DFT+DMFT study of magnetic properties in FeO at high pressures

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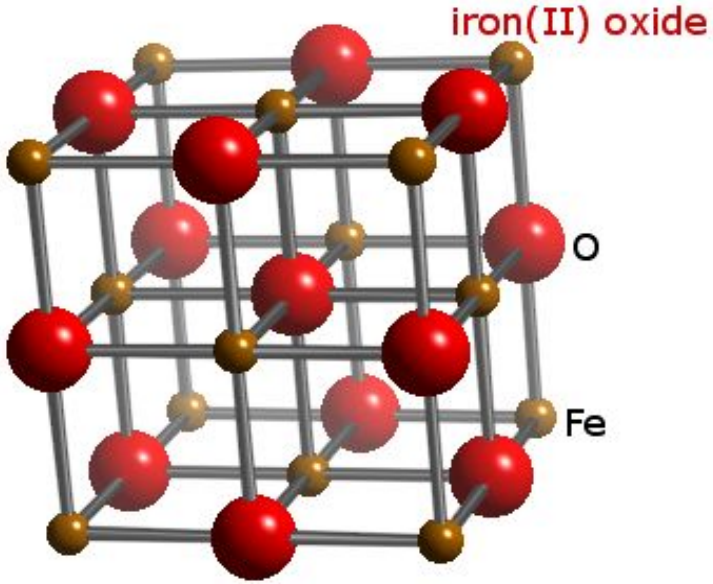
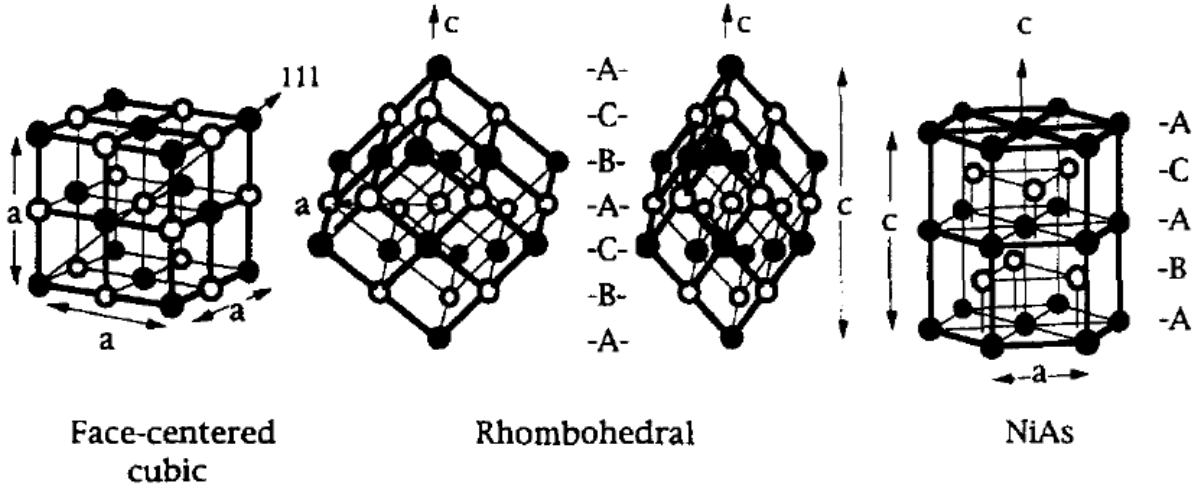
Outline

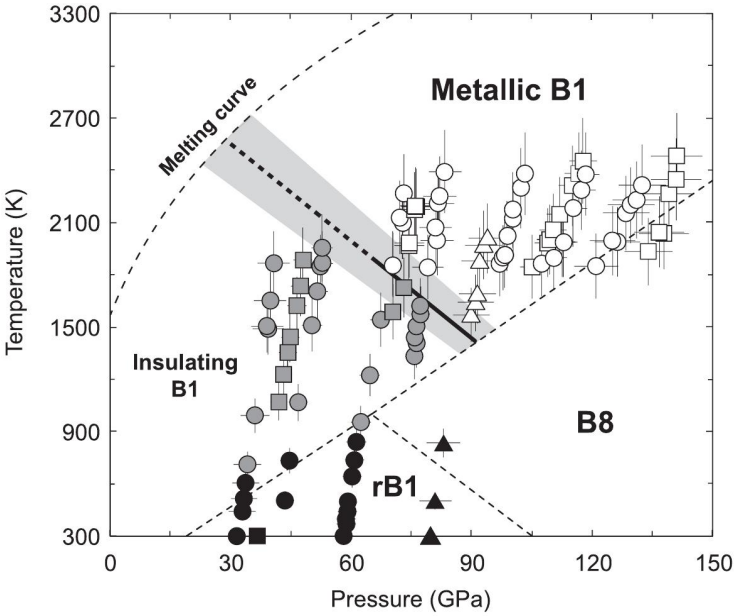
- Introductions to FeO
- Troubles of DFT calculations
- The DFT+DMFT algorithm
- Magnetic susceptibility and the Néel temperature
- Our results

Introductions to FeO

- Crystal iron(II) oxide, Fe_xO, iron vacancy x≈0.94; magnetic moment about 3.32 μ_B.
- B1, rock salt structure at ambient pressure; B1 (NaCl) → rB1 → hexagonal B8 (NiAs).
- An insulator at ambient pressure; Insulator → metal transition at high T, P.

