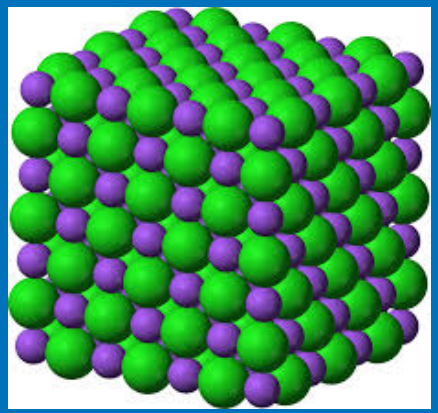
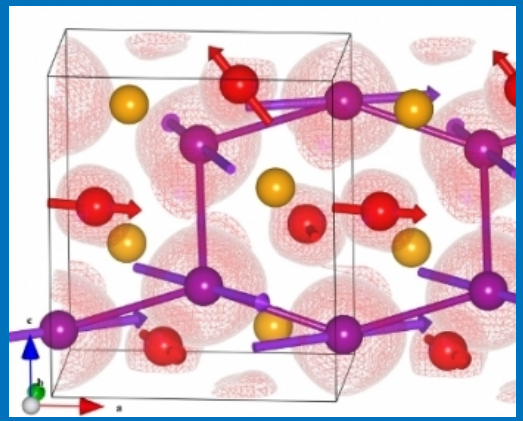
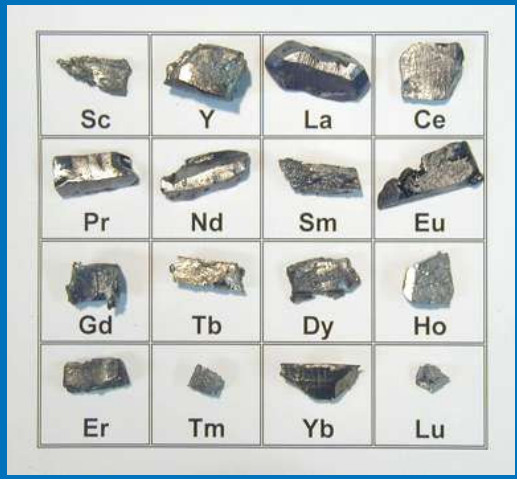
Density functional theory and slowly varying fluctuations at finite temperature to describe alloy and magnetic phase diagrams







Julie Staunton
University of Warwick

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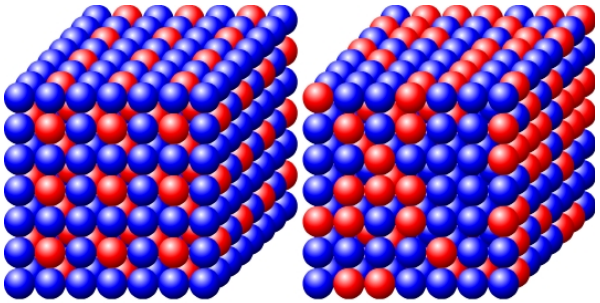
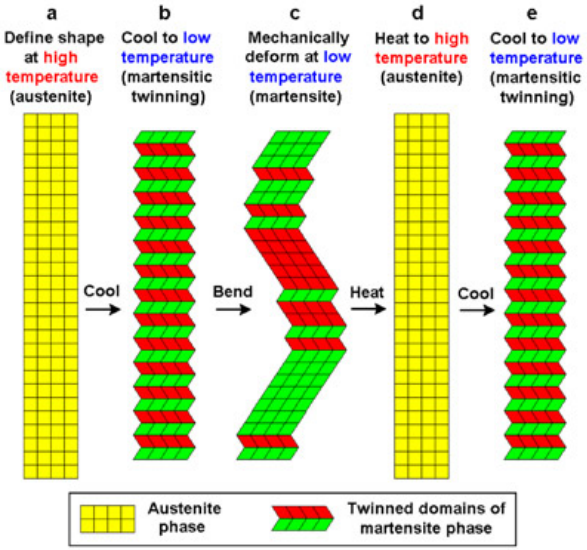
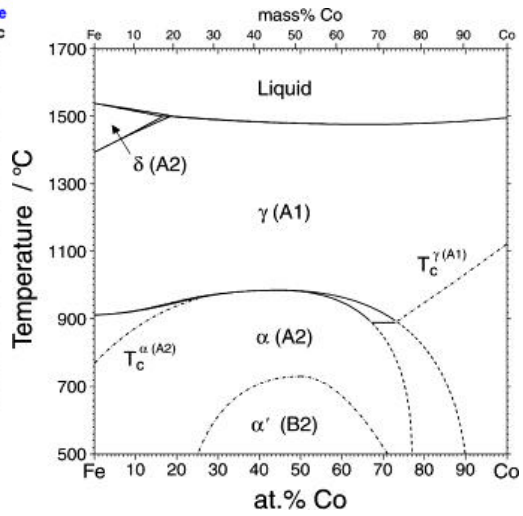
Alloy Solid Solutions and Intermetallics







- Mixing of 2 metals (Hume Rothery Rules)
  - band filling (av. no. of electrons/atom).
  - atomic size difference.
  - electronegativity -arrangement of charge around a nucleus.

