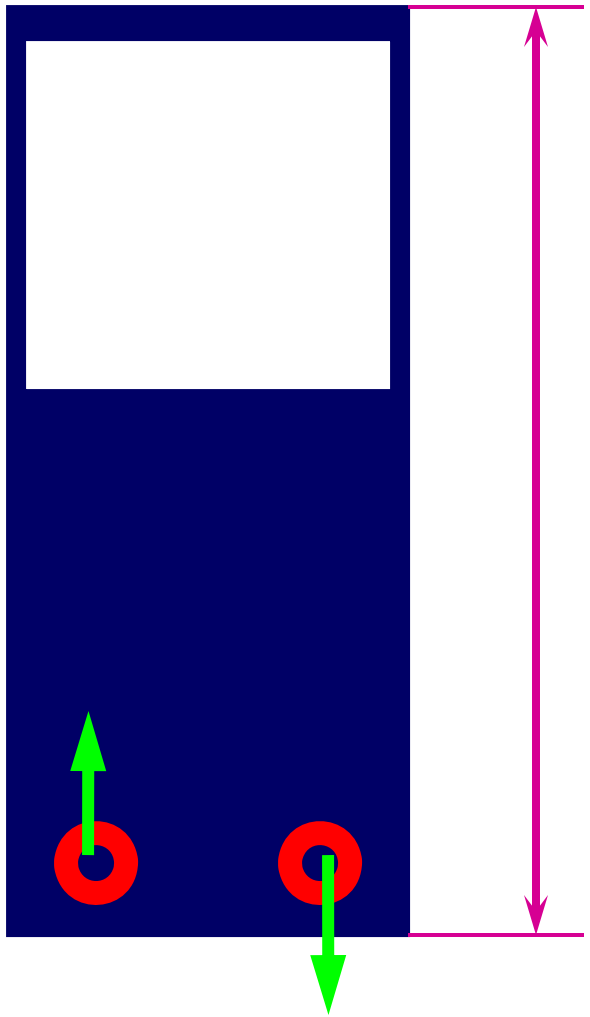
Ru



$$E_{BOND} = E_{tot}^{crystal} - E_{tot}^{atom} = \int_{valence}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

Transition metal

Ru



E_F

$$E_{BOND} = -\frac{1}{20} W N_d (10 - N_d)$$

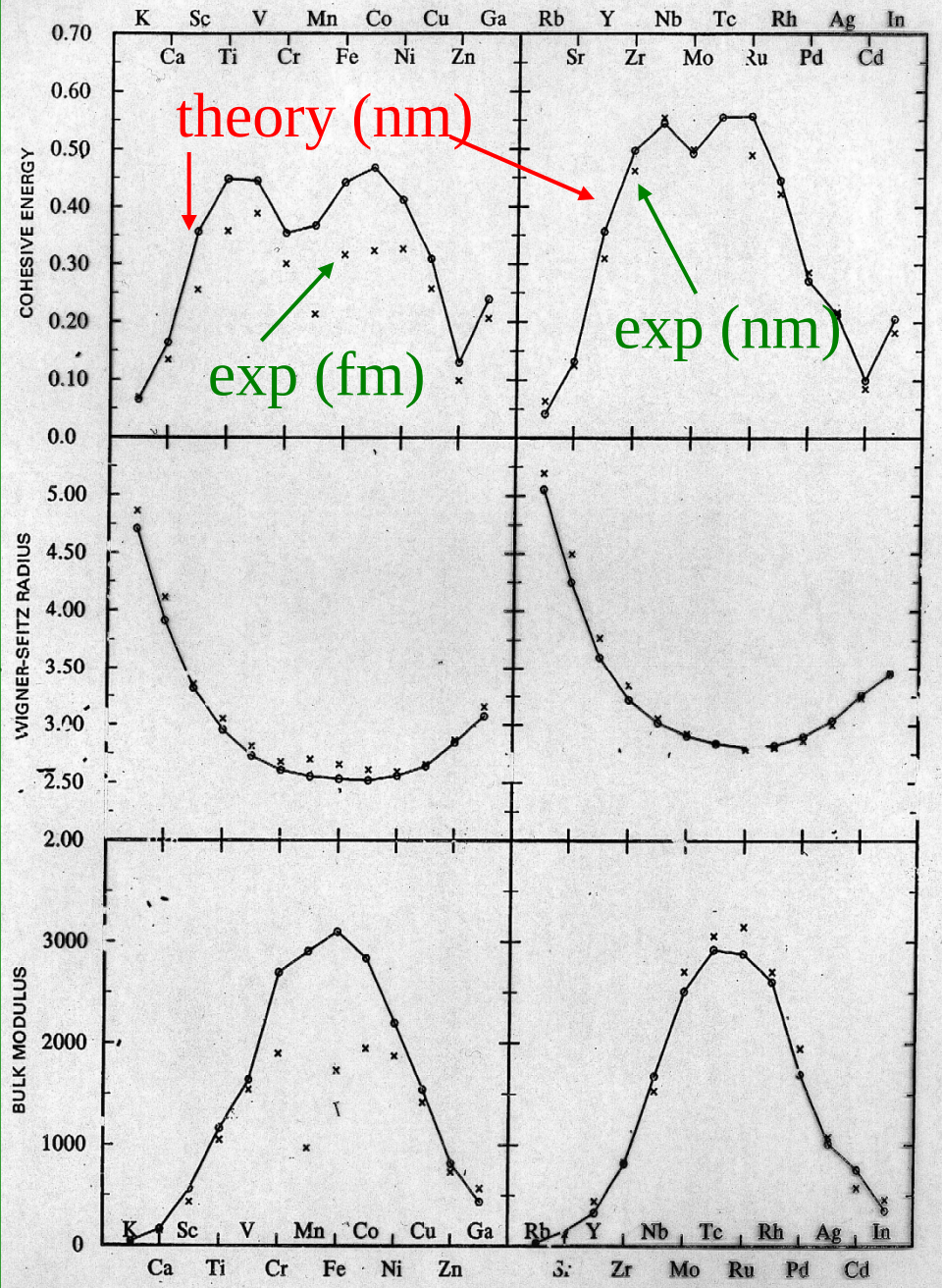
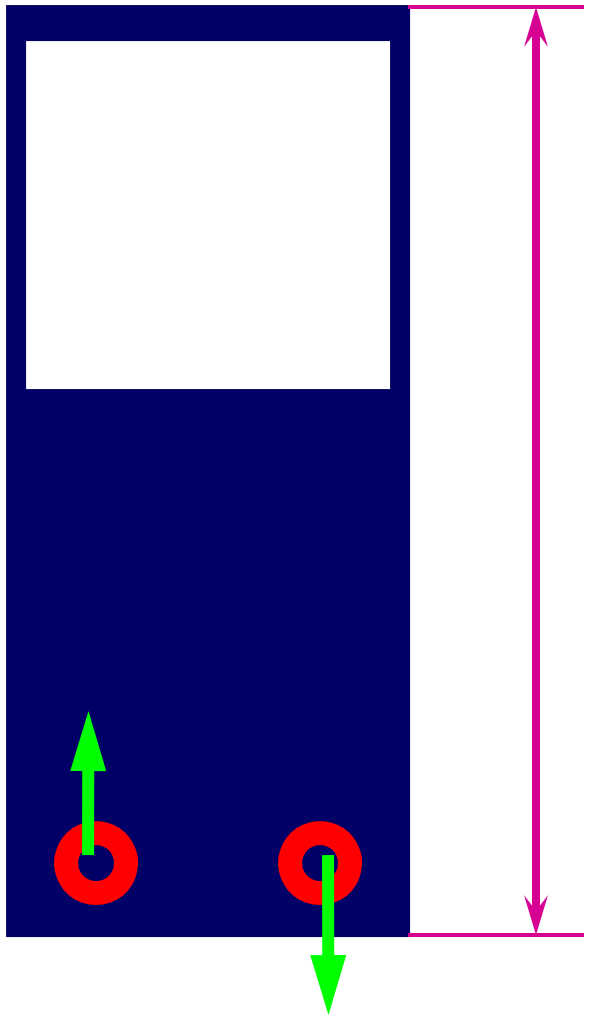


Figure 1.1 Cohesive properties. Top row- cohesive energy (Ry/atom). Middle row- Wigner-Seitz radius (a.u.). Bottom row- bulk modulus (Kbar). Measured values are indicated by crosses.

