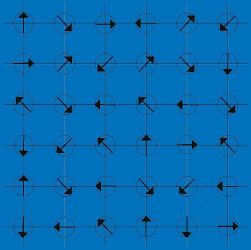
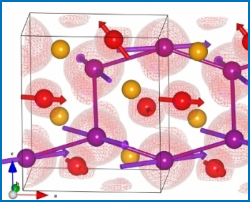
Disordered Local Moments, the Magnetocaloric Effect and Metamagnetism





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Acknowledgements

Manuel dos Santos Dias, Rudra Banerjee, Jonathan Peace (Warwick)
Zsolt Gercsi and Karl Sandeman (Imperial College)

EPSRC
Pioneering research and skills

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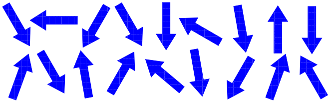
- For magnets these are local moments: $\{\hat{e}_i\}$



- $P(\{\hat{e}_i\}) = \frac{\exp[-\beta\Omega(\{\hat{e}_i\})]}{\prod_j \int d\hat{e}_j \exp[-\beta\Omega(\{\hat{e}_i\})]}$ 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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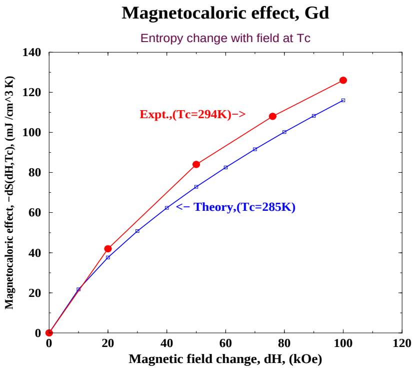
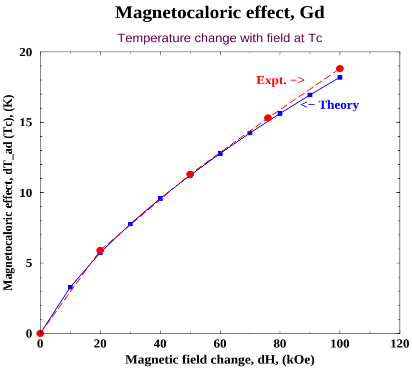
- 'First-Principles' Mean Field Theory (DLM picture), averaging using techniques adapted from theory for electrons in disordered systems (CPA).

  $P_k(\hat{e}_k) = \frac{\exp[\beta \vec{h}_k \cdot \hat{e}_k]}{\int d\hat{e}_k \exp[-\beta \vec{h}_k \cdot \hat{e}_k]}$, $\vec{m}_k = \int \hat{e}_k P_k(\hat{e}_k)\, d\hat{e}_k$.

Ab-initio modelling of the MagnetoCaloric Effect in Gadolinium





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

Magnetic interactions and structure from the DLM

- Free energy function

$$F(\{\vec{m}_i\}, \vec{B}, T) = \bar{E}(\{\vec{m}_i\}, \vec{B}) - T[\bar{S}_{mag}(\{\vec{m}_i\}, \vec{B}) + \bar{S}_{elec}(\{\hat{m}_i\}, \vec{B}, T] - \vec{B} \cdot \sum_i \mu_i \vec{m}_i$$

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- The magnetic entropy

$$\bar{S}_{mag} = -k_B \sum_i \int P_i(\hat{e}_i) \ln P_i(\hat{e}_i) d\hat{e}_i$$

and electronic entropy

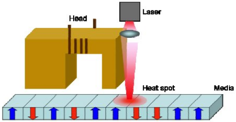
$$\bar{S}_{elec} \approx \frac{\pi^2 k_B T}{6} n(E_f; \{\vec{m}_i, \vec{B}\}),$$

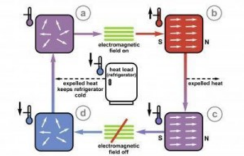
hence MCE.

- Find Free energy by finding lowest $F(\{\vec{m}_i\}, \vec{B}, T)$ for several (FM, AFM, $\cdots$) magnetic states.

Metamagnetism

- Field or temperature induced transition from antiferromagnetic to ferromagnetic state.
- Second order, first order phase transition. Tricriticality, T_t,B_t.
- Heat assisted magnetic recording. Magnetic refrigeration.