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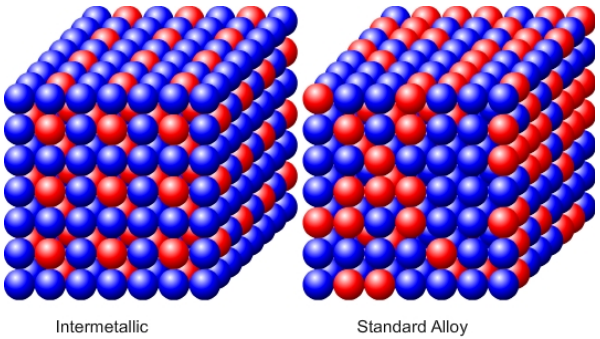

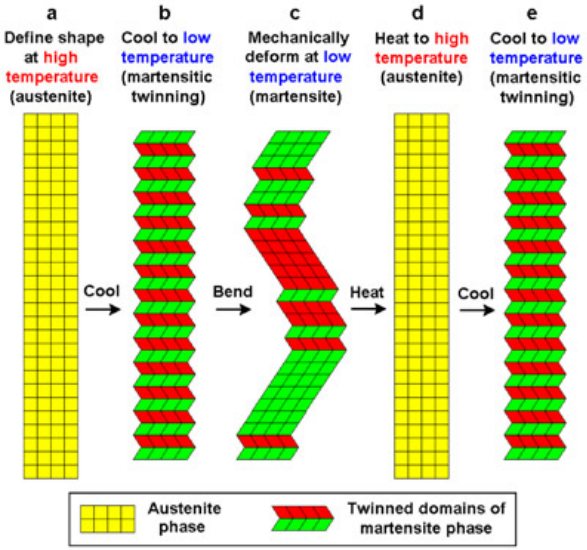

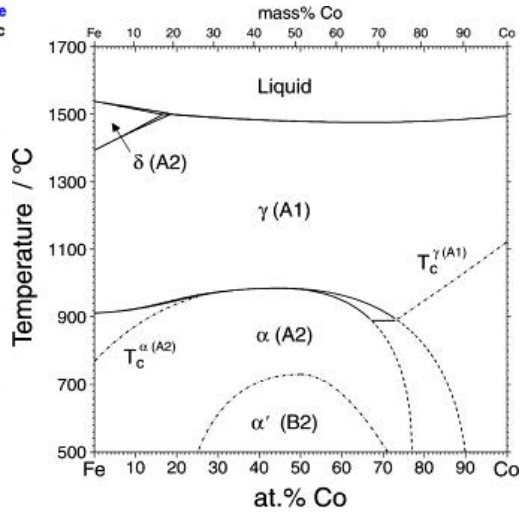

- Mixing of 2 metals (Hume Rothery Rules)
  - band filling (av. no. of electrons/atom).
  - atomic size difference.
  - electronegativity -arrangement of charge around a nucleus.
- Solid solution - lattice with each site with $x\,(1-x)$ chance of A (B) atom on it.
- Ordered arrangement - intermetallic. Affects mechanical,electrical,thermal properties etc.

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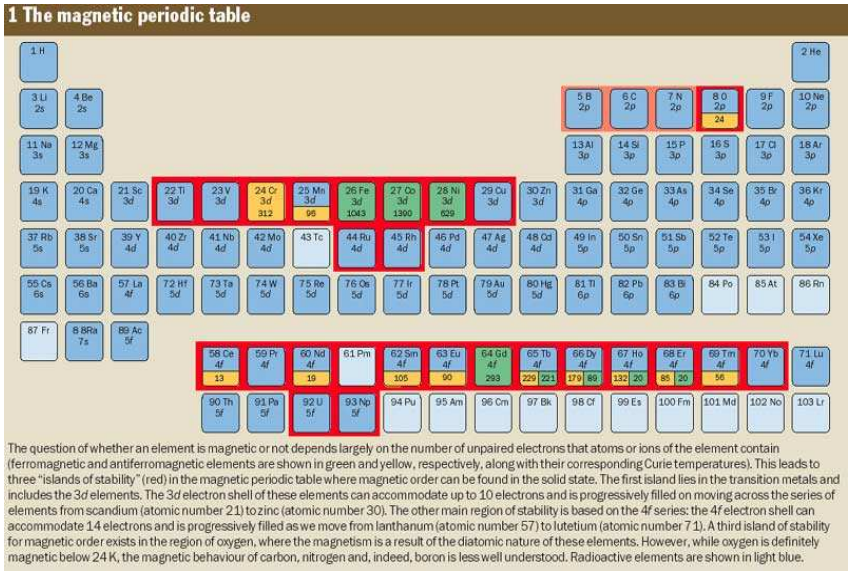
Magnetic periodic Table



M.Coey and S.Sanvito, Physics World **17**,(11), 34, (Nov. 2004)

- Transition metal d-electrons, high magnetic transition temperatures T_c.
- Rare earth f-electrons, high magnetic anisotropy, magnetisation, magnetic coercivity.