Transition metal

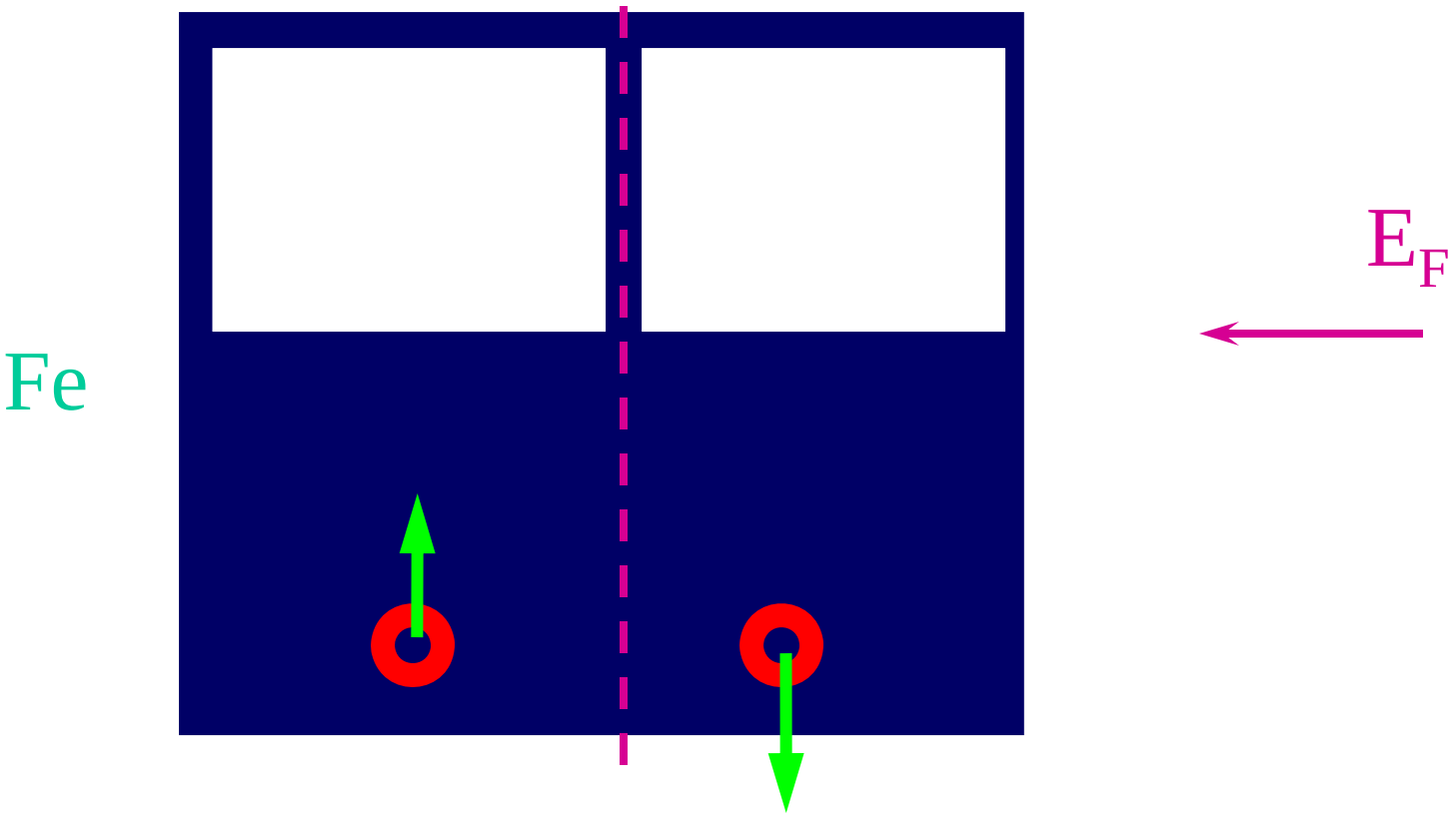
Ru



E_F

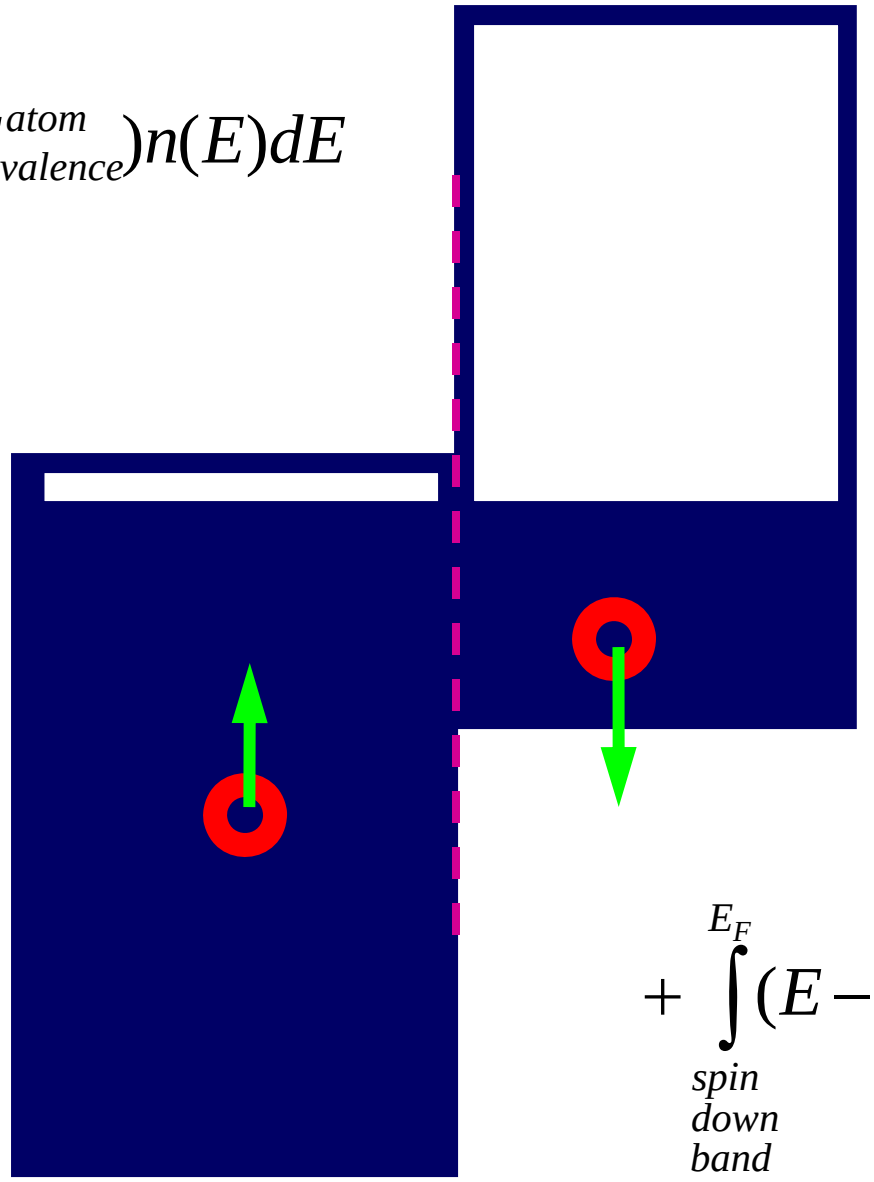
$$E_{BOND} = -\frac{1}{20} W N_d (10 - N_d)$$

Transition metal



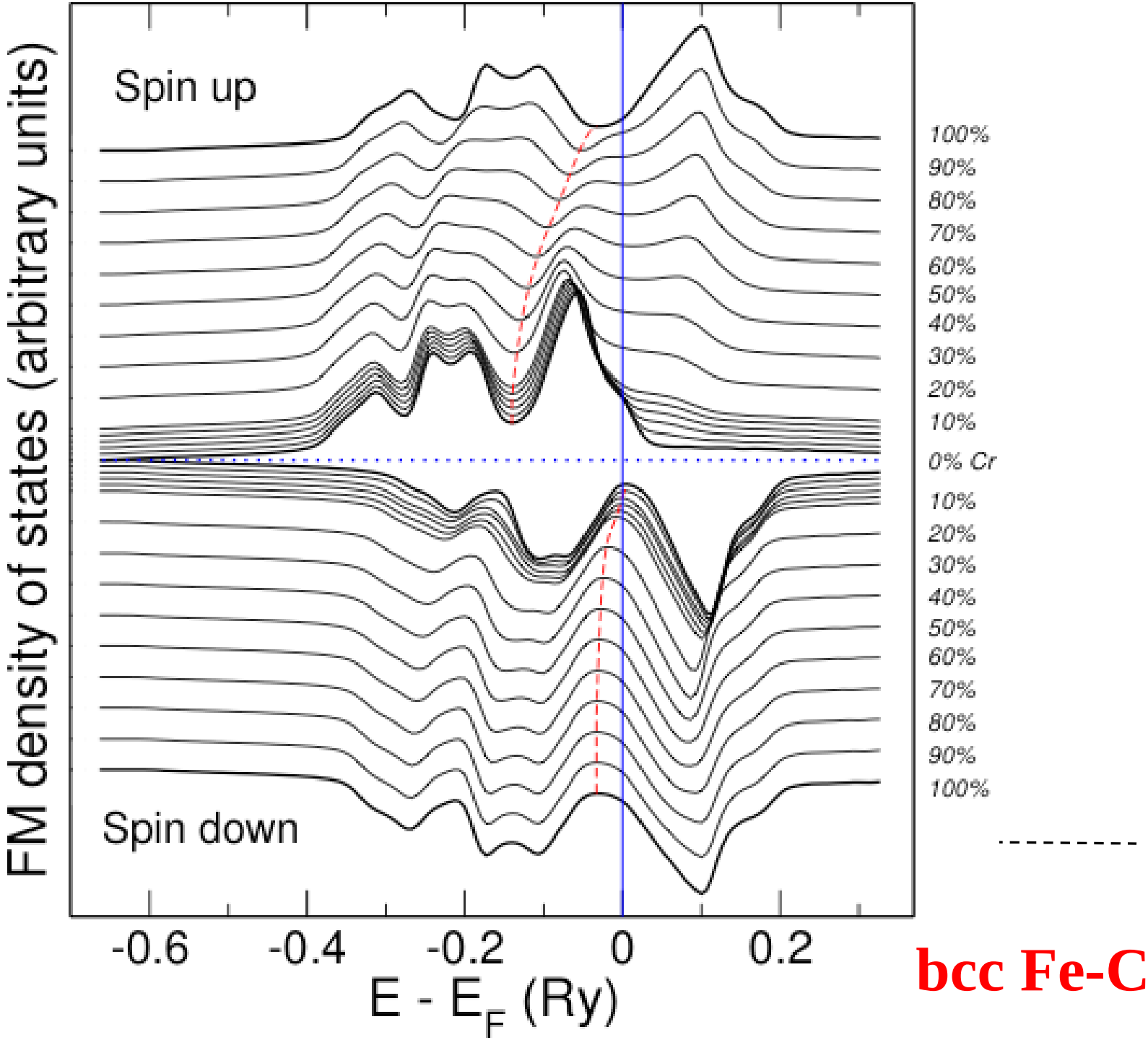
$$E_{BOND} = -\frac{1}{20} W N_d (10 - N_d)$$

$$E_{BOND} = \int_{\substack{spin\\up\\band}}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

