Disordered Local Moments, the Magnetocaloric Effect and Metamagnetism

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Acknowledgements

Manuel dos Santos Dias, Rudra Banerjee, Jonathan Peace (Warwick)
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- Temperature dependence.
  - For \( T \neq 0K \) need to identify some electronic attributes which are slowly varying (Born-Oppenheimer).
  - Separate out these modes. Statistical mechanics combined with constrained DFT-type calculations.
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• For magnets these are local moments: $\{\hat{e}_i\}$
\[ P(\{\hat{e}_i\}) = \frac{\exp[-\beta \Omega(\{\hat{e}_i\})]}{\prod_j \int d\hat{e}_j \exp[-\beta \Omega(\{\hat{e}_i\})]} \] 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 \( \Omega_0 = \sum_i \vec{h}_i \cdot \hat{e}_i \).
Disordered Local Moments and the Magnetocaloric Effect

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

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- ‘First-Principles’ Mean Field Theory (DLM picture), averaging using techniques adapted from theory for electrons in disordered systems (CPA).

\[
P_k(\hat{e}_k) = \frac{\exp[\beta \vec{h}_k \cdot \hat{e}_k]}{\int d\hat{e}_k \exp[-\beta \vec{h}_k \cdot \hat{e}_k]}, \quad \vec{m}_k = \int \hat{e}_k P_k(\hat{e}_k) d\hat{e}_k.
\]
Ab-initio modelling of the MagnetoCaloric Effect in Gadolinium

Magnetocaloric effect, Gd

Entropy change with field at Tc

Magnetocaloric effect, Gd

Temperature change with field at Tc

• Free energy function

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

\[\vec{h}_l = -\frac{\partial(\tilde{E} - T \tilde{S}_{\text{elec}})}{\partial \vec{m}_i}\] minimises \(F\).
Magnetic interactions and structure from the DLM

- Free energy function

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

- \( \hat{h}_l = -\frac{\partial (\bar{E} - T \bar{S}_{elec})}{\partial \vec{m}_i} \) minimises \( F \).

- 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, ...) 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 $|\Delta T_{ad}^{\text{max}}|$ vs. $|\Delta S^{\text{max}}|$ for several room temperature magnetic refrigerants, taken from viewpoint paper by K. G. Sandeman (Scripta Mat. 67, 566-571, (2012)).
The $\text{Fe}_{50}\text{Rh}_{50}$ solid solution orders into a B2 alloy at $T \approx 1600\text{K}$. Above $T = 0\text{K}$, the composition is $\text{Fe}_{(100 - X)}\text{Rh}_X - \text{Rh}_{(100 - X)}\text{Fe}_X$, 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 $\text{Fe}_{49}\text{Rh}_{51}$ expt. finds a FM-AF transition at 370K ($T_c = 670\text{K}$) with $|\Delta S^{max}| = 22.5 \text{ JK}^{-1} \text{ Kg}^{-1}$ at 2T.
FeRh: A little compositional disorder goes a long way · · ·

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

Incomplete B2 order: Swapping just 2% of Fe with Rh causes $T_t$ to drop to $208\text{K}$ ($T_c = 859\text{K}$). At 4% FM-AF transition has vanished.

Off stoichiometry: For $\text{Fe}_{96}\text{Rh}_{4}$-Rh, $T_t = 549\text{K}$ ($T_c = 700\text{K}$), no transition for Fe-Rh$_{96}$Fe$_4$ ($T_c = 1008\text{K}$).

For $\text{Fe}_{97}\text{Rh}_3$-$\text{Rh}_{99}\text{Fe}_1$ ($\text{Fe}_{49}\text{Rh}_{51}$) $T_t = 415\text{K}$ ($T_c = 815\text{K}$). $|\Delta S^{\text{max}}| = 20.7 \text{ J K}^{-1} \text{ Kg}^{-1}$ at 2T.
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.
- With magnetic anisotropy - first order transition into fan structure, spins oscillating about field direction or FM state.
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Itinerant electron spin model. Landau free energy expansion, coefficients describe Stoner and spin fluctuation collective electron effects.

Free energy difference $\Delta F \approx$

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

Tricritical point:

$$a(\vec{m}_0, \vec{B}_t, T_t) = 0, \quad b(\vec{m}_0, \vec{B}_t, T_t) = 0$$
CoMnSi, a metallic helical metamagnet

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


- Tricritical point observed.

- Orthorhombic structure. Large magnetoelastic effects.

- Variations, $\text{Co}_{1-x}\text{Ni}_x\text{MnSi}$, $\text{CoMn}_{1-x}\text{Cr}_x\text{Si}$, $\text{CoMnGe}_{1-x}\text{P}_x$

  (Z.Gercsi et al., PRB, 83, 174403, (2011); A.Barca et al. PRB, 87, 064410, (2013))
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: \( \vec{m}_{i}^{ch} = m \hat{x} + \Delta m_{\vec{Q}} (\cos(\vec{Q} \cdot \vec{R}_i) \hat{y} + \sin(\vec{Q} \cdot \vec{R}_i) \hat{z}) \).

- 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 \( \Delta m_{\vec{Q}} = 0 \).
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
  $$\vec{m}_{ih} = (m + \Delta m_{\vec{Q}}) \cos(\vec{Q} \cdot \vec{R}_i) \hat{x} + \Delta m_\vec{Q} \sin(\vec{Q} \cdot \vec{R}_i) \hat{y}.$$  
- Conical helix: $\vec{m}_{ch} = m \hat{x} + \Delta m_{\vec{Q}} (\cos(\vec{Q} \cdot \vec{R}_i) \hat{y} + \sin(\vec{Q} \cdot \vec{R}_i) \hat{z})$.
- Fan state: $\vec{m}_{fan} = m \hat{x} + \Delta m_{\vec{Q}} \cos(\vec{Q} \cdot \vec{R}_i) \hat{y}$.
- FM state: $\vec{m}_{FM} = m \hat{x}$ with $\Delta m_{\vec{Q}} = 0$.
- Relative difference between $F_{\text{distorted-helix}}$ and others determines presence or not of first order metamagnetic transition and $\vec{B}_c(T)$.
Metamagnetism in CoMnSi

As $d_1$ decreases, AFM correlations become stronger than FM ones. $T_N \approx 400K$. Crucially magnetic interactions weaken as $\vec{m}$ grows. This itinerant electron effective comes from the spin-polarised density induced on the Co sites.
S(2) (⃗{Q}, ⃗{m} = 0), for structures measured in neutron diffraction experiments labelled by the Mn-Mn spacing, d₁, in Å. The inset shows S(2) (⃗{Q}_\text{max}, ⃗{m}) versus FM order parameter m for d₁ = 3.07 Å. Spin-orbit coupling and magnetic anisotropic effects very small.

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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 $S^{(2)}(\vec{Q}_{\text{max}}, \vec{m})$ versus FM order parameter $m$ for $d_1 = 3.07$ Å. Spin-orbit coupling and magnetic anisotropic effects very small.

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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.

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

- Dependence of local moment interactions on overall spin polarisation of electron sea. Non-pairwise interactions.
Magnetic materials modelling

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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.