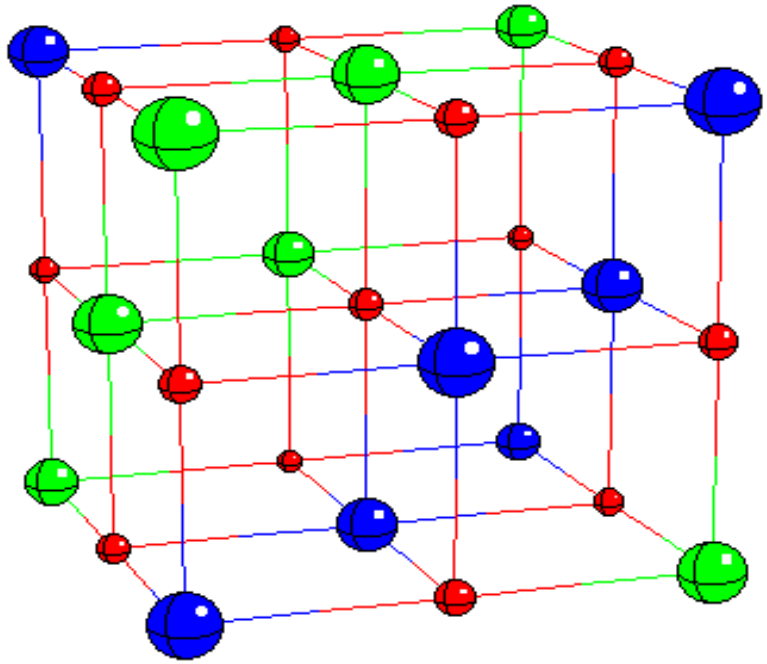




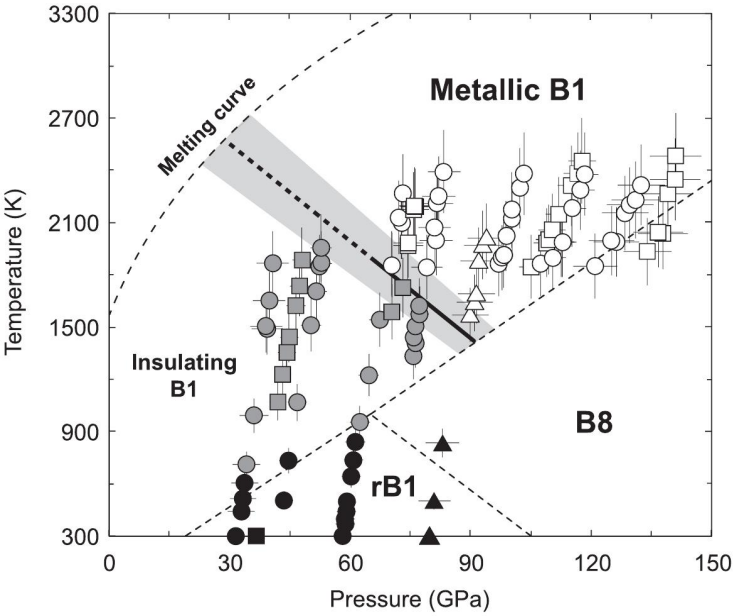


FeO phase diagram as of 2012.
From K. Ohta, R.E. Cohen et al.
Phys. Rev. Lett. 108, 026403 (2012)

Introductions to FeO



- Crystal iron(II) oxide, $Fe_{1-x}O$, iron vacancy $x \approx 0.94$; magnetic moment about 3.32 μ_B.
- B1, rock salt structure at ambient pressure; B1 (NaCl) → rB1 → hexagonal B8 (NiAs).
- An insulator at ambient pressure; Insulator → metal transition at high T, P.
- Antiferromagnetic ordering (AFM), Néel temperature 198 K; gap close above the Neel temperature.
- Magnetic transition induced by external pressure.



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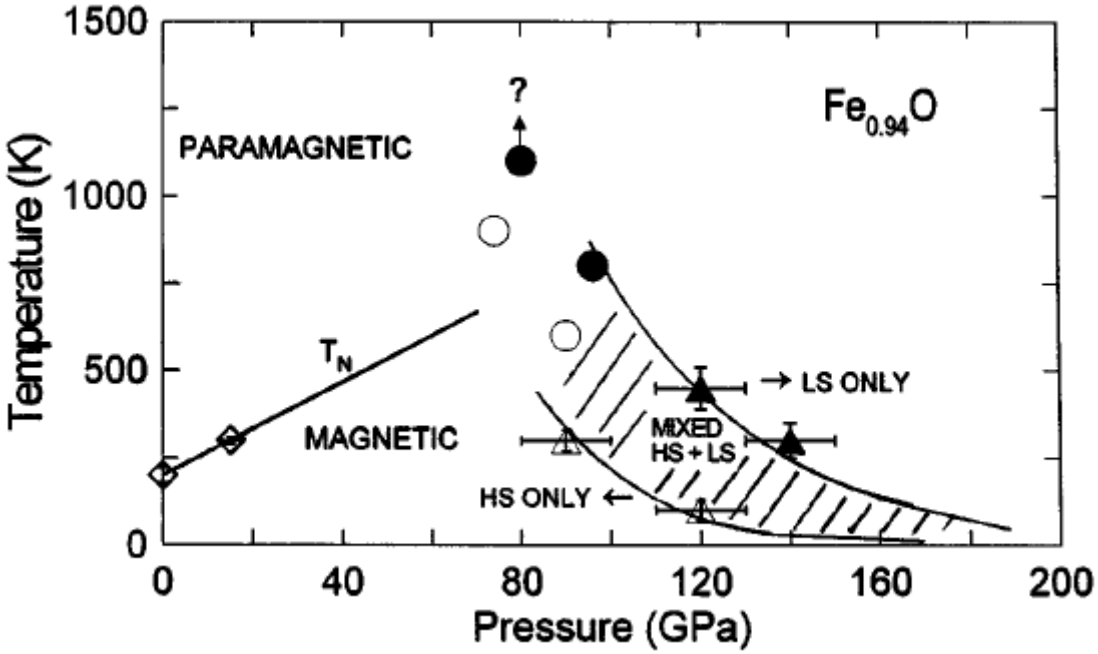
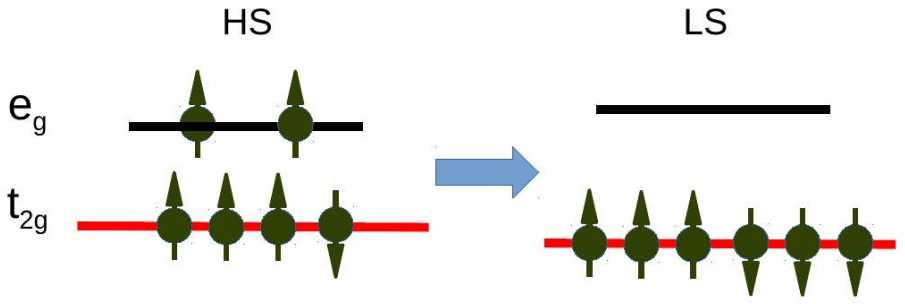
Collapse of magnetic moment in FeO

- Mössbauer spectroscopy experiment.
- Magnetic moment collapsed at P=140 GPa.
- Fe^{2+}, $3d^6$.
- high spin-low spin transition (HS-LS).