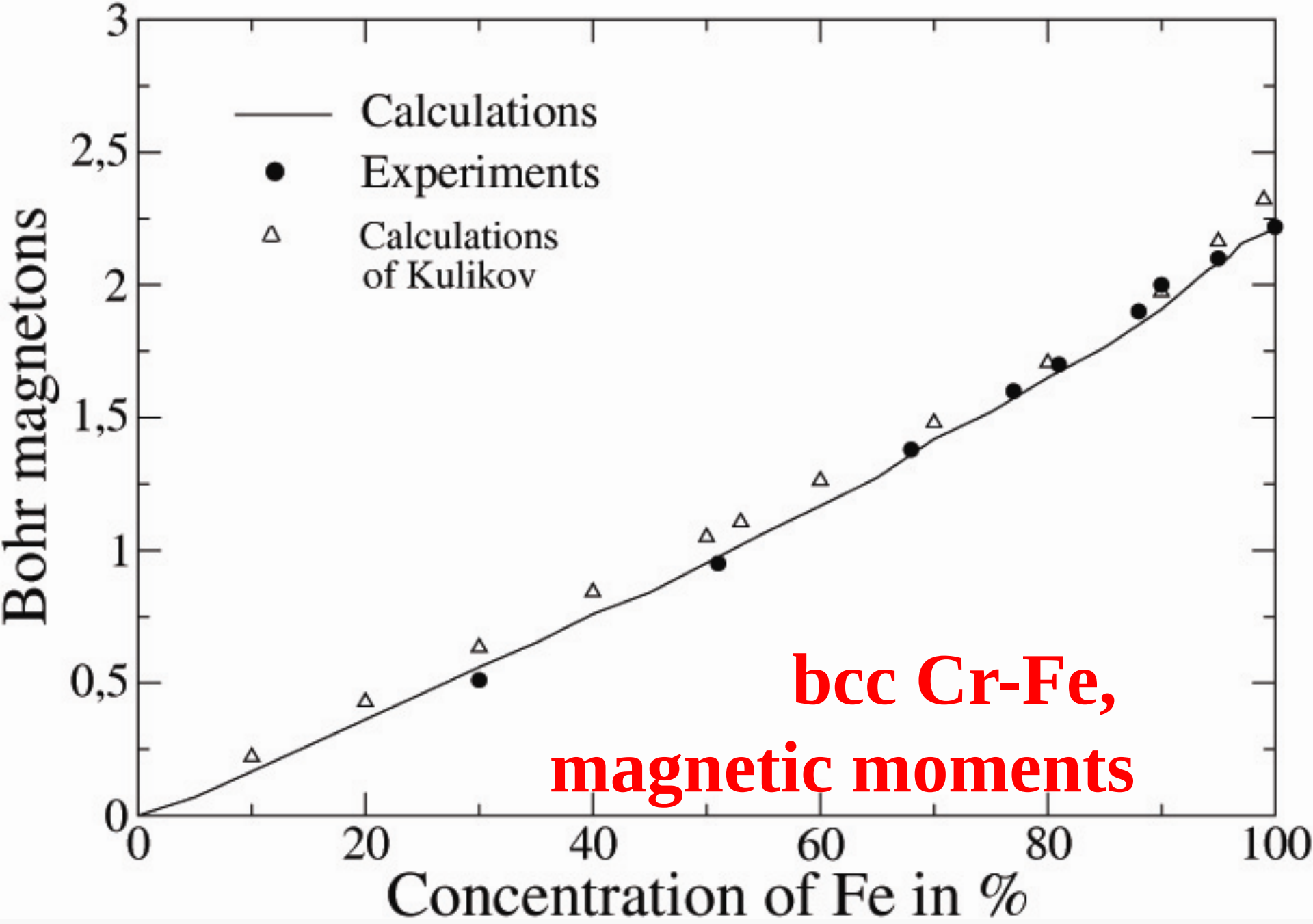


$$+ \int_{\substack{spin\\down\\band}}^{E_F} (E - E_{valence}^{atom}) n(E) dE$$

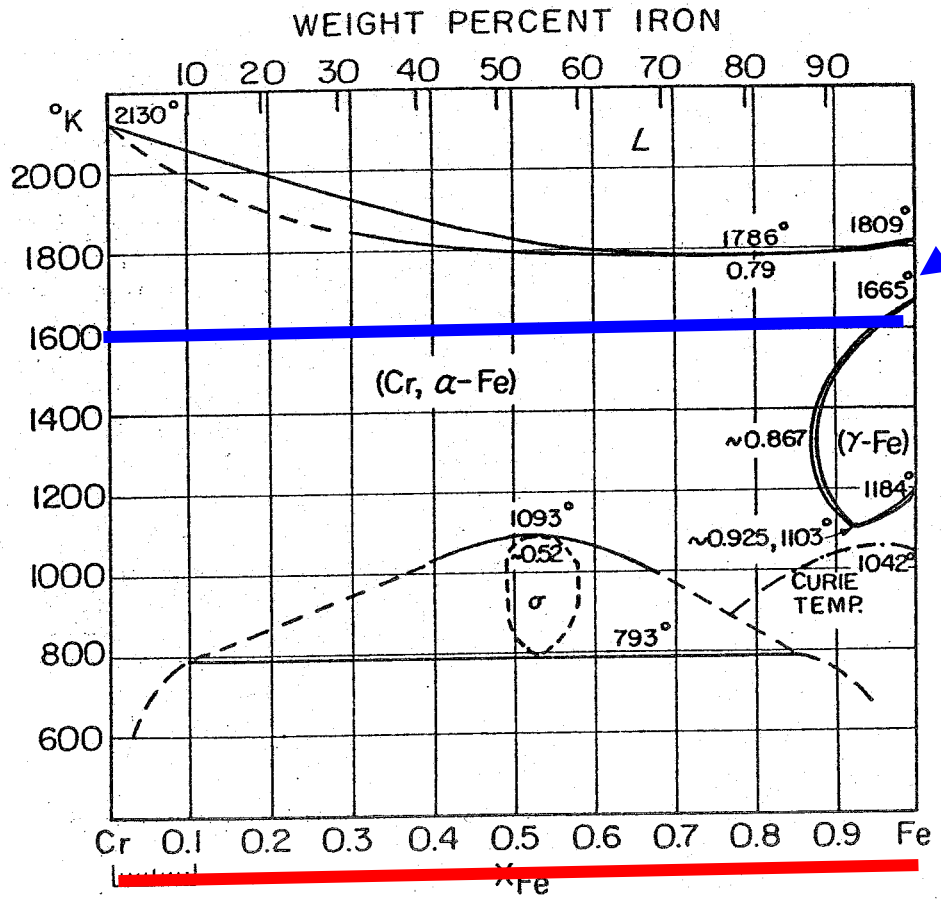
DIFFERENT PROPERTIES !!!


Spin up
Spin down
FM density of states (arbitrary units)
E - E_F (Ry)
-0.6
-0.4
-0.2
0
0.2
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0% Cr
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

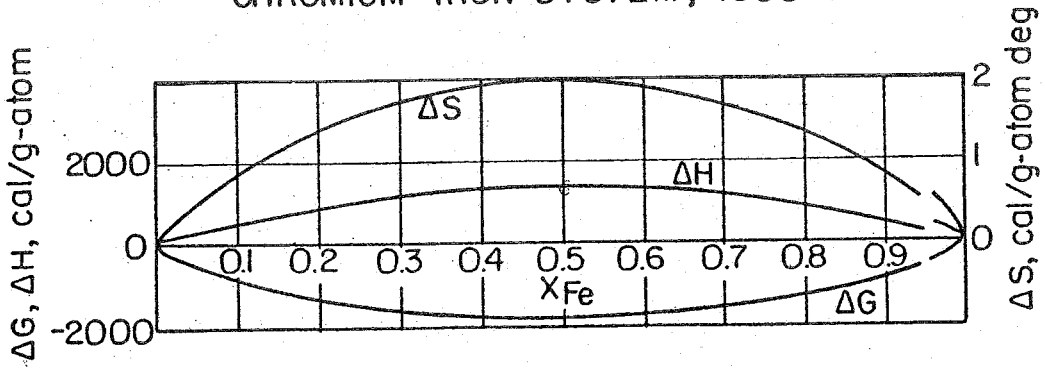
bcc Fe-Cr

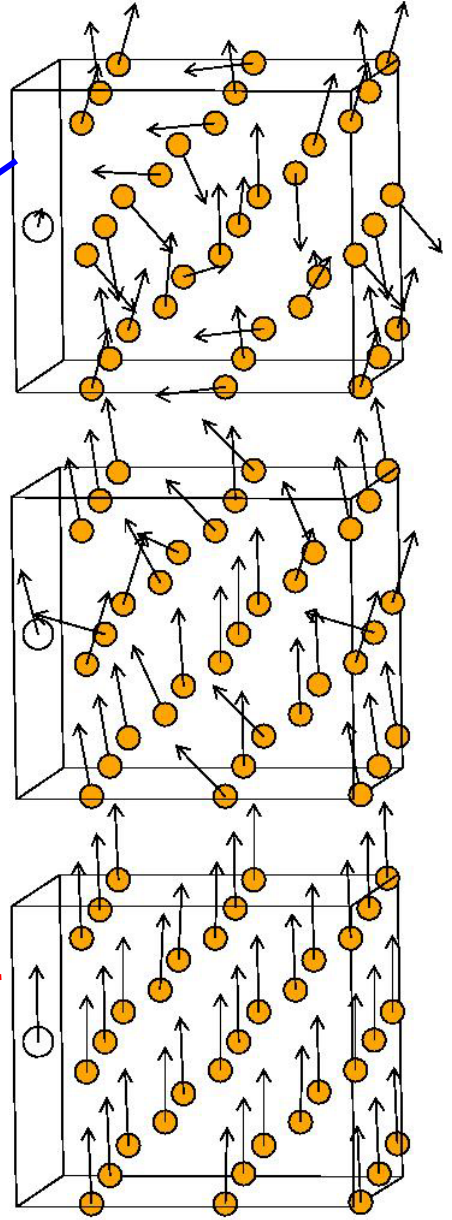


P. Olsson, I. A. Abrikosov, L. Vitos, and J. Wallenius, J. Nucl. Mater. 321, 84 (2003)



CHROMIUM -IRON SYSTEM, 1600 °K





J. Phys. F: Met. Phys. **15** (1985) 1337–1386. Printed in Great Britain

A first-principles theory of ferromagnetic phase transitions in metals†

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PHYSICAL REVIEW B **67**, 235105 (2003)