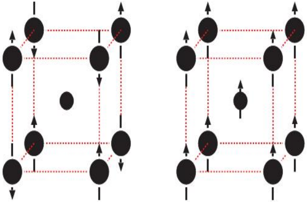


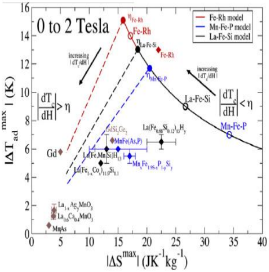


Work near T_t,B_t.

- Material with competing ferromagnetic and anti-ferromagnetic interactions. Often linked with magnetostructural effect.
- Need to control for accessible and useful T_t,B_t .

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





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

FeRh: A little compositional disorder goes a long way ⋯

- 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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- DLM Theory calculates a FM-AF transition for perfect B2 Fe-Rh at $T_t = 495$K ($T_c = 773$K). For 2T it finds $|\Delta S^{max}| = 22.2$ J K^{-1} Kg^{-1}. **40 % of this is from electronic entropy.**

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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). $|\Delta S^{max}| = 20.7$ J K^{-1} Kg^{-1} at 2T.

Metamagnetism and Helical Antiferromagnetic CoMnSi

- Local spin model of helical AFM in external magnetic field (pairwise exchange interactions and mean field theory):
  - No magnetic anisotropy - spins cant smoothly into a conical spiral towards the field's direction, 2nd. order phase transition.
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- Itinerant electron spin model. Landau free energy expansion, coefficients describe Stoner and spin fluctuation collective electron effects.
  - Free energy difference $\Delta F \approx$

$$a(\vec{m}_0, \vec{B}, T)|\Delta m_{\mathbf{Q}}|^2 + b(\vec{m}_0, \vec{B}, T)|\Delta m_{\mathbf{Q}}|^4 + c(\vec{m}_0, \vec{B}, T)|\Delta m_{\mathbf{Q}}|^6$$

  - Tricritical point:

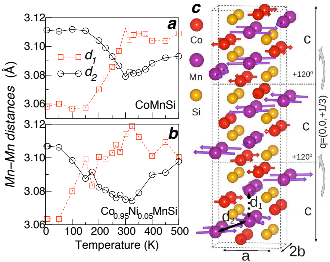
$$a(\vec{m}_0, \vec{B}_t, T_t) = 0, \qquad b(\vec{m}_0, \vec{B}_t, T_t) = 0$$

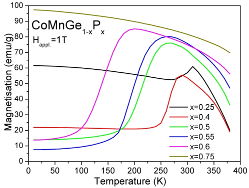
CoMnSi, a metallic helical metamagnet

- Field and T induced transition from low T incommensurate, helical AF state to high magnetisation state.

  (A.Barcza, Z.Gercsi, K.S.Knight and K.G.Sandeman, PRL, **104**, 247202, (2010))

- Tricritical point observed.
- Orthorhombic structure. Large magnetoelastic effects.





- Variations, $Co_{1-x}Ni_xMnSi$, $CoMn_{1-x}Cr_xSi$, $CoMnGe_{1-x}P_x$

  (Z.Gercsi et al., PRB,**83**, 174403, (2011); A.Barcza et al. PRB,**87**, 064410, (2013))

Magnetic states and Disordered Local Moments

- Several solutions $\{\vec{m}_i\}^{(n)}$, find lowest $F(\{\vec{m}_i\}^{(n)}, B\,\hat{x}, T)$.
- Distorted helix
  $\vec{m}_i^{dh} = (m + \Delta m_{\vec{Q}}) \cos(\vec{Q} \cdot \vec{R}_i)\hat{x} + \Delta m_{\vec{Q}} \sin(\vec{Q} \cdot \vec{R}_i)\hat{y}$.
- Conical helix: $\vec{m}_i^{ch} = m\hat{x} + \Delta m_{\vec{Q}}(\cos(\vec{Q} \cdot \vec{R}_i)\hat{y} + \sin(\vec{Q} \cdot \vec{R}_i)\hat{z})$.
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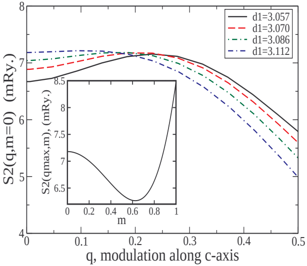
- Fan state: $\vec{m}_i^{fan} = m\hat{x} + \Delta m_{\vec{Q}} \cos(\vec{Q} \cdot \vec{R}_i)\hat{y}$.
- FM state: $\vec{m}^{FM} = m\hat{x}$ with $\Delta m_{\vec{Q}} = 0$.
- Relative difference between $F_{distorted-helix}$ and others determines presence or not of first order metamagnetic transition and $\vec{B}_c(T)$.