From M. P. Pasternak, et al.
Phys. Rev. Lett. 79, 5046 (1997)

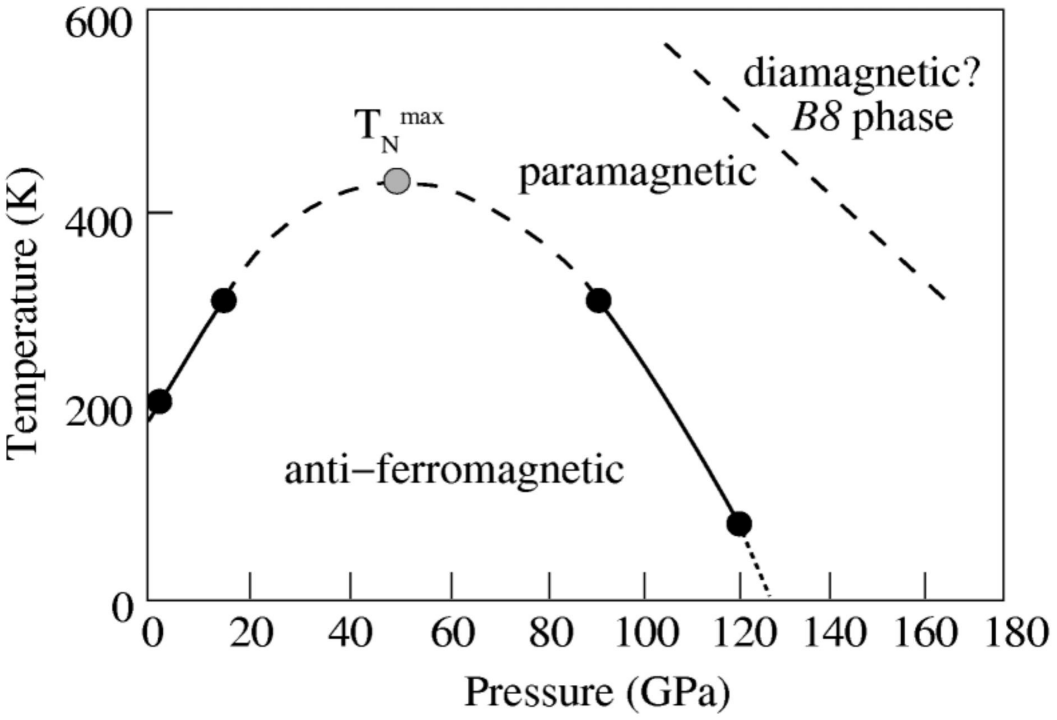
AFM to paramagnetic transition in FeO

VOLUME 83, NUMBER 20 PHYSICAL REVIEW LETTERS 15 NOVEMBER 1999

Magnetism in FeO at Megabar Pressures from X-Ray Emission Spectroscopy

James Badro, Viktor V. Struzhkin, Jinfu Shu, Russell J. Hemley, and Ho-kwang Mao

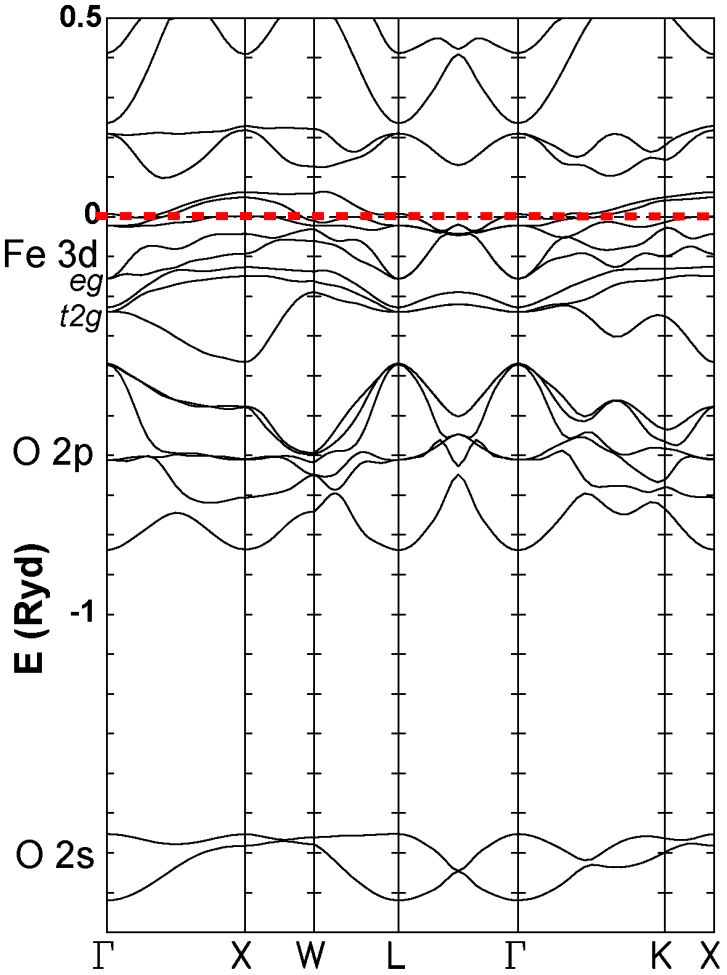
Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road N.W., Washington, D.C. 20015



From J. Badro et al., Phys. Rev. Lett. 83, 4101 (1999).

- x-ray spectroscopy experiment.
- The magnetic moments of iron preserve up to 143GPa.
- FeO experiences collapse of magnetic ordering at high pressure.
- AFM to paramagnetic transition in FeO at high pressure; a phase diagram as left.
- Which is correct? Or both?

Problems of DFT in FeO calculations



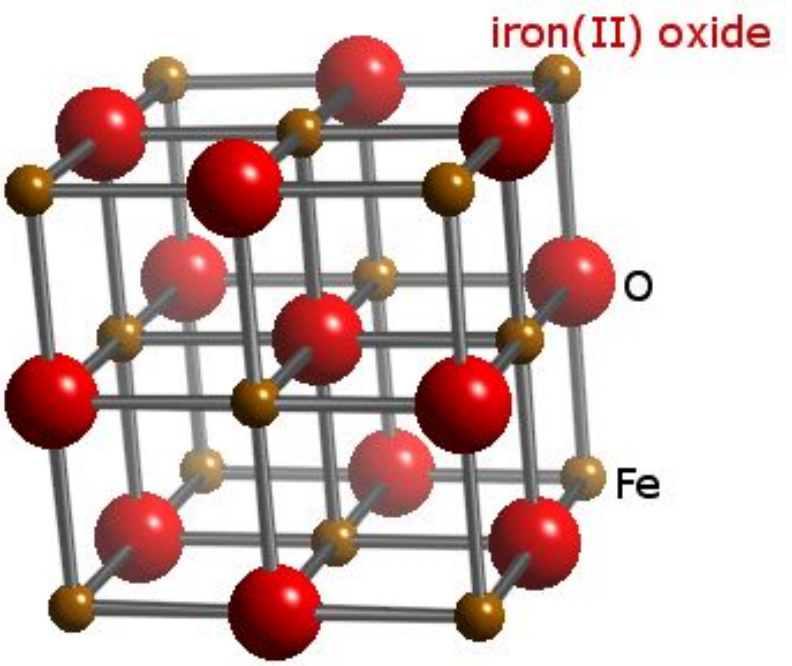
Cohen et al. (1998) High-Pressure Materials Research. Materials Research Society. **499**.

