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Spin Crossover in Ferropericlase in the Earth's Lower Mantle from *LDA + U_{SC}* Calculations

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Abstract

The high spin (HS) to low spin (LS) crossover of Fe^{2+} ions in ferropericlase, $Mg_{(1-x)}Fe_xO$ (Fp), affects mantle properties such as density, elasticity, thermal properties, element partitioning, etc. It further affects the interpretation of lower mantle velocities. Here, we introduce a framework to compute energy with the inclusion of the non-ideal mixing energy term across spin-state changes using *ab initio* DFT+ U_{SC} calculations and compare results with available experimental and computational results. We explain how this framework differs from previous calculations that use the "ideal" HS-LS mixing model, and show the importance of constraining well the energy model and the computed properties from thermodynamic relationships of Fp.

Ideal solid solution of HS and LS ferropericlase

Low spin fraction $n = n_{LS}/(n_{LS} + n_{HS})$
Ideal mixing volume $V = (1-n)V_{HS} + nV_{LS}$
Ideal mixing gibbs free energy

$$G_{ideal} = (1-n)G_{HS} + nG_{LS} + G_{mix}$$

High/low spin Gibbs free energy $G_{HS/LS} = F_{HS/LS} + PV_{HS/LS}$

$$G_{HS/LS} = F_{HS/LS}^{stat+vib} + G_{HS/LS}^{mag} + PV_{HS/LS}$$

Magnetic contribution

$$G_{mag} = -TS_{mag} = -k_B T x_{Fe}(1-n)\ln[m(2S+1)]$$

- x_{Fe} is the iron concentration
- S is iron spin quantum number
  $S = 2$ for HS and $S = 0$ for LS
- m is electronic configuration degeneracy
  $m = 3$ for HS and $m = 1$ for LS

Ideal energy of mixing

$$G_{mix} = -TS_{conf} = k_B T x_{Fe}[n\ln n + (1-n)\ln(1-n)]$$

n is calculated by minimizing G_{ideal}

$$f(P,T,n) = \Delta G_{LS-HS} + k_B T x_{Fe} \ln\left[\frac{n}{1-n}(m(2S+1))\right] = 0$$

which gives equilibrium n(P,T):

$$n = \frac{1}{1 + m(2S+1)exp\left[\frac{\Delta G_{LS-HS}}{k_B T x_{Fe}}\right]}$$

where $\Delta G_{LS-HS} = G_{LS} - G_{HS}$

Non-ideal solid solution

Non-ideal gibbs free energy

$$G_{non-ideal} = G_{ideal} + G_{ex}$$

assume the excess energy is dominated by its static part

$$G_{ex}(P,T,n) \approx H_{ex,st}(P,n)$$

n in calculated By minimizing $G_{non-ideal}$. Here, we would like to numerically solve

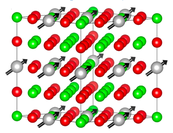
$$f(P,T,n) = \Delta G_{LS-HS} + k_B T x_{Fe} \ln\left[\frac{n}{1-n}(m(2S+1))\right] + \frac{\partial H_{ex}}{\partial n} = 0$$

Methods and calculation details

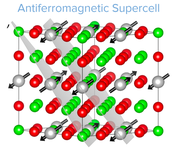
A supercell with **64** atoms for X_{Fe} = 0.1875

6 Fe, 26 Mg and 32 O atoms

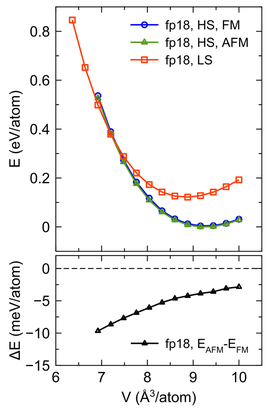
Ferromagnetic Supercell



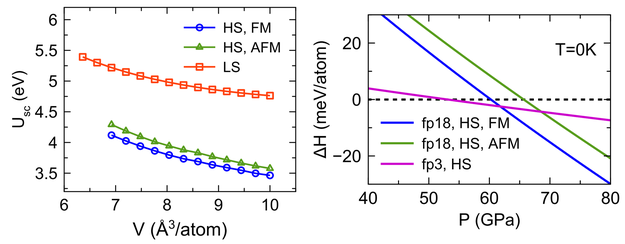
Antiferromagnetic Supercell



- DFT+U [1]
- Self-consistent U_{sc} [2]
- Density Functional Perturbation Theory + U for phonons [3]
- LDA-PAW with spin polarization
- Quantum ESPRESSO [4]
- Phonopy code [5]
- 2 × 2 × 2 k-point mesh
- qha to compute vibrational free energy [6]

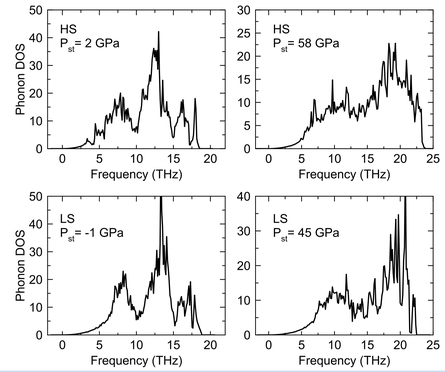


Energy, Hubbard parameters and Enthalpy



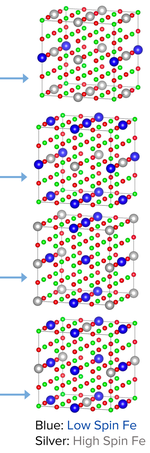
Left: E vs. V for the three states and energy difference between the HS-AFM and HS-FM. Middle: self-consistent Hubbard parameters *U* for different spin states. Right: enthalpy difference between HS and LS.