Modeling the actinides with disordered local moments

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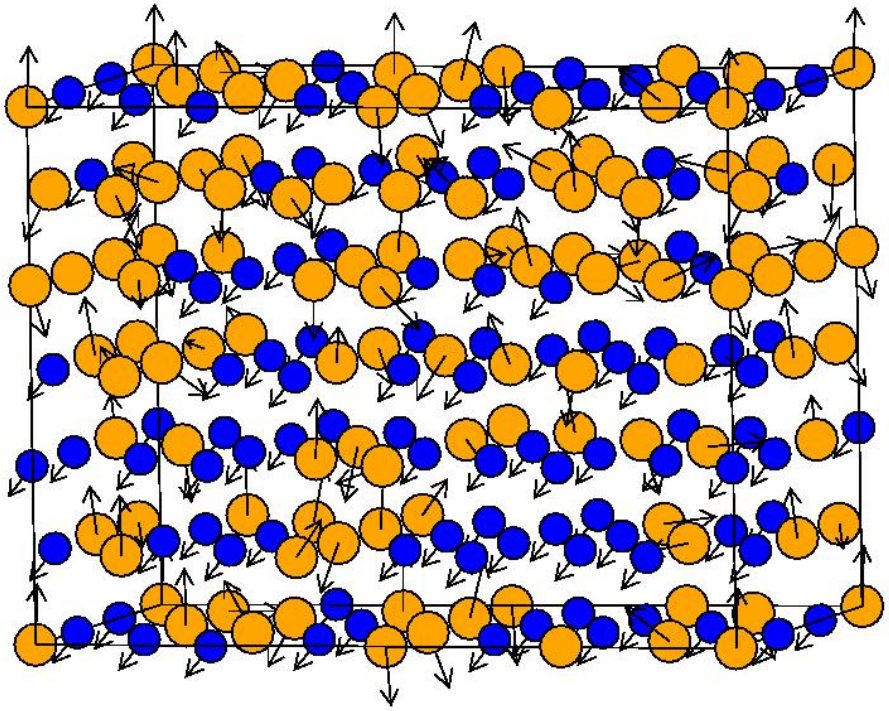
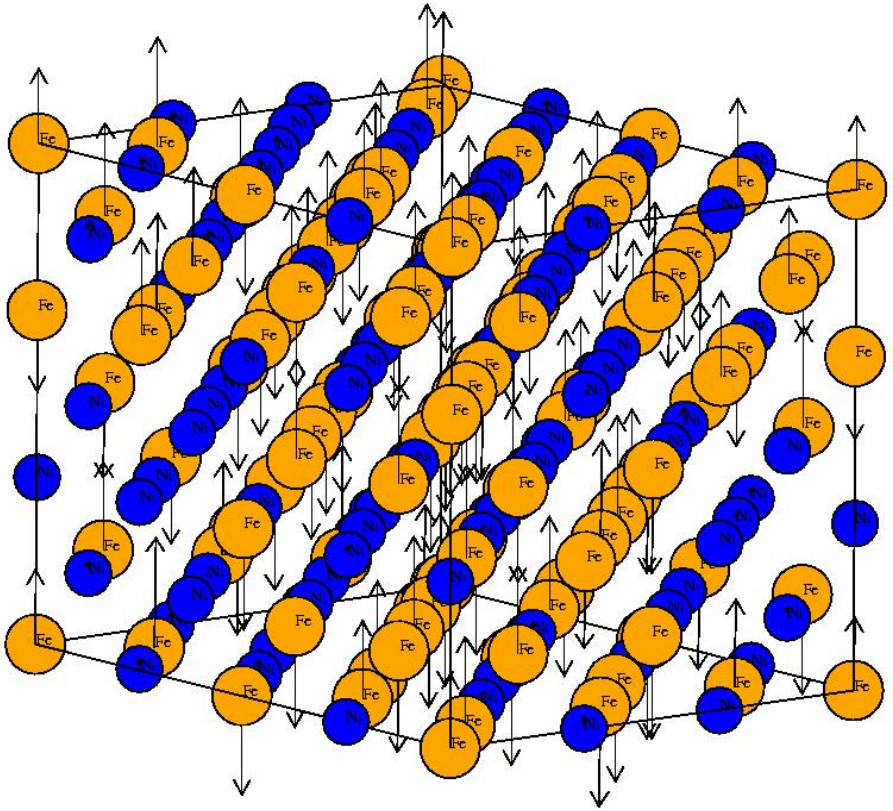
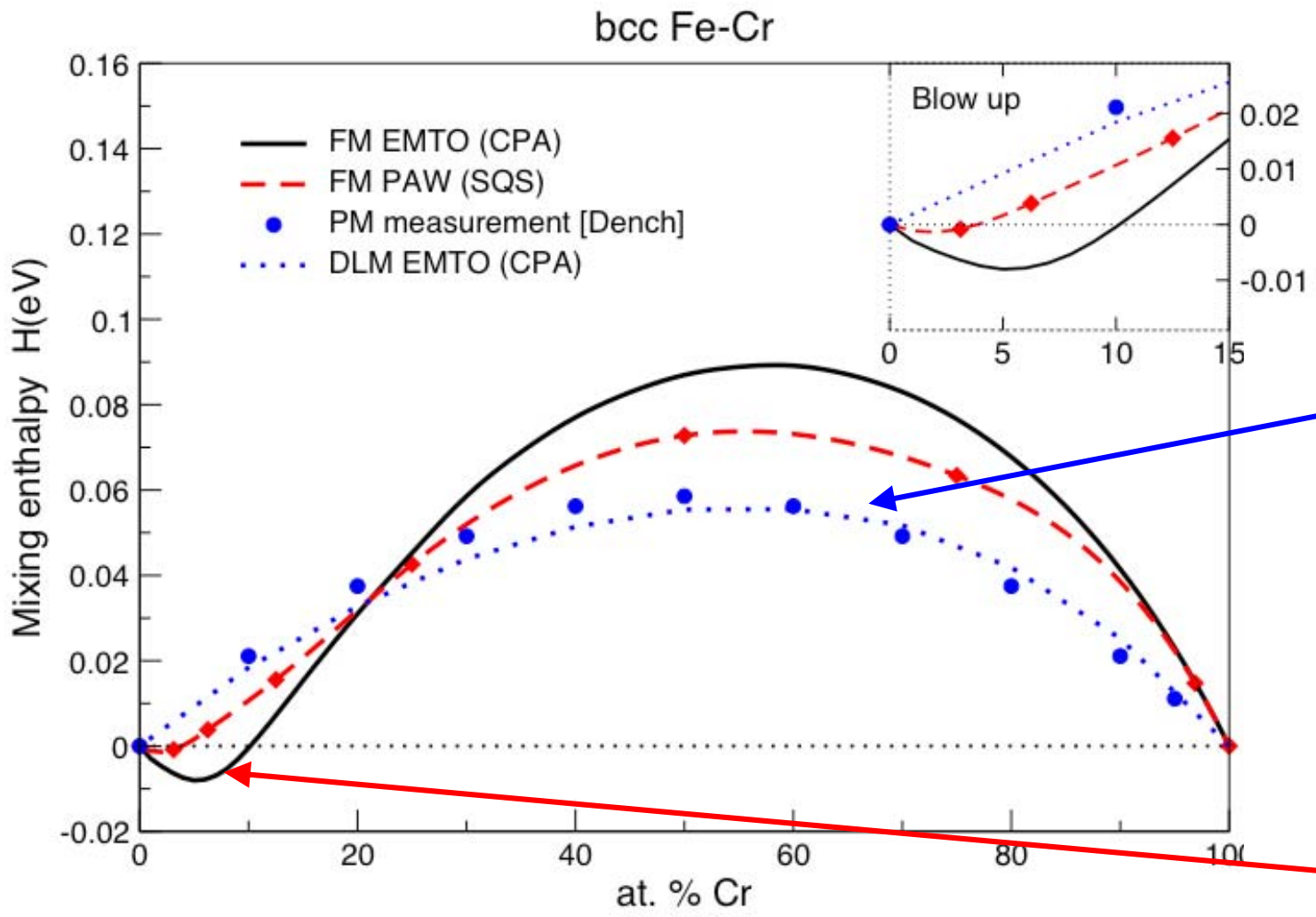
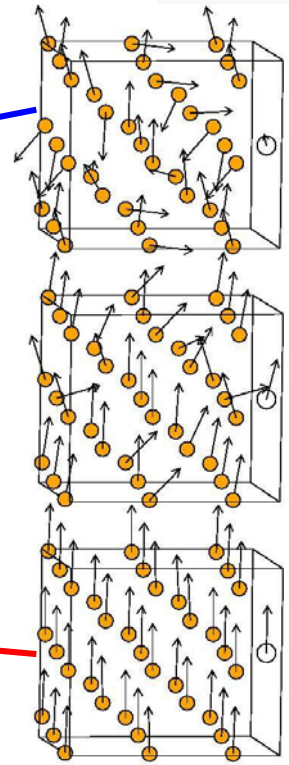
Disordered Magnetism