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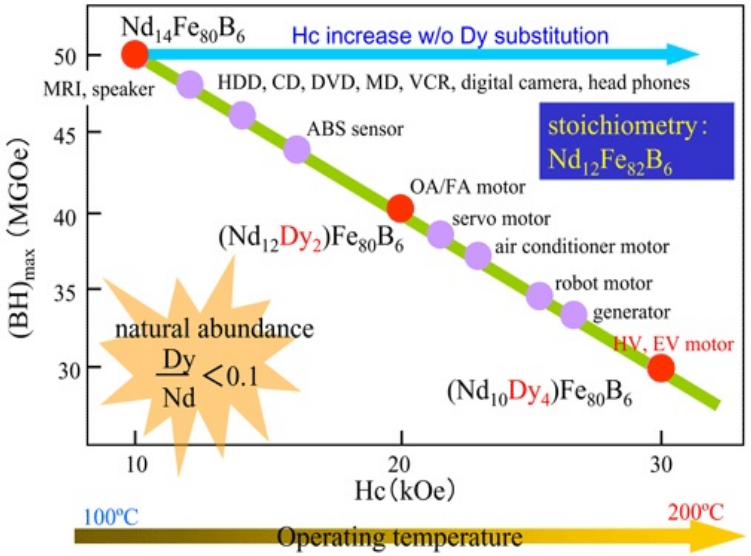
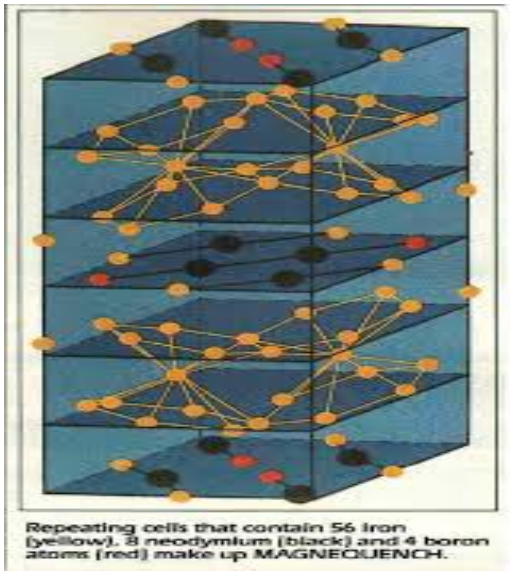
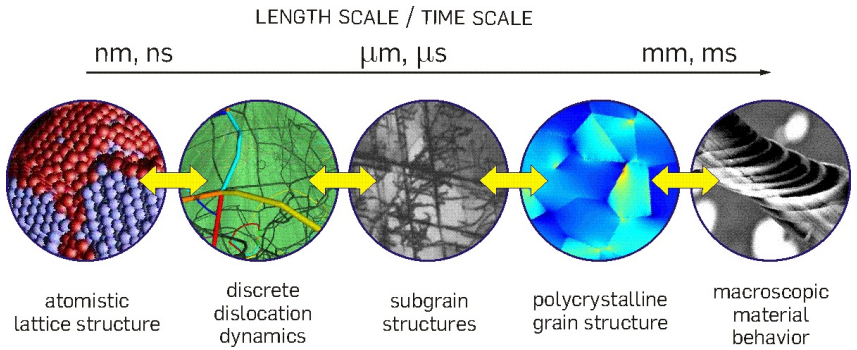
Rare earth - transition metal magnets

- Ubiquitous NdFeB







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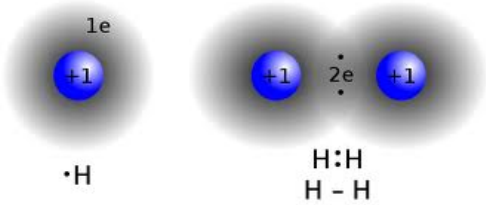
Smallest length scale processes and the **Electronic Glue**

- Ab-initio quantum description of electrons and nuclei.
- Simplest many-electron system: H_2 molecule.
- Electrostatic interactions, H^+-H^+, H^+-e, e-e.