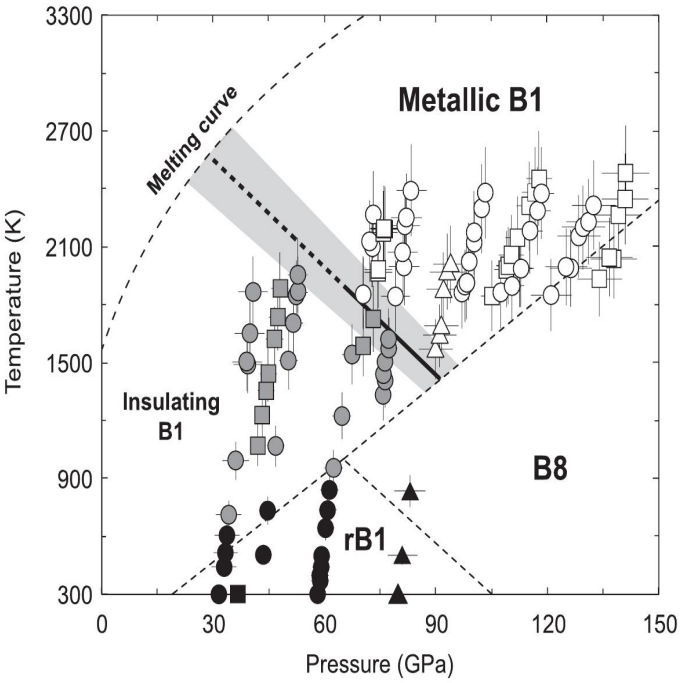
FeO is an insulator at ambient pressure

- L(S)DA/GGA etc. predict a metal.
- LDA+U does open a gap in AFM rhombohedral or lower symmetry FeO.
- LDA+U cannot give a gap in paramagnetic FeO.
- LDA+U predicts a metal → insulator transition under pressure, but not a high-spin low-spin transition. (Gramsch et al. Am. Mineral., **88**, 257 2003).
- Accuracy of LDA+U is unknown.

Problems of DFT in FeO calculations

- Atomic electronic structure of iron $3d^6 4s^2$.
- Partially filled 3d orbitals; partially localized 3d-electrons form magnetic moments.
- Strong Coulomb interactions between 3d electrons.
- Strong local correlations between 3d electrons need being included exactly; DFT fails; we choose DMFT.
- We choose B1 structure of FeO; no strain; no iron deficiency.
- Due to cubic lattice two sets of degenerated orbitals: e_g and t_{2g}.





The DFT+DMFT formalism

DFT for crystal

$$\left(-\nabla^2 + V^{DFT} + \bar{\Sigma}_k(\omega)\right)\psi_{k\omega_n i}(r) = \epsilon_{k\omega_n i}\psi_{k\omega_n i}(r)$$

DMFT for local interactions

$$\frac{1}{\omega - E_{imp} - \Sigma_{imp} - \Delta} = G^{imp} = \sum_k P_k \left(i\omega + \mu - H^{DFT} - \hat{E}\bar{\Sigma}\right)^{-1}$$

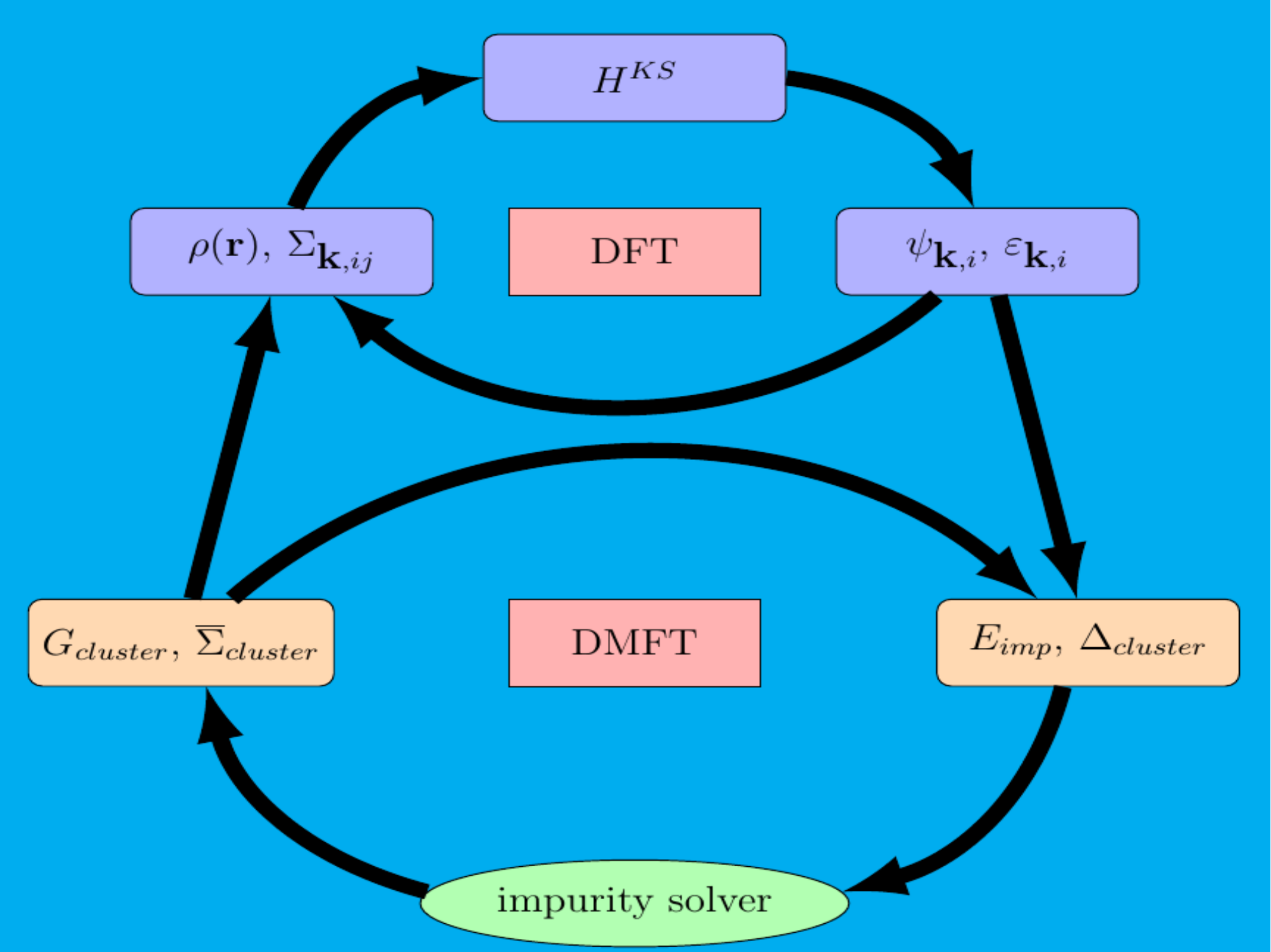
- WIEN2k LAPW code for DFT.
- Continuous Time Quantum Monte Carlo (CTQMC) as impurity solver.
- Fully self-consistent in charge density ρ, chemical potential μ, impurity levels E_{imp}, hybridization Δ, and self-energy Σ.
- Fully localized limit double-counting.