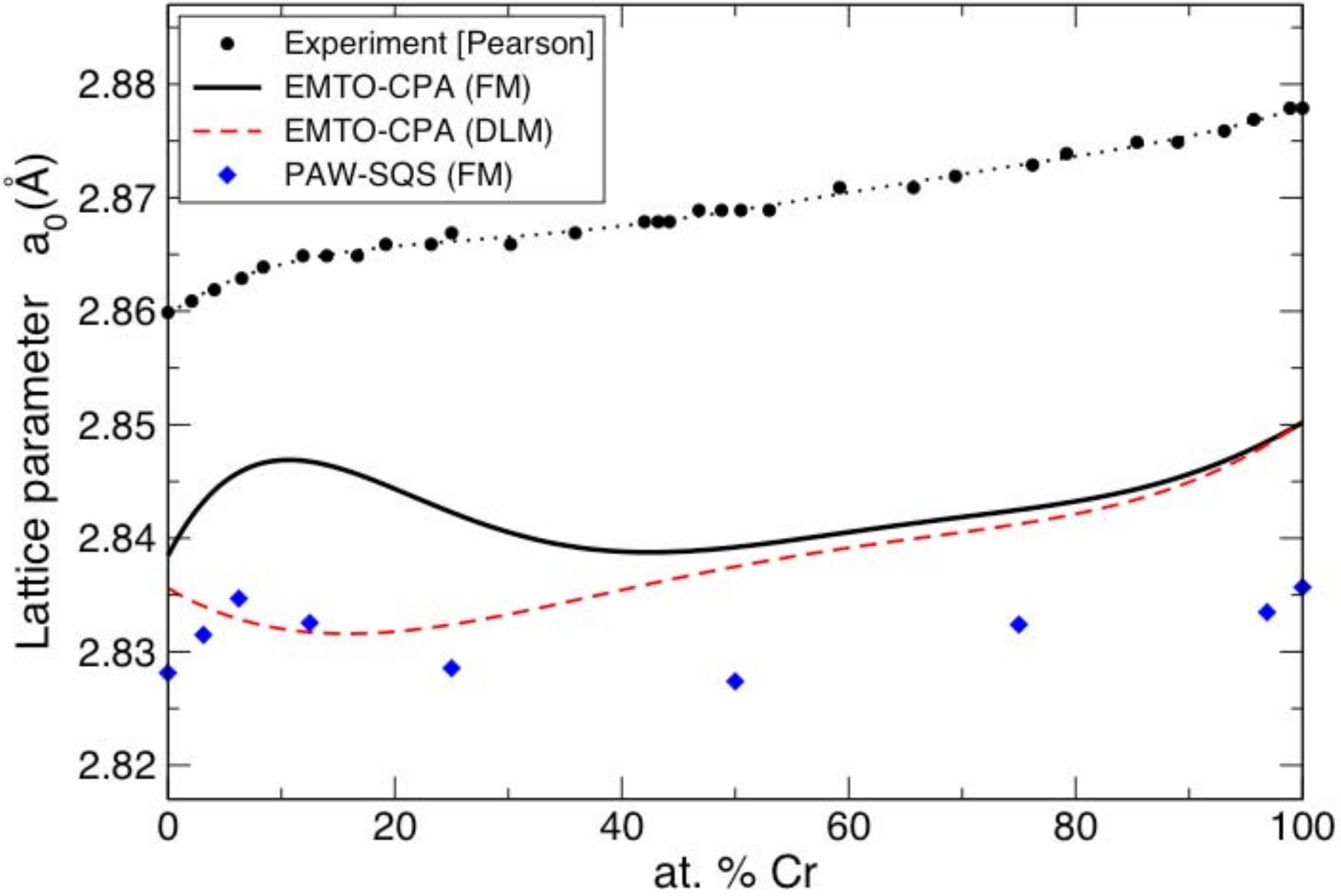


Disordered Local Moment Model

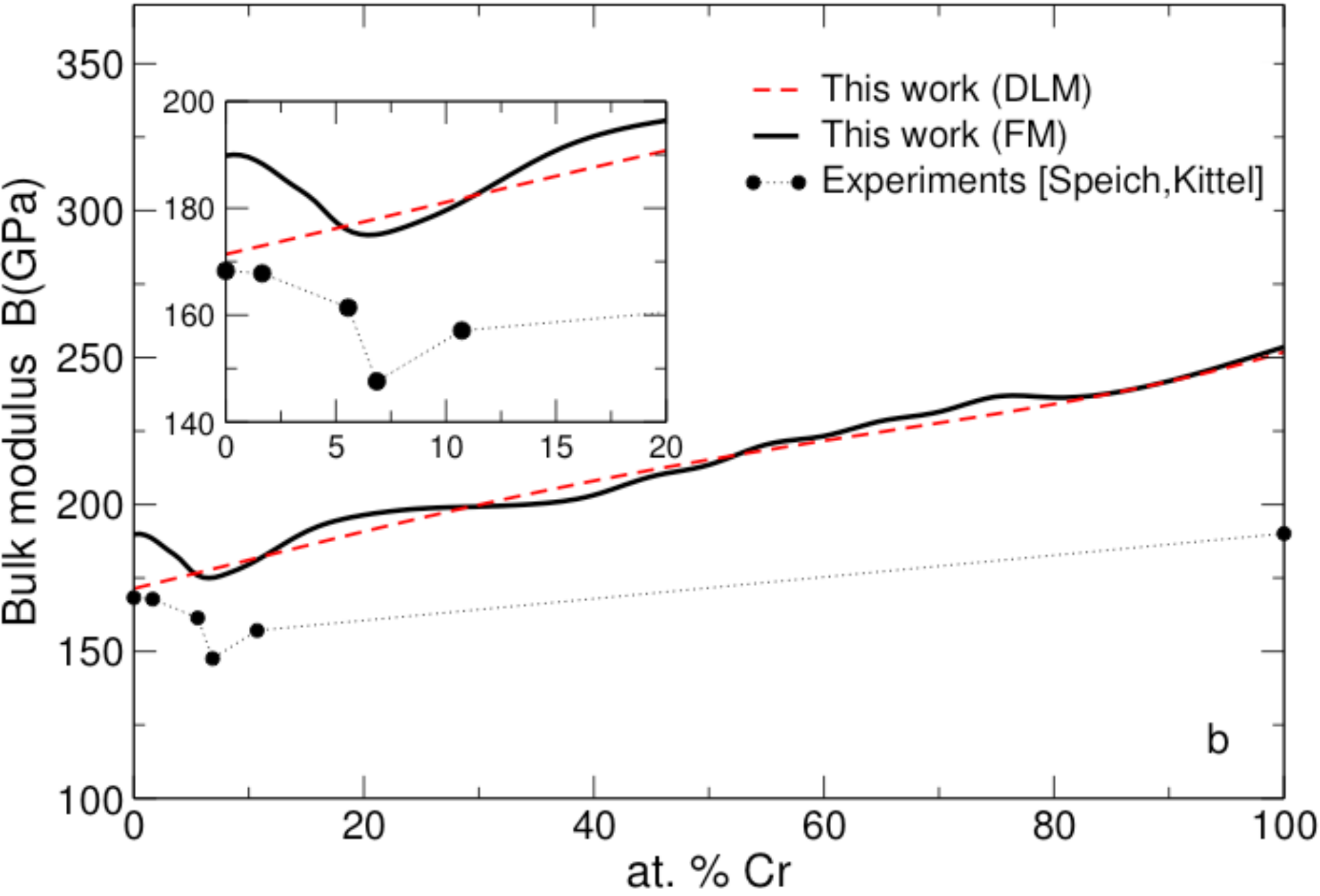




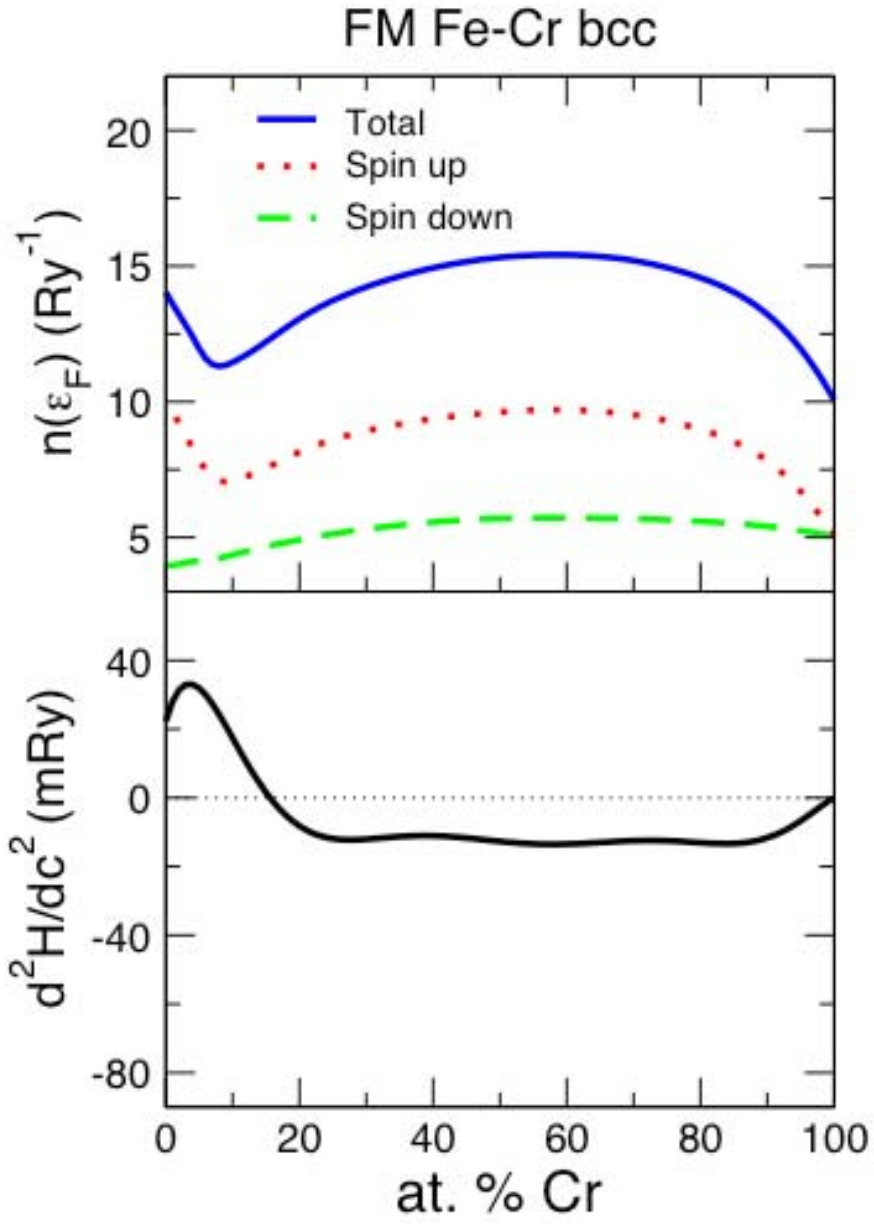
P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B 73, 104416 (2006)