- Assume protons move much more slowly than electrons. Electrons glue protons together.
- Deal with electrons' spins. Pauli Exclusion Principle.
- Good but approximate description. More complex materials??
- Add computational power and tractable method.

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Materials Modelling and Density Functional Theory

- $\Omega[\rho, \vec{m}]$, Energy minimised by ground state charge, ρ and magnetisation, $\vec{m}$, densities.
- Many interacting electrons described in terms of non-interacting electrons in effective fields (Kohn Sham).

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  - Separate out these modes. Statistical mechanics combined with constrained DFT-type calculations.

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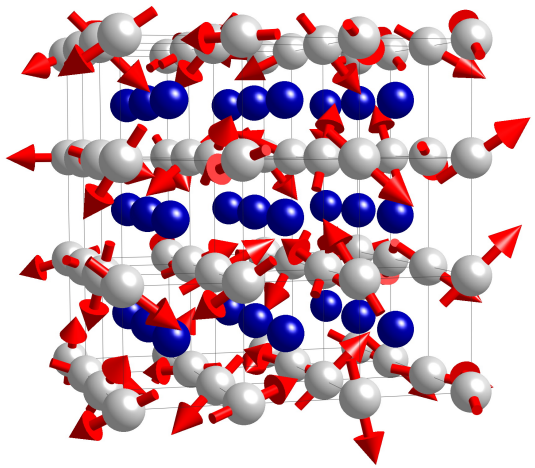
- For magnets these are local moments: $\{\hat{e}_i\}$



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Finding the interactions amongst the Disordered Local Moments - DLM-DFT

- $P(\{\hat{e}_i\}) = \frac{\exp[-\beta\Omega(\{\hat{e}_i\})]}{\prod_j \int d\hat{e}_j \exp[-\beta\Omega(\{\hat{e}_i\})]}$ where $\Omega(\{\hat{e}_i\})$ is the electronic grand potential from SDFT.

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- Choose 'reference' Hamiltonian $\Omega_0\{\hat{e}_i\}$ and use Feynman Inequality $F \leq F_0 + \langle \Omega - \Omega_0 \rangle^0$ with $\Omega_0 = \sum_i \vec{h}_i \cdot \hat{e}_i$,

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- 'First-Principles' Mean Field Theory (DLM picture), averaging using techniques adapted from theory for electrons in disordered systems (CPA).
  $P_k(\hat{e}_k) = \frac{\exp[\beta\vec{h}_k \cdot \hat{e}_k]}{\int d\hat{e}_k \exp[-\beta\vec{h}_k \cdot \hat{e}_k]}$, $\vec{m}_k = \int \hat{e}_k P_k(\hat{e}_k)\, d\hat{e}_k$.
- Free energy: $F(\{\vec{m}_i\}, \vec{H}^{app.}, T) =$
  $\bar{\Omega}(\{\vec{m}_i\}, \vec{H}^{app.}) - T\bar{S}_{mag}(\{\vec{m}_i\}, \vec{H}^{app.}) - \vec{H}^{app.} \cdot \sum_i \mu_i \vec{m}_i$

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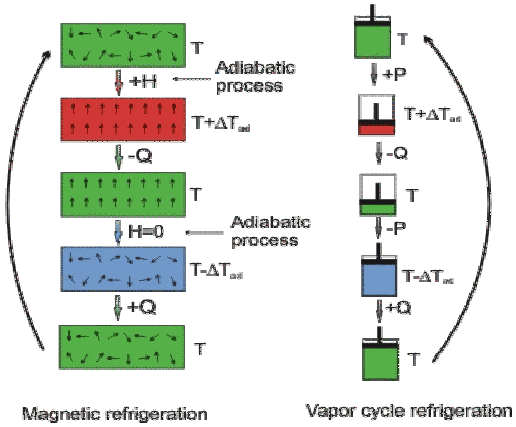
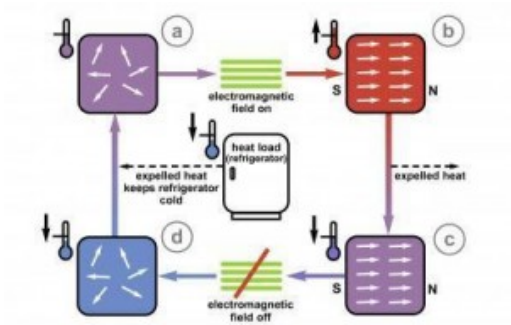
Magnetic Refrigeration - a promising cooling technology





- Magnetic, electronic and lattice entropy interchanging when magnetic field is turned on and off.
- Need materials that respond strongly to modest magnetic fields.
- Large effect when magnetic state changes. Magnetism coupled to another property.
- Rare earth, transition metal magnetic refrigerants.