$$\bar{\Sigma} = \Sigma - \Sigma_{DC}$$

$$\bar{\Sigma}_{k,ij} = \sum_{\tau,LL'} \bar{E}(ji,\tau LL')\,\bar{\Sigma}_{LL'}$$

- Code by Kristjan Haule,

  http://hauleweb.rutgers.edu/downloads/


H^{KS}
$\rho(\mathbf{r})$, $\Sigma_{\mathbf{k},ij}$
DFT
$\psi_{\mathbf{k},i}$, $\varepsilon_{\mathbf{k},i}$
$G_{cluster}$, $\overline{\Sigma}_{cluster}$
DMFT
E_{imp}, $\Delta_{cluster}$
impurity solver

Magnetic susceptibility and the Néel temperature

The bulk magnetic susceptibility is required to detect the AFM ordering:

$$\boxed{\chi_q(T) \propto (T - T_N)^{-1}}$$

in which q is the moment, is the Néel temperature.

But all data from DMFT are localized on the impurity site:

Singlet-particle quantities:

Dressed Green's function $G_{loc}(\omega)$, self-energy $\Sigma(\omega)$.

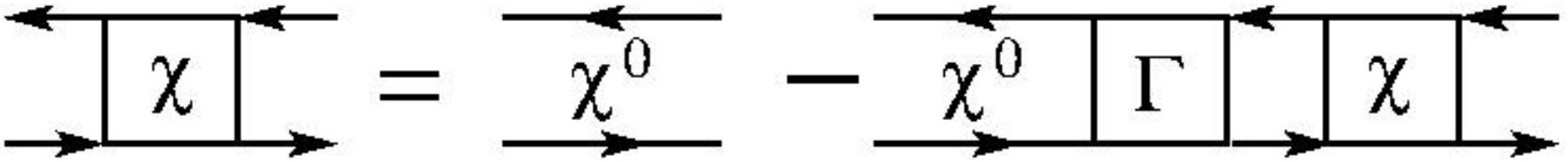
Two-particle quantities:

Susceptibilities, including magnetic susceptibility $\chi_{loc}(\omega, \omega', \nu)$.

How to extract bulk quantities from local quantities?

Magnetic susceptibility and the Néel temperature

Bethe-Salpeter equation:



$$\chi = \chi^0 - \chi^0 \Gamma(\omega, \omega', \nu)\chi$$

Or equivalently,

$$\chi^{0-1} - \chi^{-1} = \Gamma(\omega, \omega', \nu)$$

Irreducible vertex Γ(ω, ω', ν) is local in space

Used for bulk magnetic χ

$$\chi_{loc}^{0-1} - \chi_{loc}^{-1} = \Gamma(\omega, \omega', \nu) = \chi_q^{0-1} - \chi_q^{-1}$$

Magnetic susceptibility and the Néel temperature

Bare local magnetic susceptibility

$$\chi^0_{loc}(\omega, \omega', \nu) = -G_{loc}(\omega) G_{loc}(\omega + \nu) \delta_{\omega,\omega'}$$

Bare bulk magnetic susceptibility

$$\chi^0_q(\omega, \omega', \nu) = -\sum_k G_k(\omega) G_{k+q}(\omega + \nu) \delta_{\omega,\omega'}$$

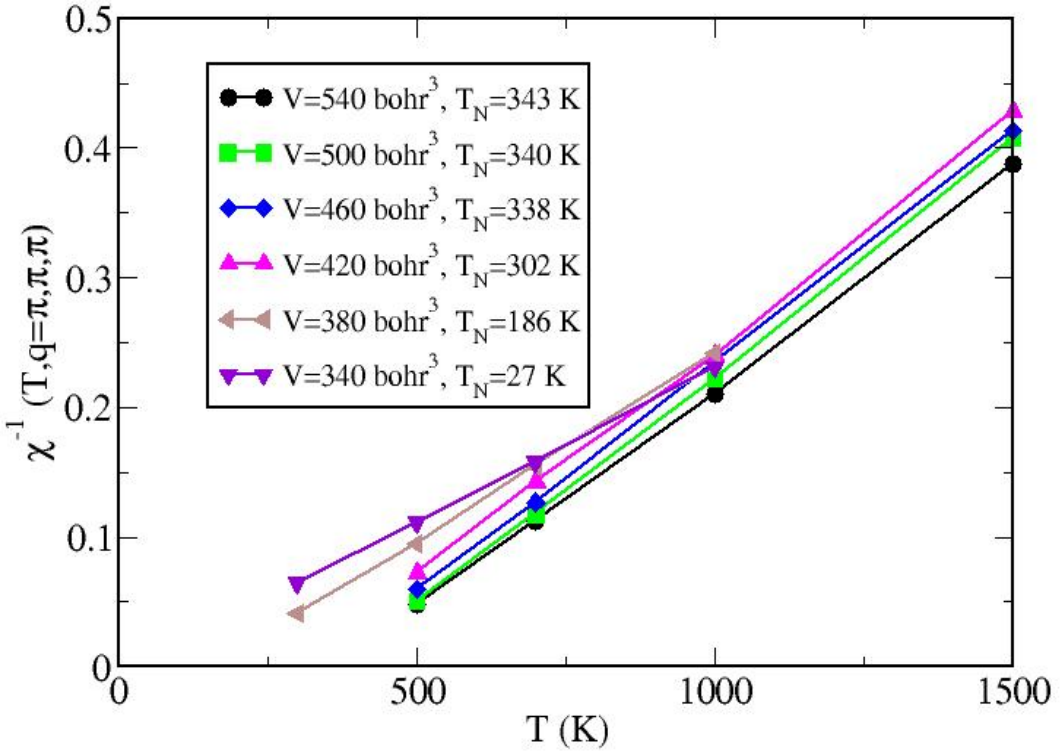
The bulk magnetic susceptibility is calculated

$$\chi_q^{-1} = \left(\chi^0_q\right)^{-1} - \left(\chi^0_{loc}\right)^{-1} + \chi^{-1}_{loc}$$

