Spin state and structural stability of ferropericlase up to 30 Mbar

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INTRODUCTION

• As a solid solution of MgO and FeO [$(Mg_{1-x},Fe_x)O$] ferropericlase(fp) might be a major mantle forming phase terrestrial type exoplanets.

• The properties of fp are well characterized within the range of condition typical of the Earth's interior but they need to investigated also in a much broader pressure/temperature range achieved in the interior of larger planets.

• The interplay between a structural change and the spin-state change in iron makes it a non-trivial task.

METHODS

• LDA+U: treat the strong on-site Coulomb interaction of localized electrons in iron oxides, which is not correctly described by standard (LDA or GGA) DFT calculations.

$$E = E_{LDA} + \frac{U}{2}\sum_{I,\sigma} Tr[\boldsymbol{n}^{I,\sigma}(1-\boldsymbol{n}^{I,\sigma})]$$

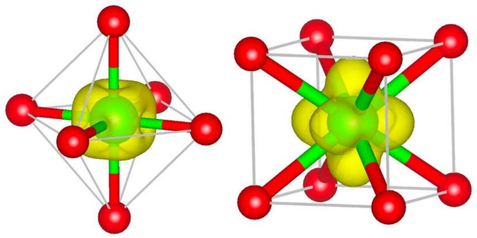
• Phonon calculations were performed using the finite-displacement method implemented in the Phonopy code[1] with the LDA+U calculations from Quantum ESPRESSO. The electronic entropy at high temperatures was obtained using the Mermin functional[2,3]. The final Gibbs free energy computed with the quasi-harmonic approximation calculations, i.e.

$$G(P,T) = G^{QHA}(P,T)$$
$$= H(P,T) - T(S_{elec} + S_{vib} + S_{mag})$$

• For the face-centered cubic phase, B1 phase, we constructed a $2\times2\times2$ supercell with 64 atoms with one iron atom corresponding to the iron concentrations X_{Fe}=0.03125 (fp3). Similarly, a $2\sqrt{2}\times2\sqrt{2}\times4$ supercell has been constructed for B2 phase, which is a body-centered cubic phase. Ferrous iron is the form of iron in both B1 and B2 phase.

STATIC RESULTS

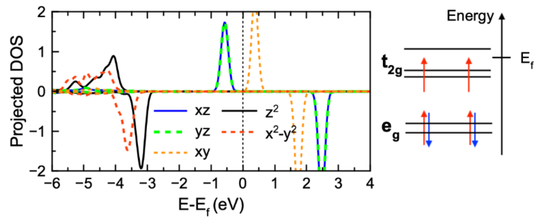
• In the B1 structure, the t_{2g} orbitals have lower energy than e_g orbital. However, in the B2 structure, e_g orbitals have lower energy than t_{2g} orbitals. The lower energy of e_g orbitals in B2 is due to the change of the polyhedron surrounding ferrous iron (Fe^{2+}).



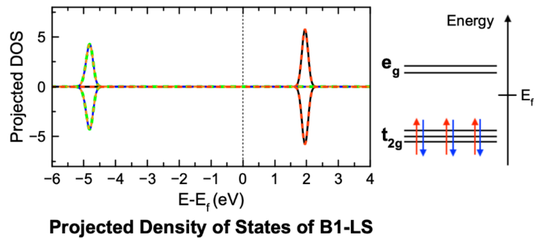
t_{2g} orbitals in octahedra coordinate (B1)

e_{2g} orbitals in cubic coordinate (B2)

• In the B2 structure, four of the six d-electrons of Fe^{2+} occupy the e_g orbital with spin up and spin down. The remaining two electrons occupy two of the three t_{2g} orbitals. Such an occupancy leads to an intermediate-spin state, with S=1.



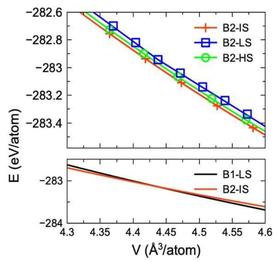
Projected Density of States of B2-IS



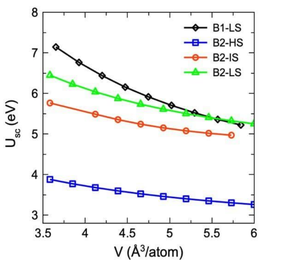
Projected Density of States of B1-LS

• The corresponding self-consistent Hubbard parameters display a strong dependences on volume, structure, and spin states.

