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Planetary Interiors: Brucite Phase Transition

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Introduction

Brucite, $Mg(OH)_2$, is a hydrous mineral with a role in the transportation of water in the Earth's interior. It is has the P$\bar{3}$m1 structure shown in Figure 1. Due to the layered structure of P$\bar{3}$m1, it is expected to form a superionic state, where the hydrogen ions (protons) are free to move in the layer, before decomposing into magnesium oxide (MgO) and water. Recent studies have found a stable phase at higher pressure [1]. This is the $P4_32_12$ structure shown in Figure 2. This should allow Brucite to be stable deeper in the Earth's mantle and play a more important role in the transport of water. This project is a study into this phase transition and the stability of the both phases.

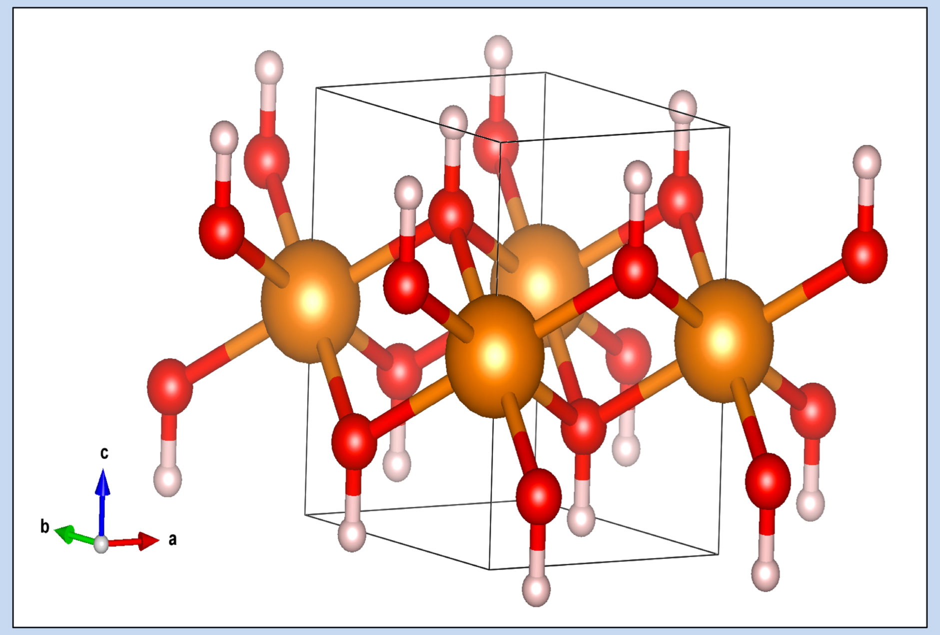

Figure 1: P$\bar{3}$m1 structure

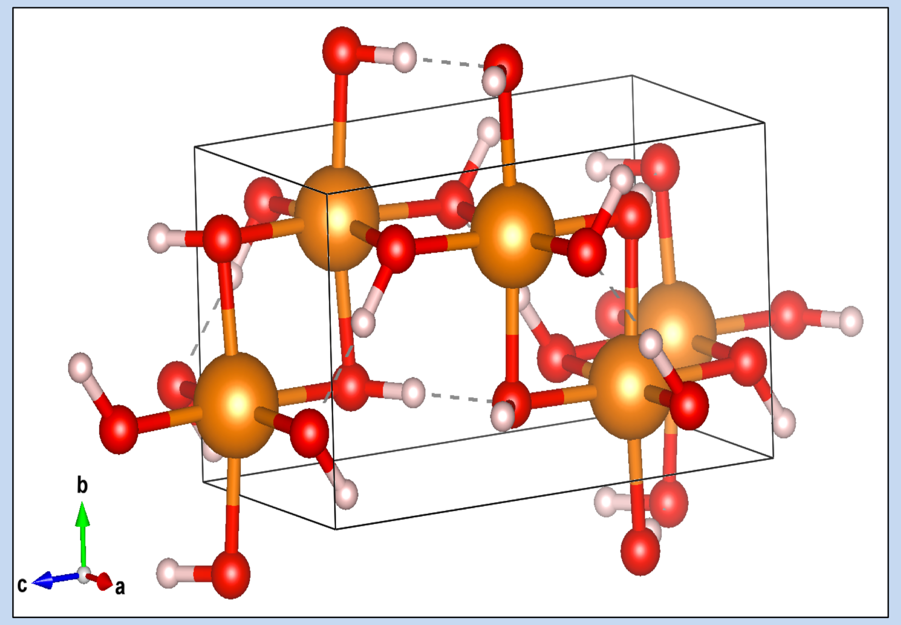

Figure 2: $P4_32_12$ structure

Methods

Structure optimisations at various pressures were carried out and their energies compared to find when the $P4_32_12$ phase becomes more favourable. Molecular dynamics simulations using density functional theory (DFT) were then carried out at various temperatures on these optimised structures. The mean square displacement (MSD), diffusion constants, radial/partial distribution functions (RDF/PDF), hydrogen distributions and simulations were studied to classify the states.