AFM ordering in FeO, q=(π, π, π), ν=0

$$\sum_{\omega,\omega'} \chi_q(\omega, \omega') = \chi_q(T) \propto (T - T_N)^{-1}$$

Results: AFM ordering



AFM ordering in FeO, q=(π, π, π), ν=0

$$\sum_{\omega,\omega'} \chi_q(\omega,\omega') = \chi_q(T) \propto (T - T_N)^{-1}$$

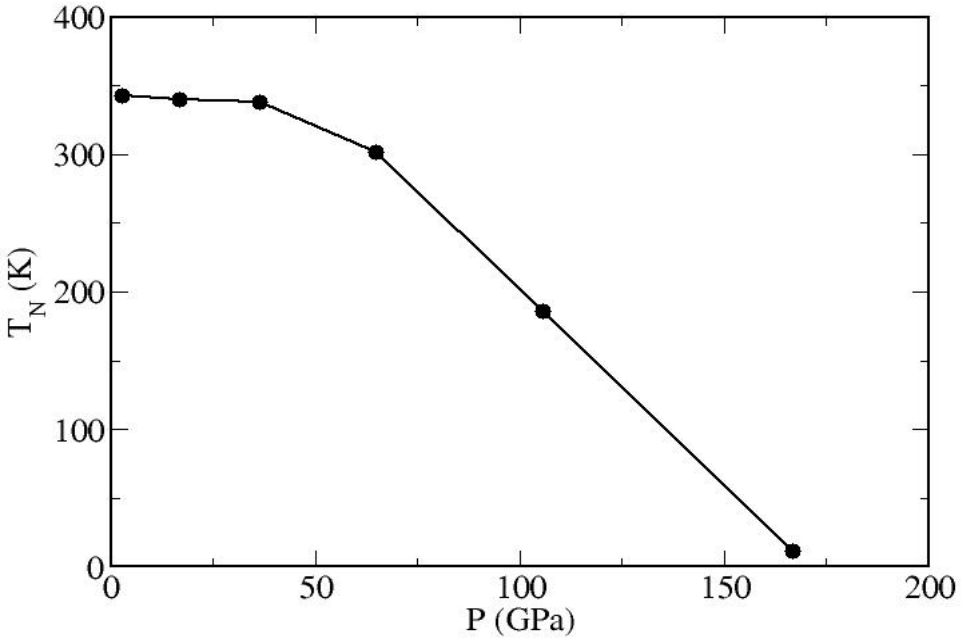
Hubbard U = 7 eV
Hund's J from Yukawa potential

There is AFM ordering as the temperature is decreased; as the extrapolation of inverse bulk magnetic $\chi^{-1} \rightarrow 0$, $T=T_N$.

The Néel temperature decreases monotonically as volume of FeO is decreased.

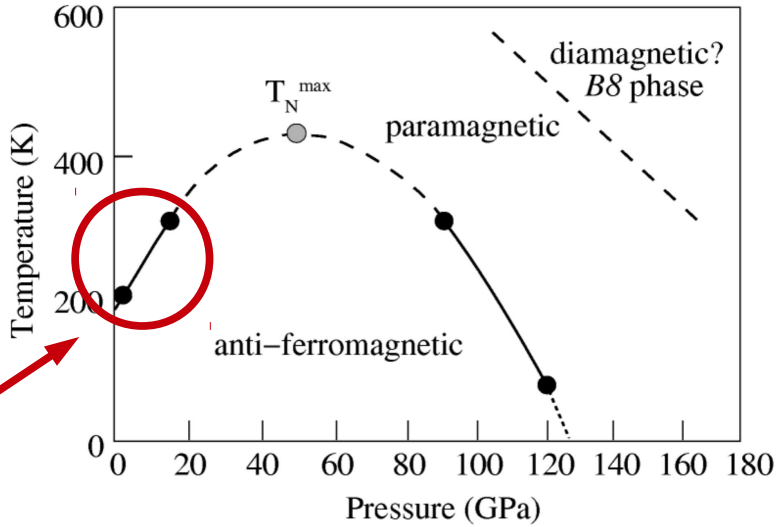
P-V-T given by Mie-Grüneisen equations of state, from R. A. Fischer et al. Earth and Planetary Science Letters 304, 496–502 (2011).

Results: Néel temperature vs. pressure



The Néel temperature decreases slowly at P< 46 GPa, then quickly decays until reaches T_N=0 K at about 320 bohr^3, 170 GPa.