• The B2-IS state has lower energy than the B2-HS and B2-LS states at all pressures in static calculations. Furthermore, there is a structural transition between B1-LS and B2-IS in fp3.

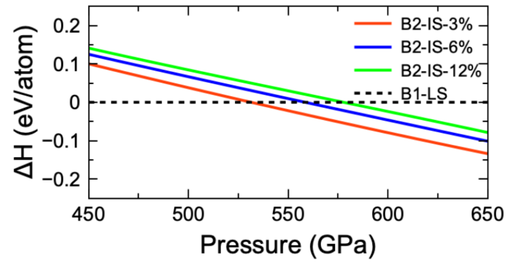


E-V curve of FP3



Self-consistent Hubbard parameters

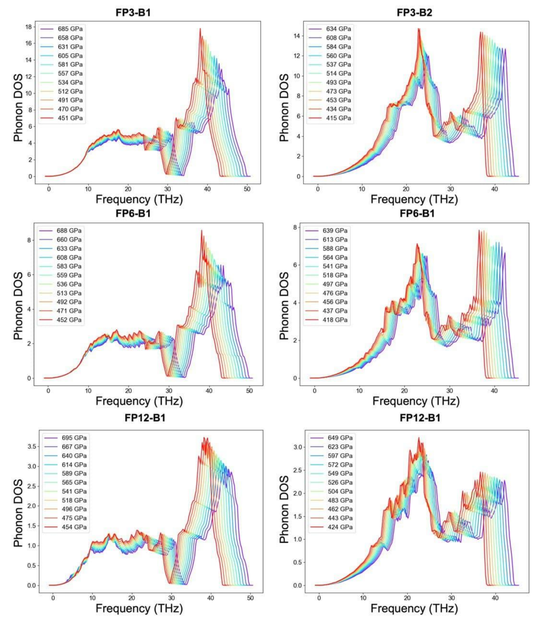
• The current LDA+U_{SC} calculations produce concentration dependent B1-LS to B2-IS transition pressures: 526 GPa, 568 GPa, and 576 GPa in fp3, fp6, and fp12, respectively.



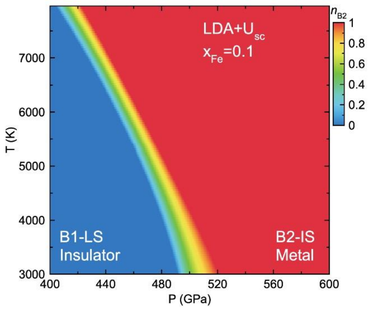
PHONON RESULTS

• Phonon calculations are performed with LDA+U_{SC} at several volumes in both B2-IS and B1-LS states for fp3, fp6, and fp12.

•No imaginary frequency is found in either B2-IS states or B1-LS states within the chosen pressure range. Therefore, both B2-IS and B1-LS states of fp with up do 12.5% iron are dynamically stable.



•To obtain the phase boundary at finite temperatures, we further included the vibrational entropy S_{vib} and electronic entropy S_{elec} described by the Mermin functional..

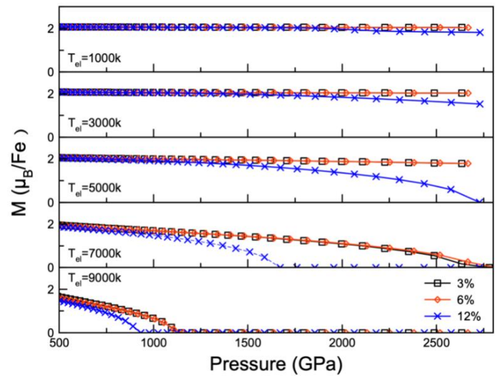


TRANSITION TO B2-LS

•The B2-IS phase is stable up to 2.5 TPa with Tel=1000K.

•With increasing electronic temperature, the electronic entropy destroy magnetization.

•At Tel=5000K, there are signs of a transition between B2-IS to B2-LS for XFe=12%. With higher electronic temperatures and higher Fe concentrations, the IS-LS transition pressure decreases.



SUMMARY AND ACKNOWLEDGMENT

•The intermediate-spin state is the ground state of fp in the B2 structure.

•The self-consistent Hubbard parameters U obtained from LDA+Usc calclations depends strongly on pressure, structure, and spin state.

•There is possible transition from B2-IS to B2-LS in fp system, which depends on the electronic temperature.

This work is supported by the National Science Foundation with Grant No. NSF awards EAR_1918126.

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