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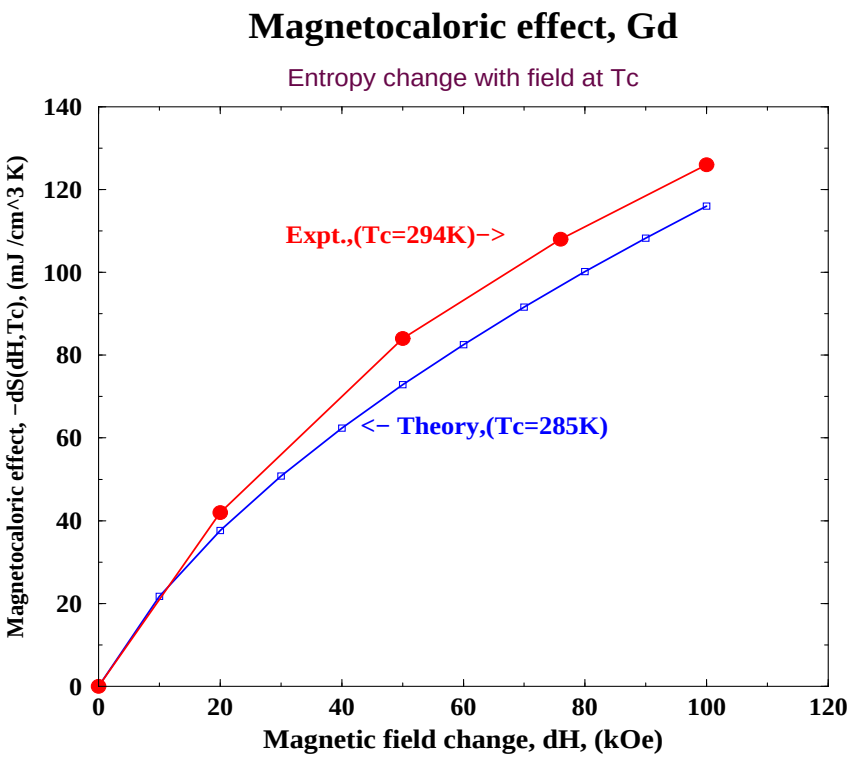
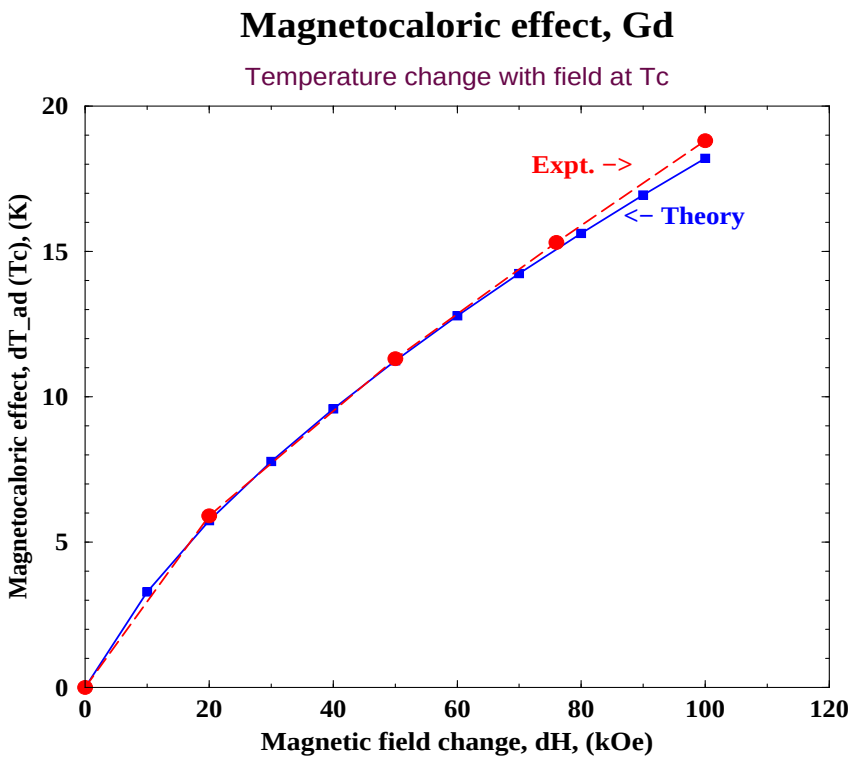
Ab-initio modelling of the MagnetoCaloric Effect in Gadolinium





Experimental results from K.Gschneidner Jr. et al., Rep.Prog.Phys. 68, (2005), 1479-1539

Theory: J.B.Staunton et al, Journal of Physics-Condensed Matter 26, 274210, (2014).