P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B 73, 104416 (2006)



P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B 73, 104416 (2006)



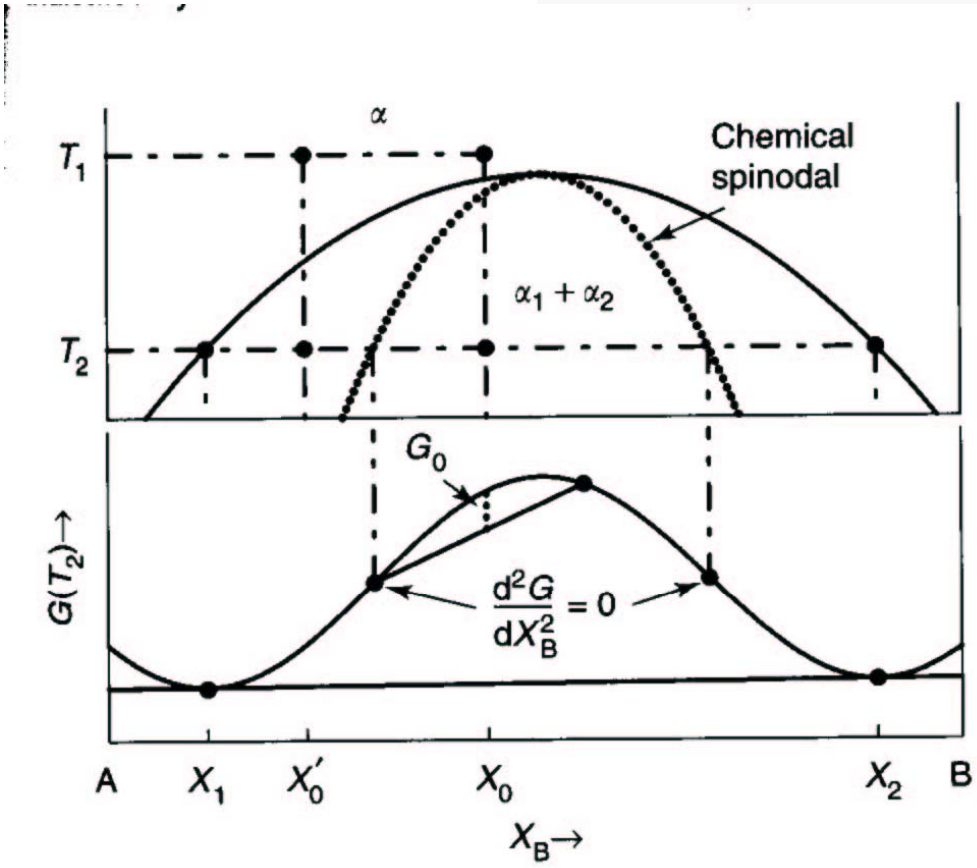


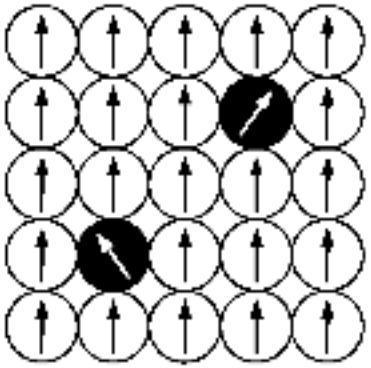
Figure 9 (a) Schematic phase diagram and (b) free energy vs. composition diagram for alloys between the spinodal points, which are unstable and can decompose into two coherent phases α_1 and α_2 without overcoming an activation energy barrier. Alloys between the miscibility gap and the spinodal are metastable and can decompose only after nucleation of the other phase.

P. Olsson, I. A. Abrikosov, and J. Wallenius, Phys. Rev. B 73, 104416 (2006)

Exchange parameters

Pair exchange parameter

$\Theta/2$



i

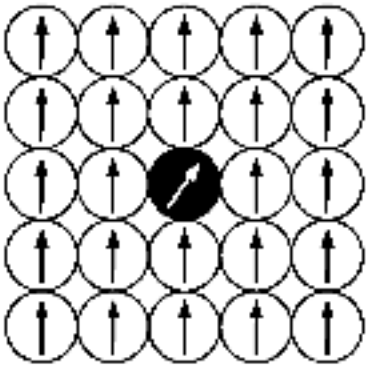
$J_{ij} > 0$ $\uparrow\uparrow$

j

< 0 $\uparrow\downarrow$

Effective exchange parameter

Θ



i = 0

$$J_0 = \sum_{j \neq 0} J_{0j}$$

$$H = -\sum_{i,\, j \neq i} J_{ij} \sigma_i \sigma_j$$

Effect of magnetism on phase stability in Fe-Cr system: a model

Chemical and magnetic interactions:

$$H = \frac{1}{2}\sum_{ij}\left\{\left(v_{ij}^{AA} - 2\sigma_i^A\sigma_j^A J_{ij}^{AA}\right)c_i^A c_j^A + 2\left(v_{ij}^{AB} - 2\sigma_i^A\sigma_j^B J_{ij}^{AB}\right)c_i^A(1-c_j^A) + \left(v_{ij}^{BB} - 2\sigma_i^B\sigma_j^B J_{ij}^{BB}\right)(1-c_i^A)(1-c_j^A)\right\}$$

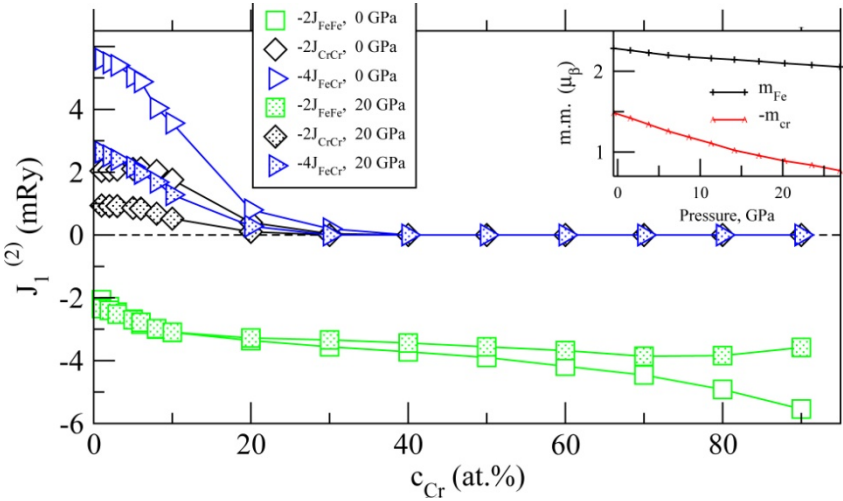
Configurational part

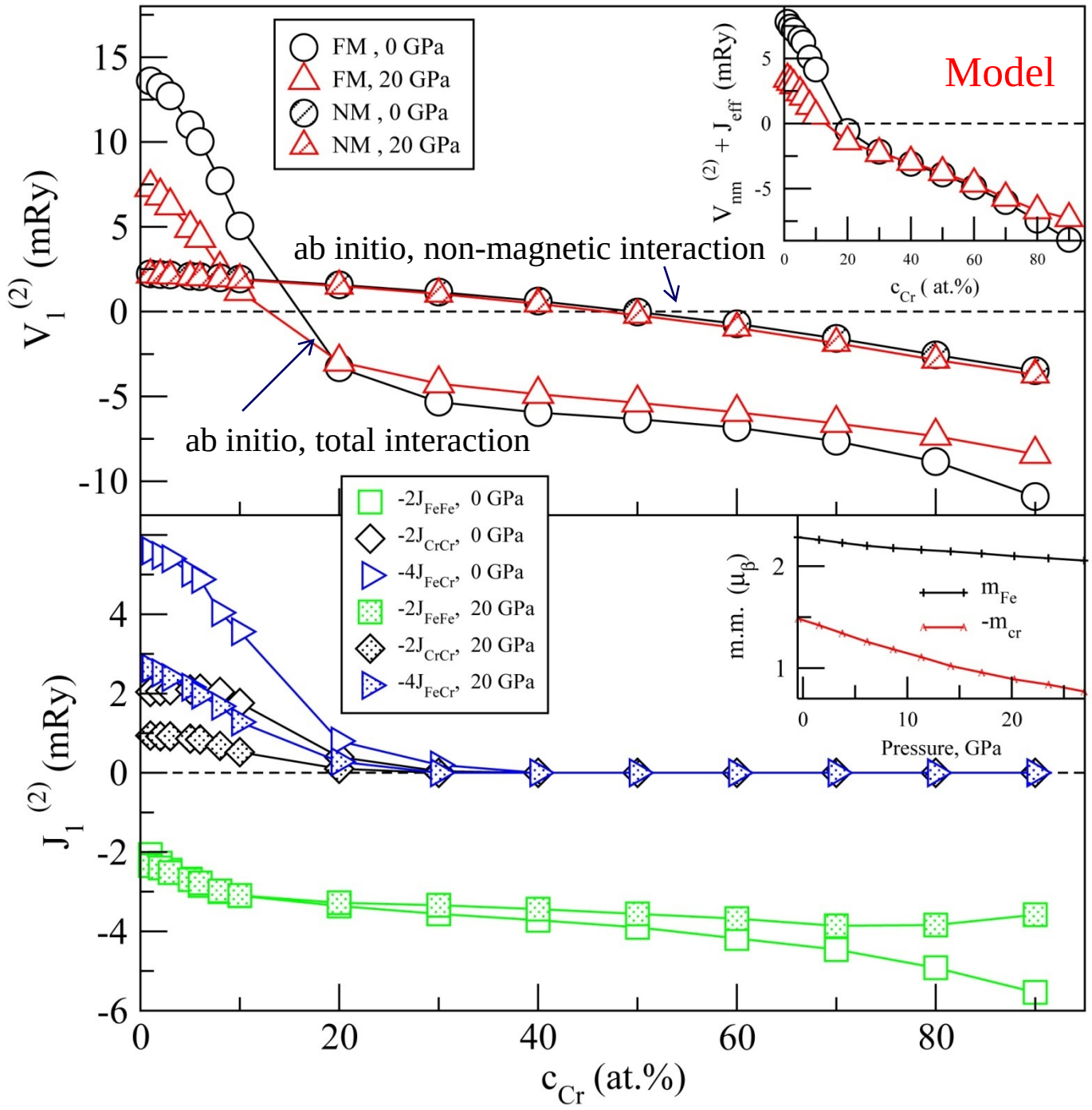
$$H_{conf} = \frac{1}{2}\sum_{ij} V_{ij} c_i^A c_j^A \qquad V_{ij} = V_{ij}^{chem} + V_{ij}^{magn}$$