Metamagnetism in CoMnSi



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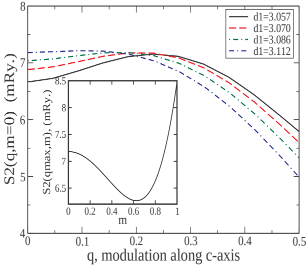

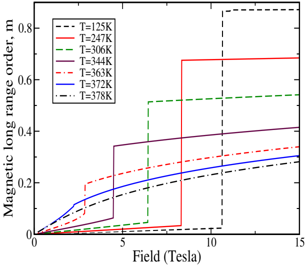

- $S^{(2)}(\vec{Q}, \vec{m} = 0)$, for structures measured in neutron diffraction experiments labelled by the Mn-Mn spacing, d_1, in Å. The inset shows $S^{(2)}(\vec{Q}_{max}, \vec{m})$ versus FM order parameter m for $d_1 = 3.07$ Å. Spin-orbit coupling and magnetic anisotropic effects very small.
- As d_1 decreases, AFM correlations become stronger than FM ones. $T_N \approx 400$K. Crucially magnetic interactions weaken as $\vec{m}$ grows. This itinerant electron effective comes from the spin-polarised density induced on the Co sites.

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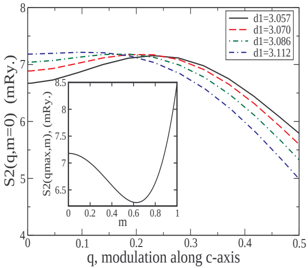

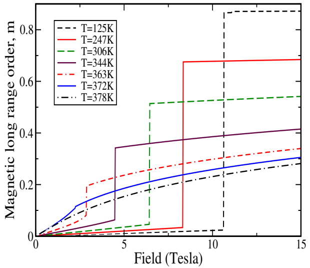

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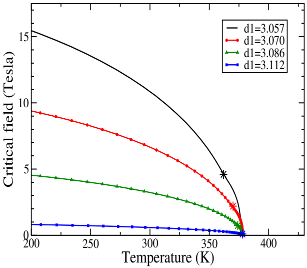
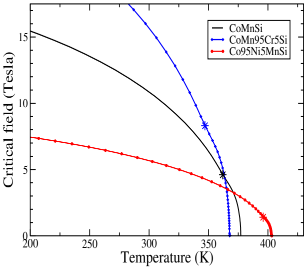
- m versus applied field for several temperatures for $d_1 = 3.07$ Å. *A tricritical point is indicated at 372K, 2 Tesla*.

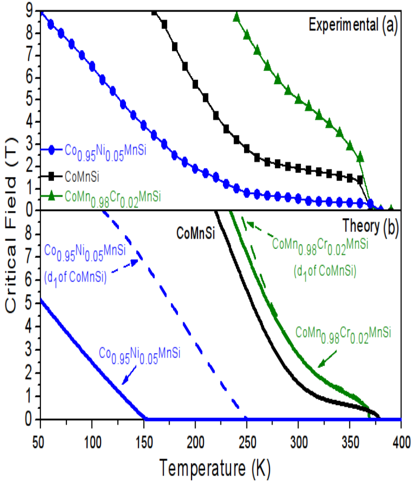
Critical field to switch HAFM to FM/fan state





- The critical field B_c for transition between a helical AFM and a FM state versus T.
- The critical field B_c for $Co_{0.95}Ni_{0.05}MnSi$ (adding electrons) and $CoMn_{0.95}Cr_{0.05}Si$ (removing electrons) with $d_1 = 3.06$ Å.

Test against experiment



Further details: J. B. Staunton et al., PRB 87, 125115(R), (2013).

Magnetic materials modelling

- Summary:
  - Slowly varying local moments in sea of ‘fast’ electrons.
  - Theory of metallic magnetism at finite temperatures.
    - MCE of Gd around second order FM transition.
    - Application to B2-ordered FeRh. First order FM to AF transition. *Strong variation with compositional disorder.*
    - Application to orthorhombic CoMnSi helical antiferromagnet.
    - Competing FM and incommensurate AF Mn - Mn interactions. Tricriticality, enhanced magnetocaloric and magnetostructural effects.
      First order metamagnetic phase transition without anisotropy.
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- Outlook:
  - Find new adaptive magnetic materials.
  - Materials modelling tool for magnetic refrigeration materials.
  - Nanostructuring magnetic properties.
  - Electronic effects, temperature and spintronics.