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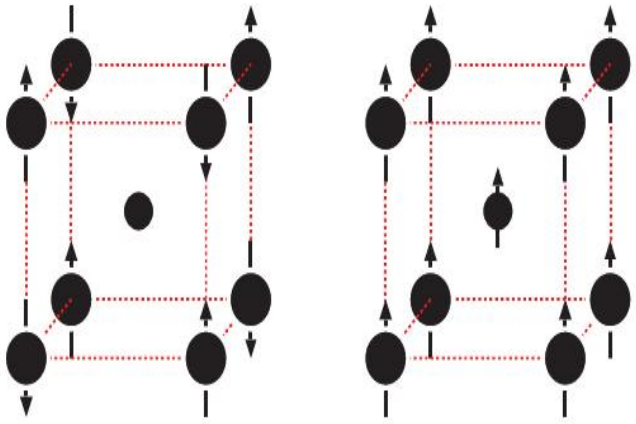
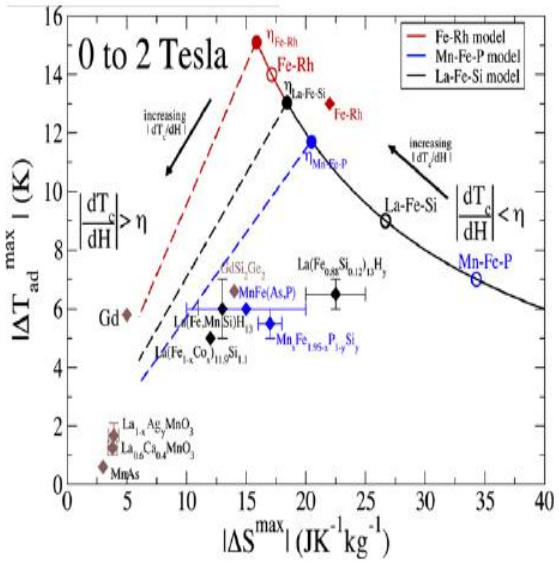
Fe-Rh - a 'two-faced' magnetic alloy





Magnetic states of the ordered B2 (CsCl) alloy Fe-Rh and experimental data for $|\Delta T_{ad}^{max}$ vs. $|\Delta S^{max}|$ for several room temperature magnetic refrigerants, (K. G. Sandeman (Scripta Mat. **67**, 566-571, (2012))).

Metamagnetic transition occurs in tight compositional range, $Fe_{48}Rh_{52}$ to $Fe_{51}Rh_{49}$, preparation-route dependent, impurities.

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FeRh: A little compositional disorder goes a long way $\cdots$

- The $Fe_{50}Rh_{50}$ solid solution orders into a B2 alloy at $T \approx 1600$K. Above $T = 0$K, the composition is $Fe_{(100-X)}Rh_X$-$Rh_{(100-X)}Fe_X$, where $X \neq 0$, the ordering incomplete.
- Away from stoichiometry and where compositional ordering is not complete, there can be Fe atoms on 'Rh' sites.
- Dramatic effect on magnetic properties, phase coexistence and broadening of 1st order transition. For $Fe_{49}Rh_{51}$ expt. finds a FM-AF transition at 370K ($T_c = 670$K) with $|\Delta S^{max}| = 22.5$ J K^{-1} Kg^{-1} at 2T.

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J.B. Staunton et al. Phys. Rev. B 89, 054427, (2014).

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- Incomplete B2 order: Swapping just 2% of Fe with Rh causes T_t to drop to 208K ($T_c = 859$K). At 4% FM-AF transition has vanished.
- Off stoichiometry: For $Fe_{96}Rh_4$-Rh, $T_t = 549$K ($T_c = 700$K), no transition for Fe-$Rh_{96}Fe_4$ ($T_c = 1008$K).
- For $Fe_{97}Rh_3$-$Rh_{99}Fe_1$ ($Fe_{49}Rh_{51}$) $T_t = 415$K ($T_c = 815$K). $|\Delta S^{max}| = 20.7\ \mathrm{J\,K^{-1}\ Kg^{-1}}$ at 2T.

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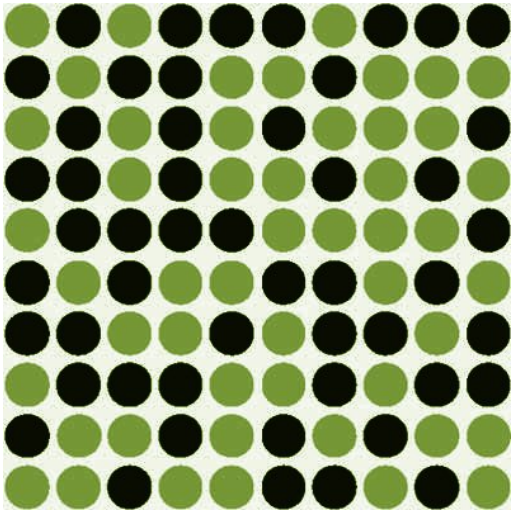
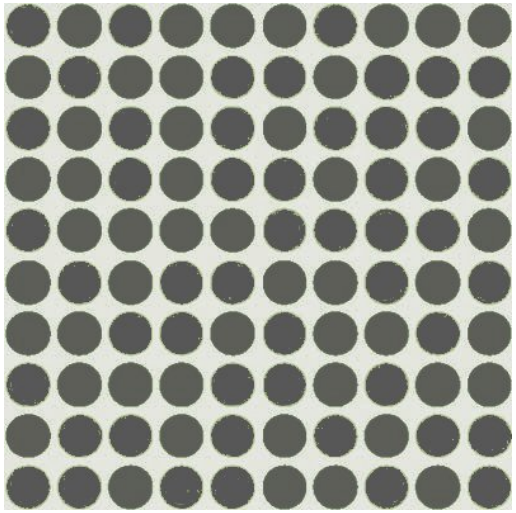
Electrons and Disorder - An Effective Lattice