For a fixed magnetic configuration $\left(\sigma_i^A = \sigma_A; \sigma_i^B = \sigma_B\right)$:

$$V_{ij}^{chem} = v_{ij}^{AA} + v_{ij}^{BB} - 2v_{ij}^{AB}$$

$$V_{ij}^{magn} = -2\left[\sigma_A^2 J_{ij}^{AA} - 2\sigma_A\sigma_B J_{ij}^{AB} + \sigma_B^2 J_{ij}^{BB}\right]$$




FM , 0 GPa
FM, 20 GPa
NM , 0 GPa
NM , 20 GPa
Model
ab initio, non-magnetic interaction
ab initio, total interaction
$V_1^{(2)}$ (mRy)
$V_{nm}^{(2)} + J_{eff}$ (mRy)
c_{Cr} (at.%)
-2J$_{FeFe}$, 0 GPa
-2J$_{CrCr}$, 0 GPa
-4J$_{FeCr}$, 0 GPa
-2J$_{FeFe}$, 20 GPa
-2J$_{CrCr}$, 20 GPa
-4J$_{FeCr}$, 20 GPa
$J_1^{(2)}$ (mRy)
m.m. (μ_β)
m$_{Fe}$
-m$_{cr}$
Pressure, GPa
c_{Cr} (at.%)

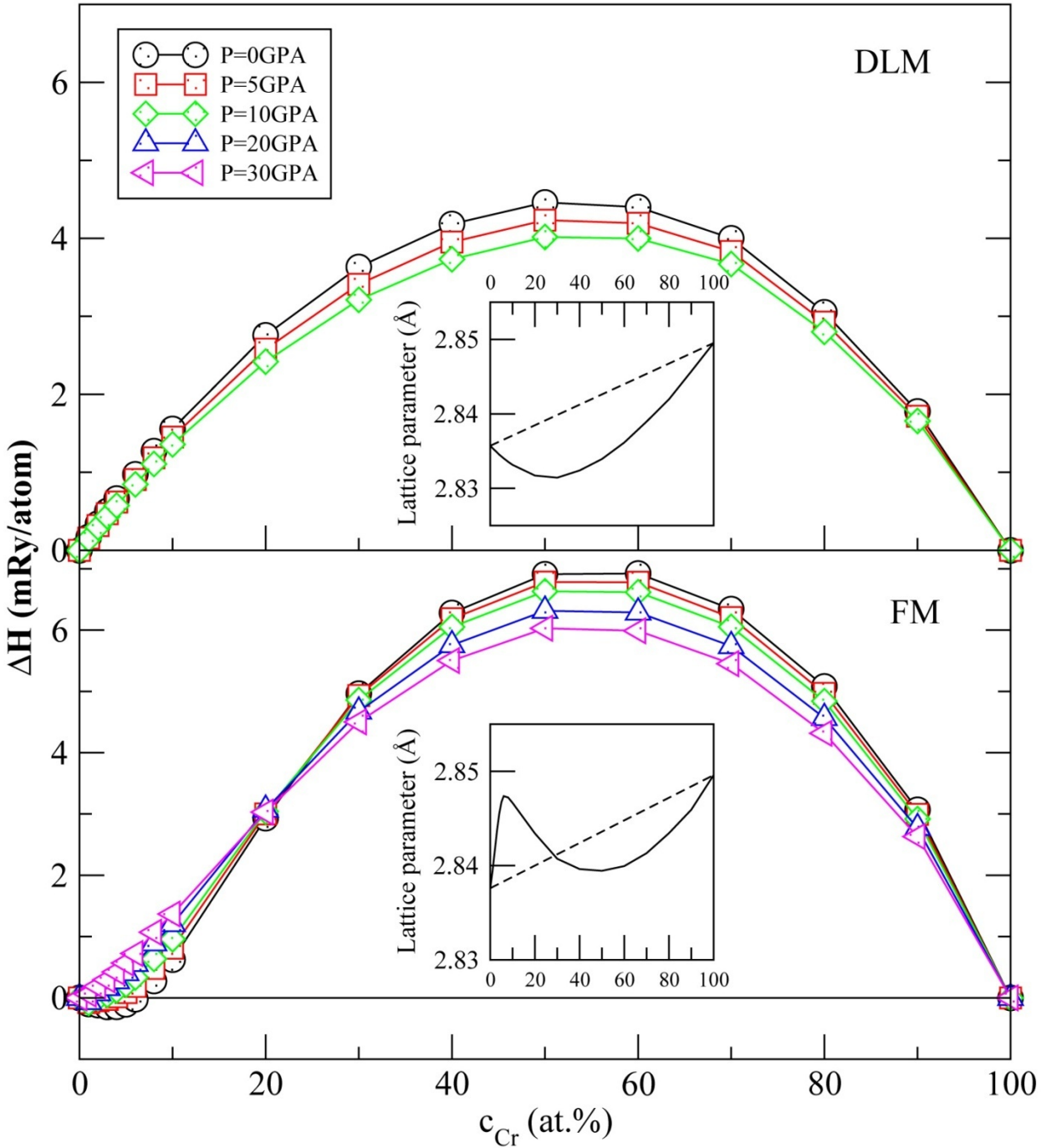
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$\Delta G = G_{\mathrm{Ti}_{1-x}\mathrm{Al}_x\mathrm{N}} - (1-x)G_{\mathrm{TiN}} - xG_{\mathrm{AlN}}$$

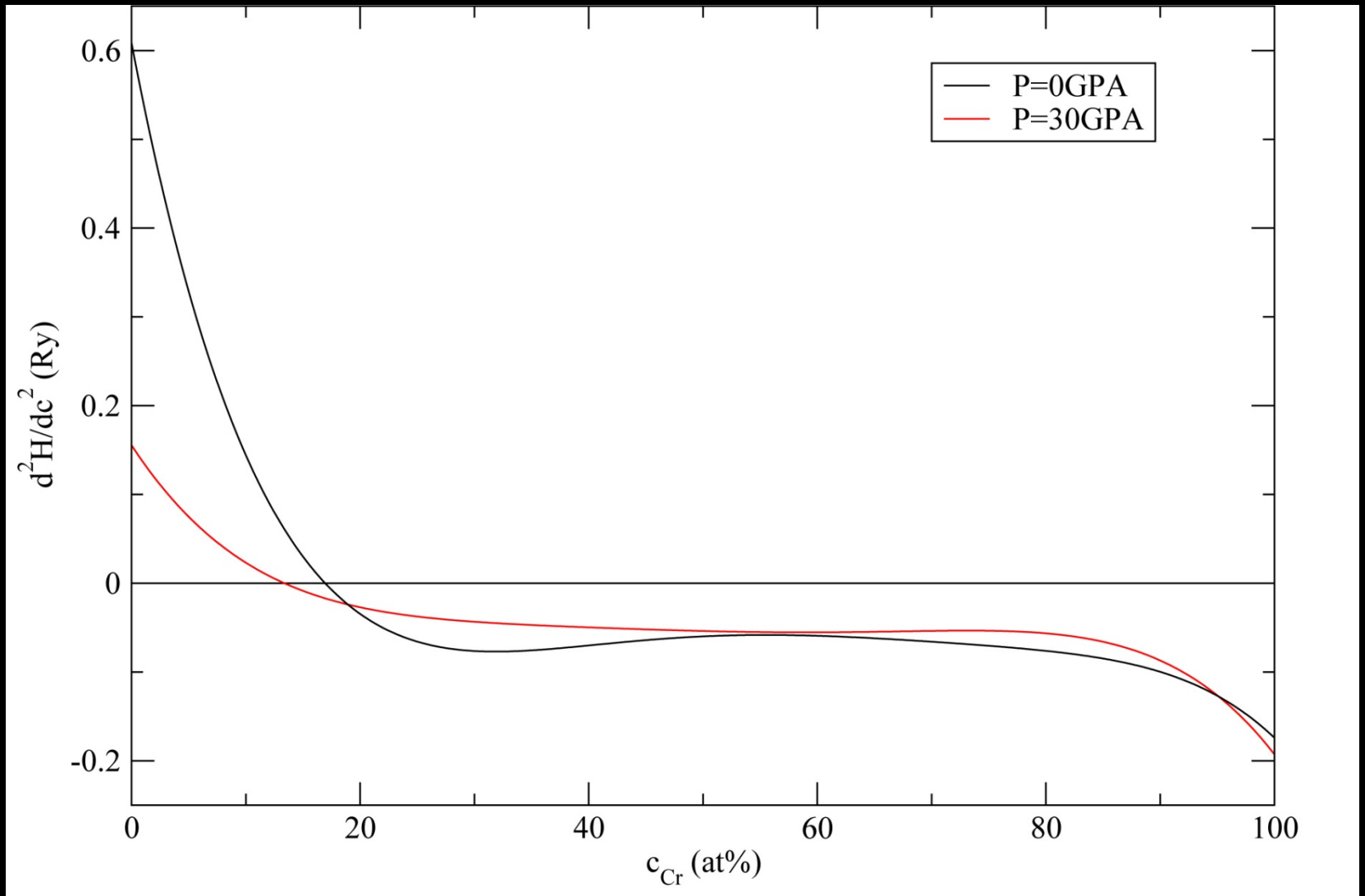
$$\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V$$

$$\Delta V = V_{\mathrm{Ti}_{1-x}\mathrm{Al}_x\mathrm{N}} - (1-x)V_{\mathrm{TiN}} - xV_{\mathrm{AlN}}.$$