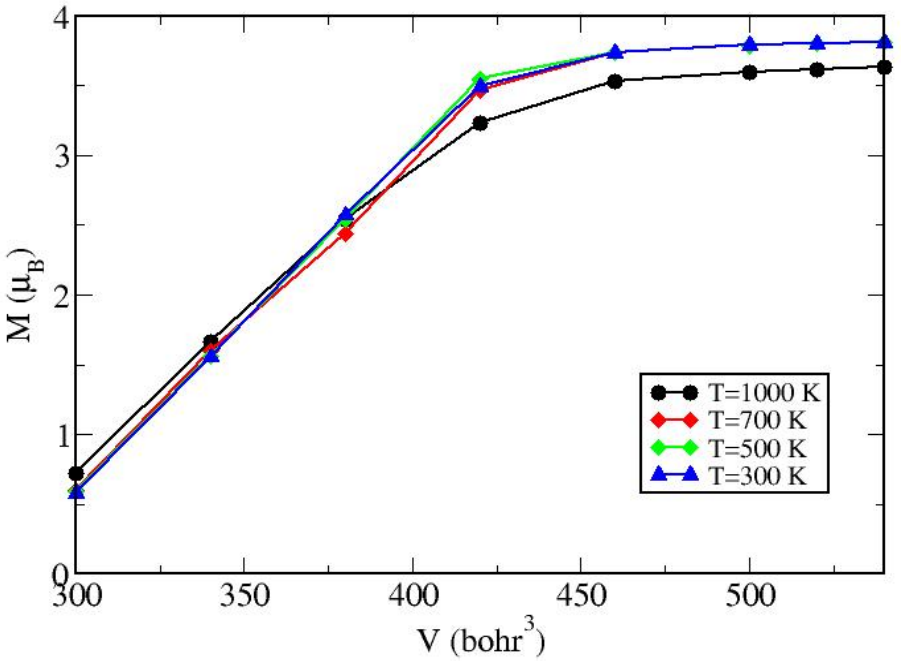
T_N=200 K

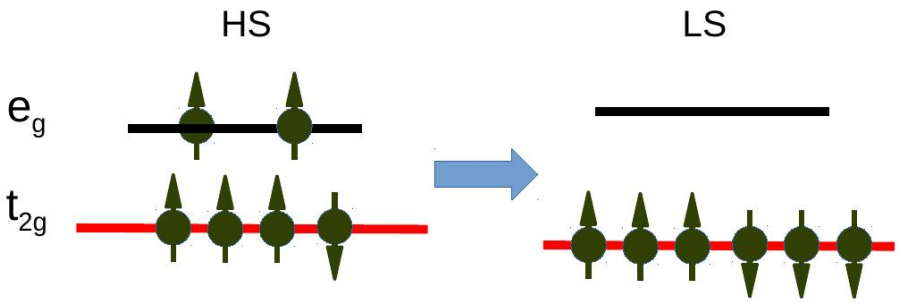


The Néel temperature at ambient pressure from DFT+DMFT is T_N=343 K, higher than experimental result T_N=200 K.

In experiment T_N is enhanced with increased pressure up to 15 GPa; missing in our calculations.

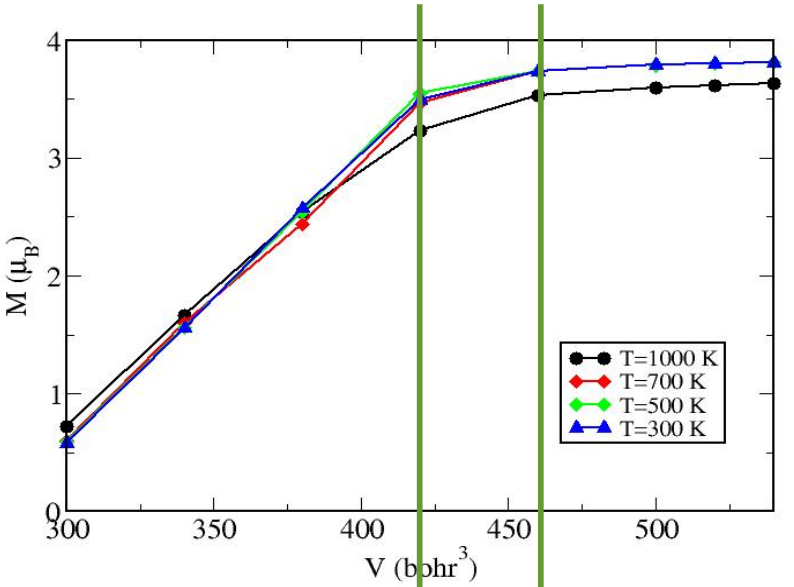
Results: magnetic moment vs. volume

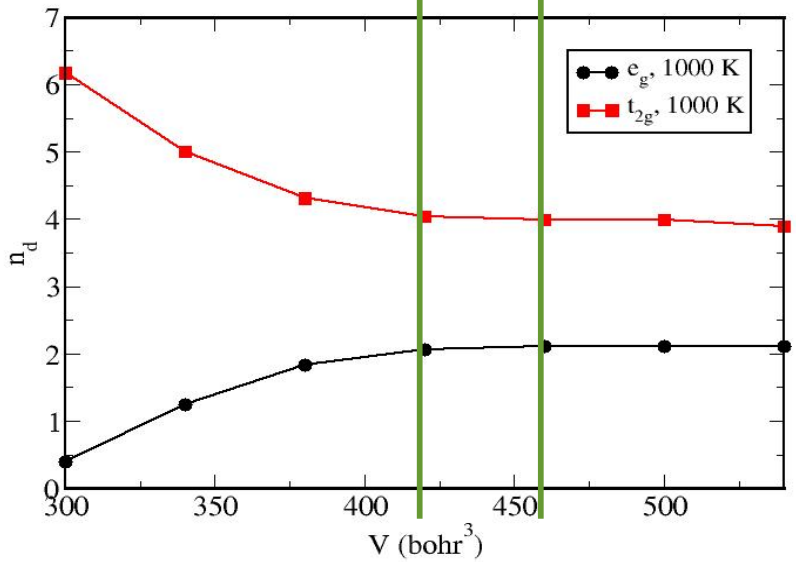




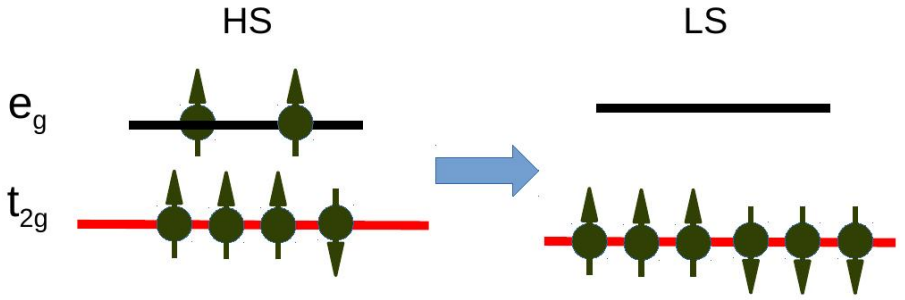
- Magnetic moments of FeO decrease as volume is decreased.
- The M vs. V lines start to converge as temperature is lower than 1000 K; indicate the collapse of magnetic moments is a crossover.
- The collapse of magnetic moments, or the HS-LS crossover is consistent with previous DFT calculations.
- Coexistance of two kinds of magnetic transitions in FeO under pressure: paramagnetic-AFM and HS-LS