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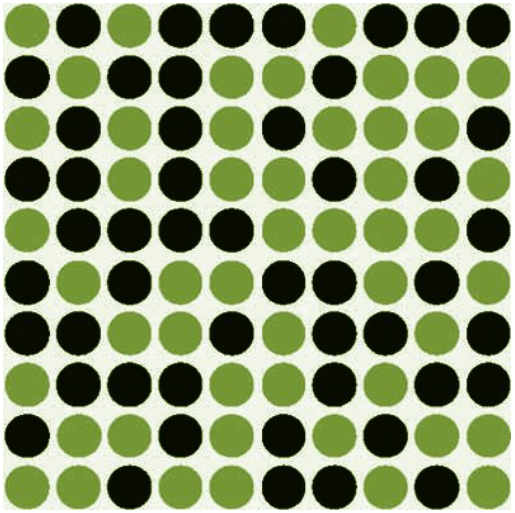

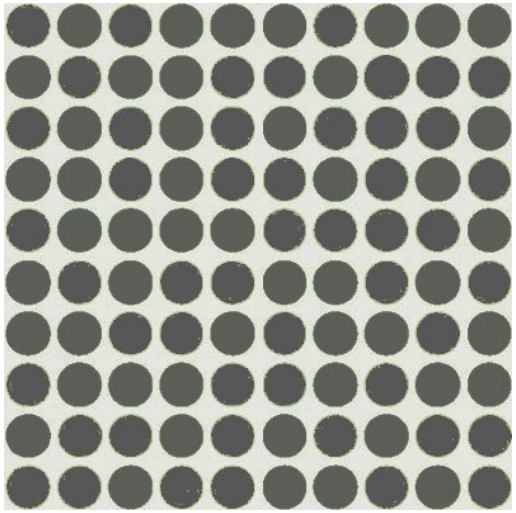

- $< G_{ij} >= G^0_{ij} + \sum_{kl} G^0_{ik} \Xi_{kl} < G_{lj} >$
- $\bar{G}(\mathbf{k}) = \frac{1}{N} \sum_j < G_{ij} > e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)} = (G^{0,-1}(\mathbf{k}) - \Xi(\mathbf{k}))^{-1}$
- G^η_{ii} is Green function for embedded impurity.
- $\sum_\eta P(\eta) G^\eta_{ii} = \bar{G}_{ii} \approx < G_{ii} > \rightsquigarrow$
  Coherent Potential Approximation for Ξ_i.

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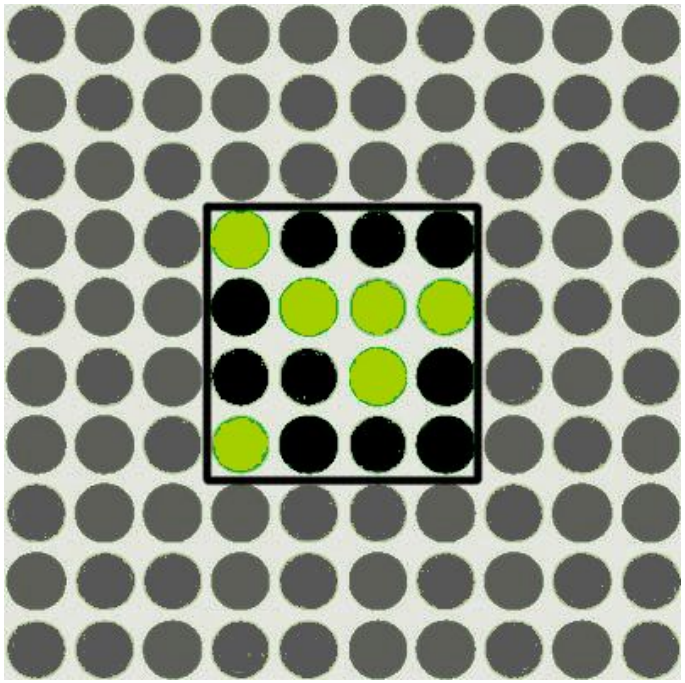
Cluster Approximation