Vibrational DOS for HS and LS



Unique configurations

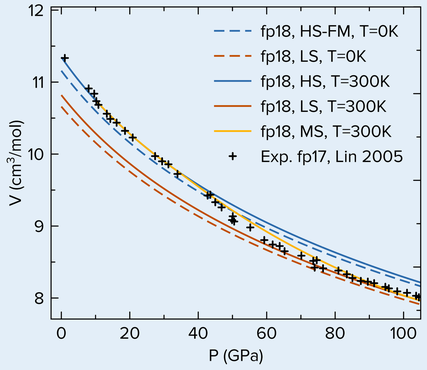
Low spin fraction n	Space group of unique configurations	Number of equivalent configurations
$\frac{1}{6}$	#123 P4/mmm	1
$\frac{1}{3}$	#123 P4/mmm	6
	#131 P4_2/mmc	6
	#139 I4/mmm	3
$\frac{1}{2}$	#123 P4/mmm	6
	#221 Pm-3m	2
	#47 Pmmm	12
$\frac{2}{3}$	#123 P4/mmm	6
	#131 P4_2/mmc	6
	#139 I4/mmm	3
$\frac{5}{6}$	#123 P4/mmm	1



Blue: Low Spin Fe
Silver: High Spin Fe

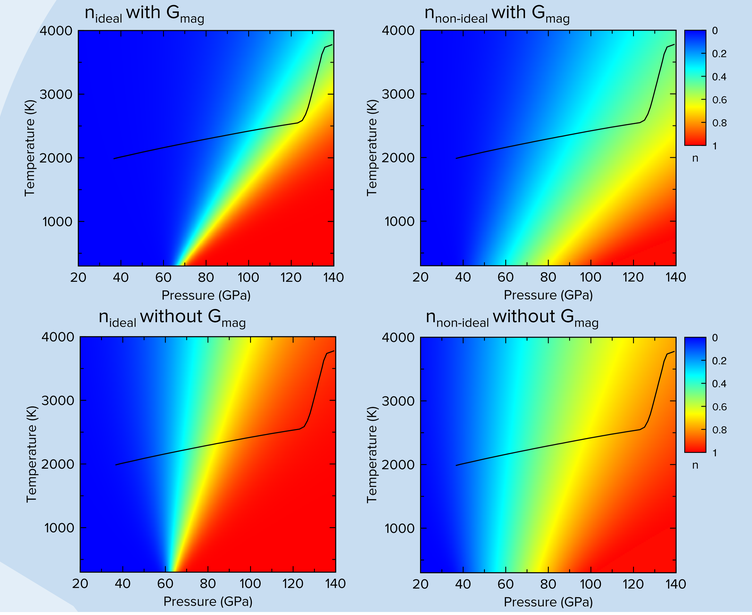
Equation of state at 300 K

Compression curve of fp18. The experimental data is at 300 K with x_{Fe}=17% ferropericlase [7].



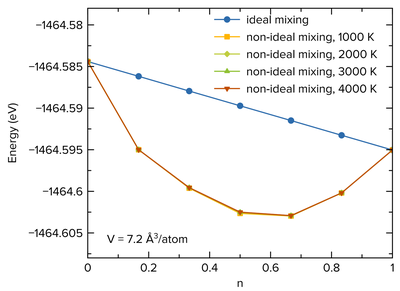
Spin-Crossover LS fraction n

Temperature-dependent spin-crossover ranges with X_{Fe}=18.75% based on the different models as labelled. The black line indicates the geotherm [8, 9].



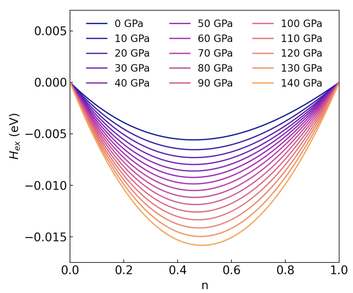
Non-ideal Mixing – Methods

Compute the MS static energy through the weighted average using Boltzmann factor of the unique configurations at each n



Use polynomial 3rd order to fit $H_{ex}(n)$

- $H_{ex}(n=0) = 0$ and $H_{ex}(n=1) = 0$
- $H_{ex}(n) = a\,n^3 + b\,n^2 - (a+b)\,n$



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Acknowledgements

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