Results: occupancy of d-electrons vs. volume



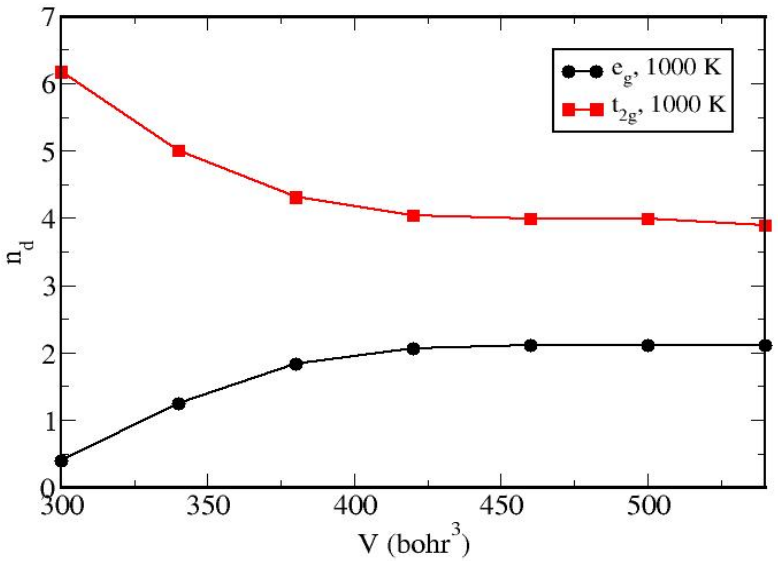


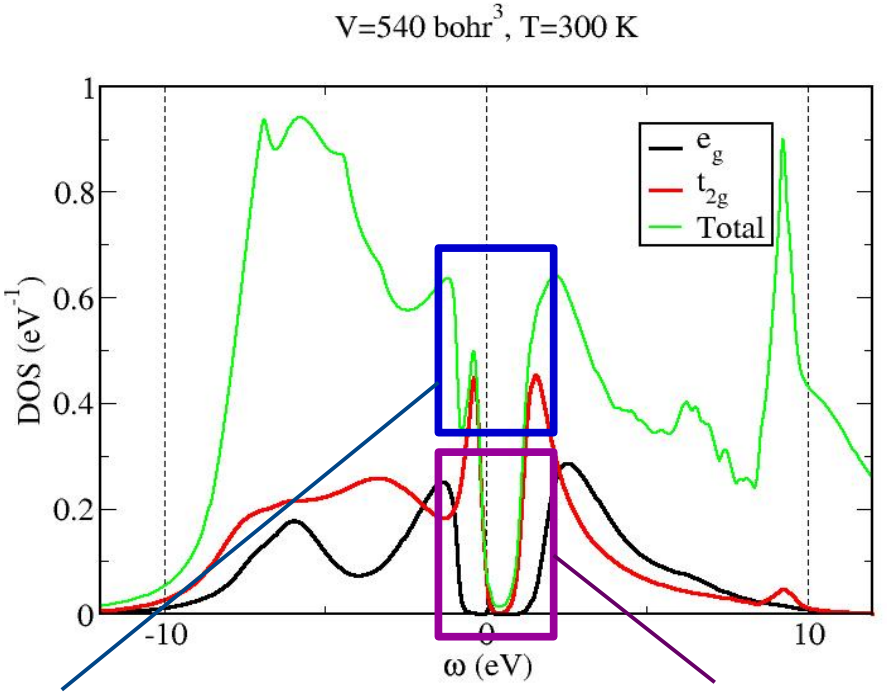
- As volume is decreased, electrons on the e_g orbitals transfer to the t_{2g} orbitals.
- The HS-LS crossover is due to the partitioning and pairing of electrons among the e_g and the t_{2g} orbitals.
- Why there is charge transfer from the e_g orbitals to the t_{2g} orbitals?



Results: DOS

300 bohr^3 540 bohr^3

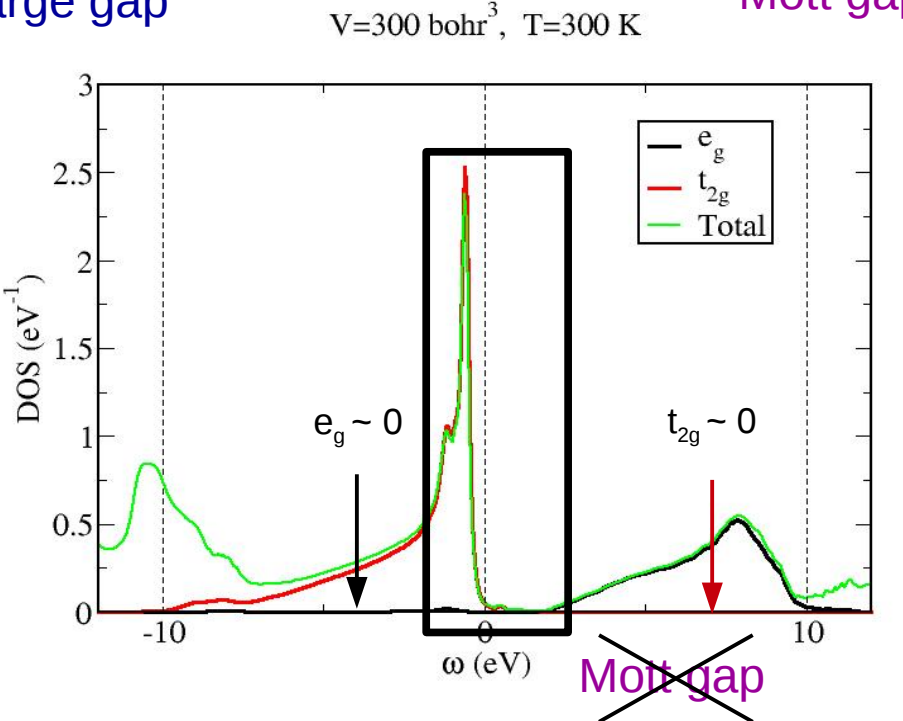




Charge gap

Mott gap

- Charge transfer among the e_g and the t_{2g} orbitals due to DOS transfer among the e_g and the t_{2g} orbitals.
- At V=540 bohr^3, FeO are both Mott and charge transfer insulator.
- At V=260 bohr^3, all d-electrons at E_f, still insulator but no Mott gap.



Mott gap

Conclusions

- There are two kinds of magnetic transitions in FeO under pressure: paramagnetic-AFM transition and the HS-LS crossover.
- The Néel temperature approaches zero at about 320 $bohr^3$, 170 GPa, where the HS-LS crossover is not finished, and the magnetic moments are finite.
- The collapse of magnetic moments is due to the charge transfer among the e_g and the t_{2g} orbitals when external pressure is increased.
- FeO is Mott and charge transfer insulator at ambient pressure; at high pressure FeO is still an insulator, but without Mott gap.
- Constrained LDA for U and J ...

Thank You

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