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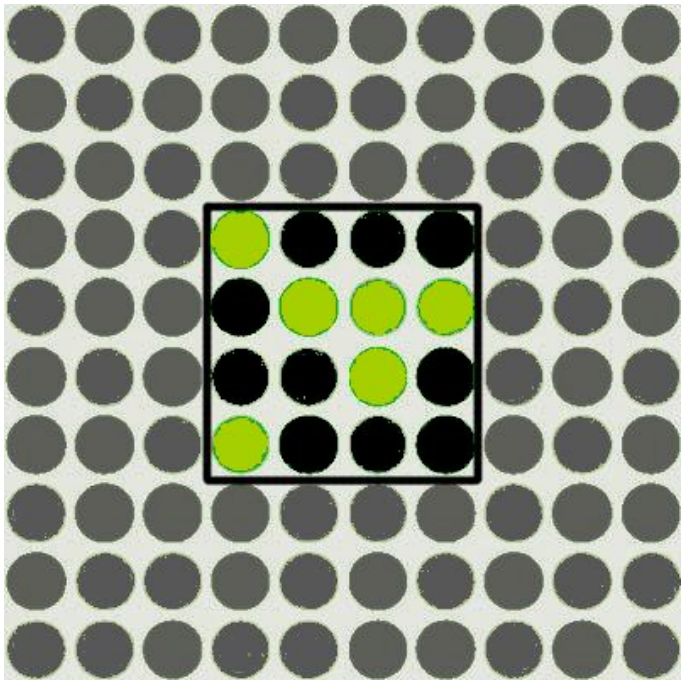

- $G^{\eta}_{IJ} = [\underline{G}^{0,-1} + \underline{\Xi} - \underline{V}^{\eta}]^{-1}_{IJ}$
- $\sum_{\eta} P(\eta) G^{\eta}_{IJ} = \hat{G}_{IJ} \approx < G_{IJ} >$

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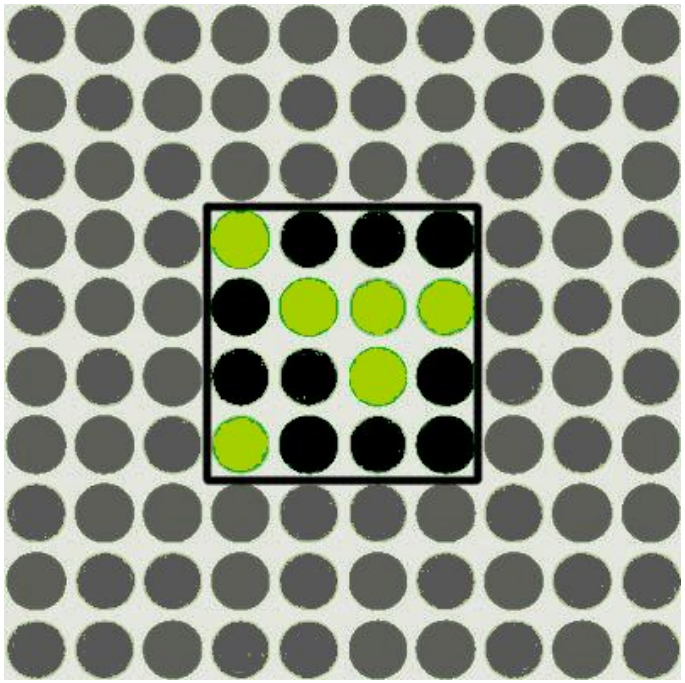

- $G^{\eta}_{IJ} = [\underline{G}^{0,-1} + \underline{\Xi} - \underline{V}^{\eta}]^{-1}_{IJ}$
- $\sum_{\eta} P(\eta) G^{\eta}_{IJ} = \hat{G}_{IJ} \approx < G_{IJ} >$
- $\hat{G}_{IJ} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \int [G^0(\mathbf{k}) - \Xi(\mathbf{K}_n]^{-1} e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} d\mathbf{k}_n.$

D.A.Rowlands et al. Phys. Rev. B 67, 115109, (2003); Phys. Rev. B 73, 165122, (2006);

J.B.Staunton et al. JPCM 26, 274210, (2014).

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Magnetic materials modelling

- Summary:
  - Slowly varying local moments in sea of 'fast' electrons.

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  - Application of similar ideas to alloy phase diagrams.
- Outlook:
  - Ab-initio short- and long-range order in alloys, magnets
  - Find new adaptive magnetic materials.
  - Materials modelling tool for magnetic refrigeration materials, permanent magnets etc..
  - Nanostructuring magnetic properties.
  - Electronic effects, temperature and spintronics.

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Acknowledgements

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Thank you for your attention!