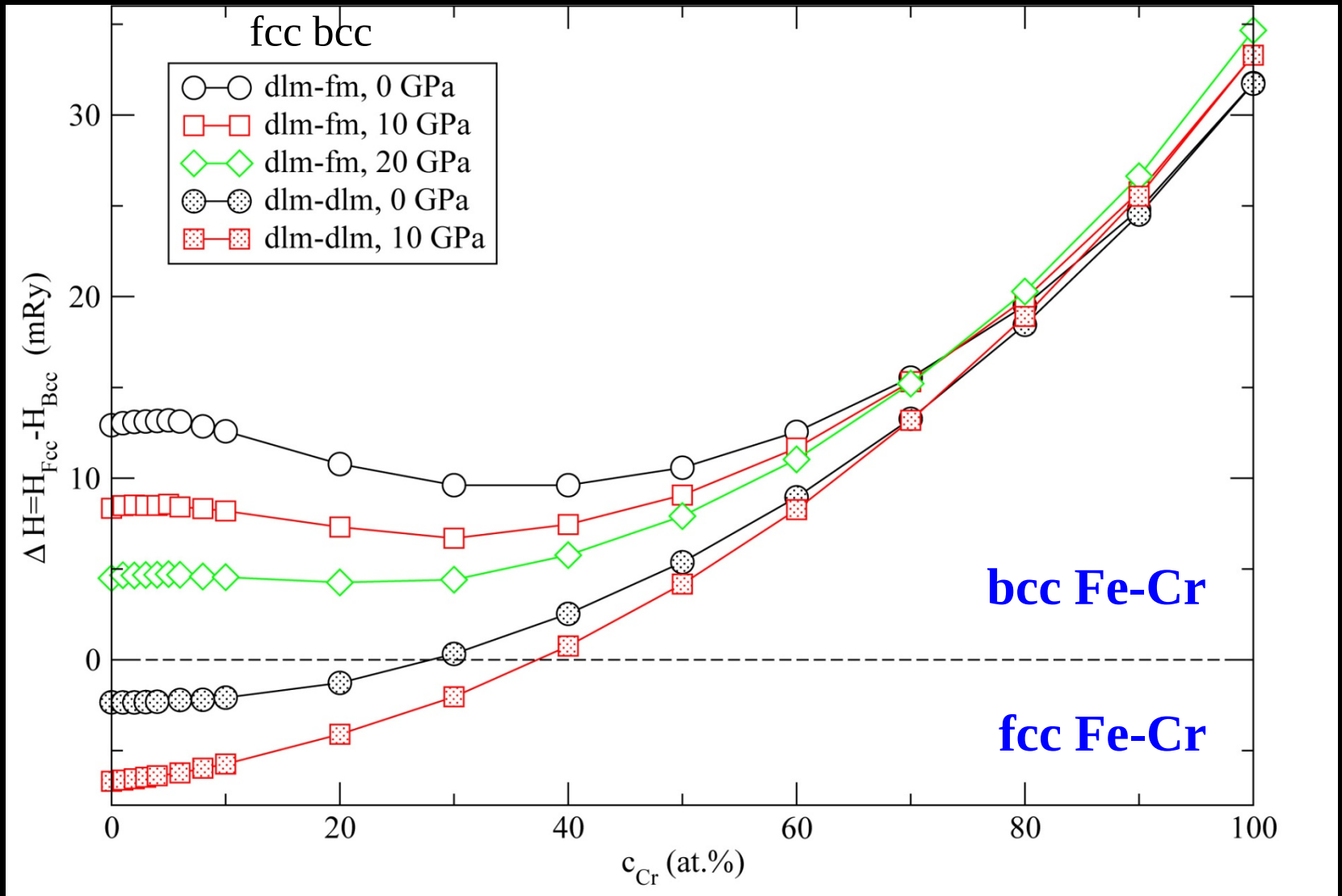
B. Alling, M. Oden, L. Hultman, and I. A. Abrikosov, Appl. Phys. Lett. **95**, 181906 (2009).

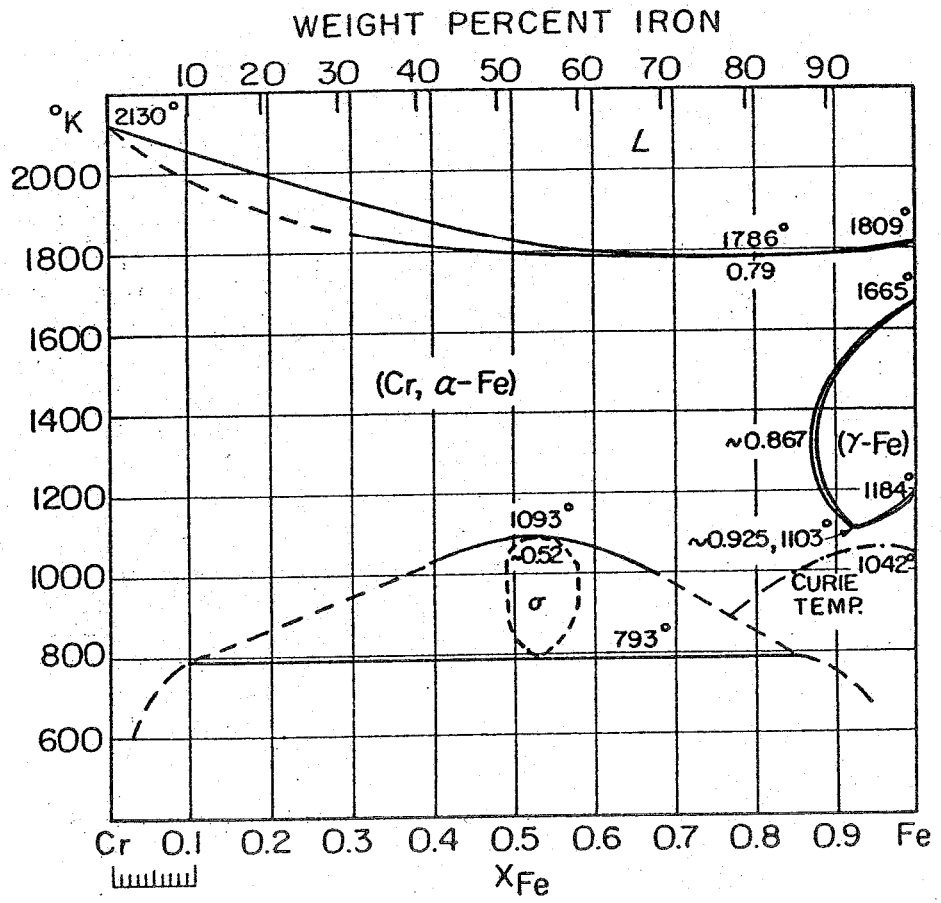

P=0GPA
P=5GPA
P=10GPA
P=20GPA
P=30GPA
DLM
FM
ΔH (mRy/atom)
c_Cr (at.%)
Lattice parameter (Å)
2.85
2.84
2.83
0
20
40
60
80
100
0
2
4
6

Effect of pressure on the tendency towards the spinodal decomposition in bcc Fe-Cr alloys

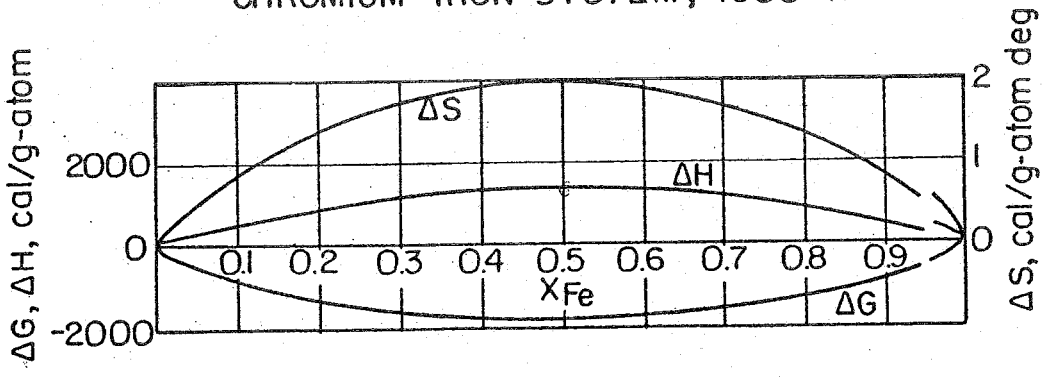


Effect of pressure on the structural energy differences in Fe-Cr alloys





CHROMIUM - IRON SYSTEM, 1600 °K



CONCLUSIONS :

- Reliable tools have been developed for first-principles theoretical treatment of (magnetic) solution phases.
- First-principles simulations can be carried out for real materials of technological importance. The results allow for the cautious optimism.
- Choice of the methodology depends on the problem at hand.
- The mixing enthalpy for paramagnetic Fe-Cr alloys is positive at all concentrations, in excellent agreement with experiment. On the contrary, ferromagnetic bcc Fe-Cr alloys are anomalously stable at low Cr concentrations.
- The stabilization of Fe-rich Fe-Cr alloys comes essentially from magnetic effects, and it is suppressed with pressure.
- Therefore, magnetic effects must be taken into account in simulations.