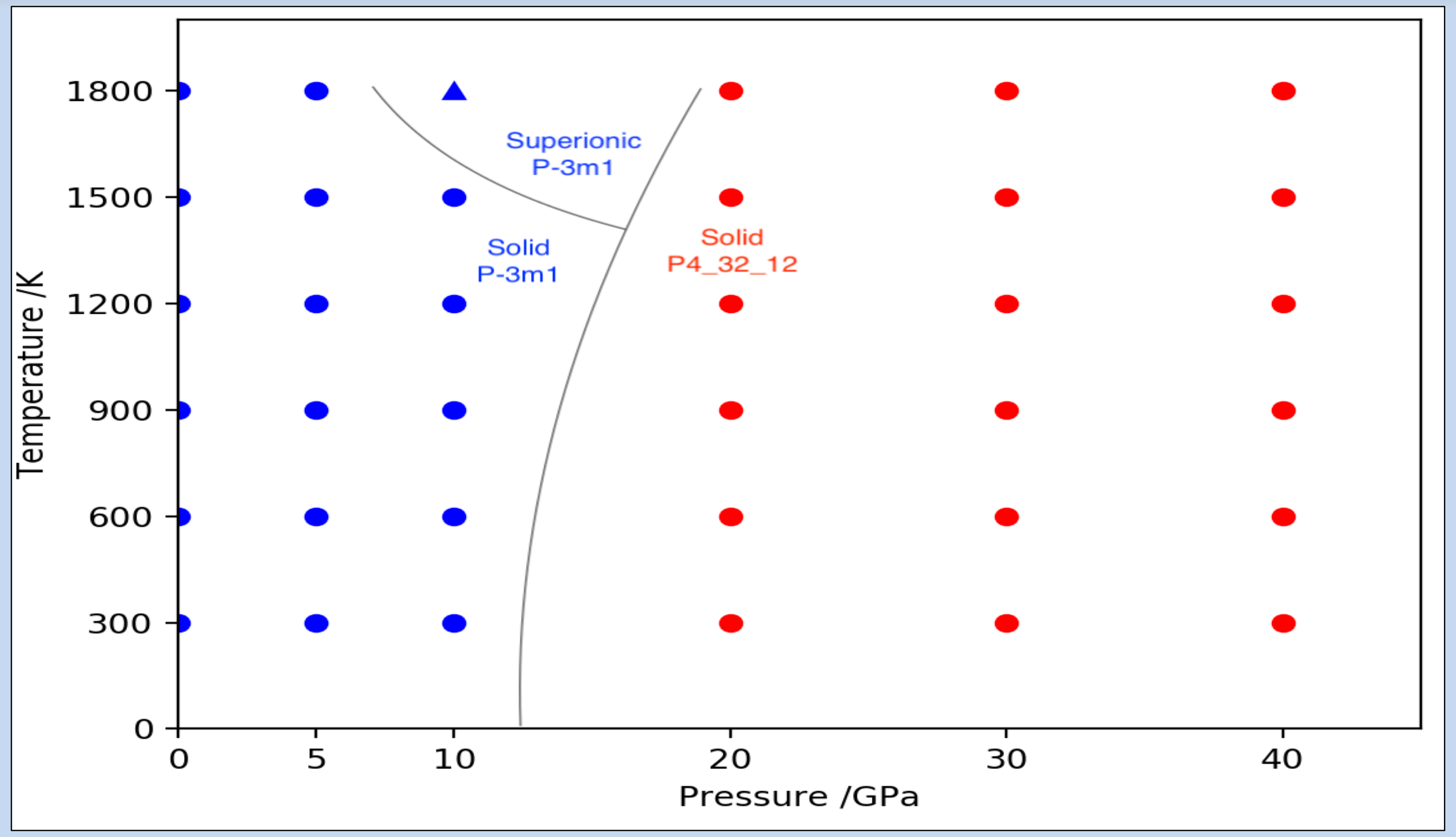

Figure 6: PT diagram approximation for Brucite

Results

The phase transition is at roughly 12 GPa at 0 K based on the energy of the optimised states shown in Figure 3. The P$\bar{3}$m1 phase was found to be solid up to 10 GPa and 1800 K except for exactly at 10 GPa and 1800 K, where the protons become superionic. The proton diffusion constant of the superionic state is 0.230 $Å^2ps^{-1}$, which is proportional to the gradient of the MSD line in Figure 4. The liquid shape of the RDF in Figure 5 is also result of the free moving protons but more solid Mg and O ions. The $P4_32_12$ phase was found to be solid between 20-40 GPa up to 1800 K.

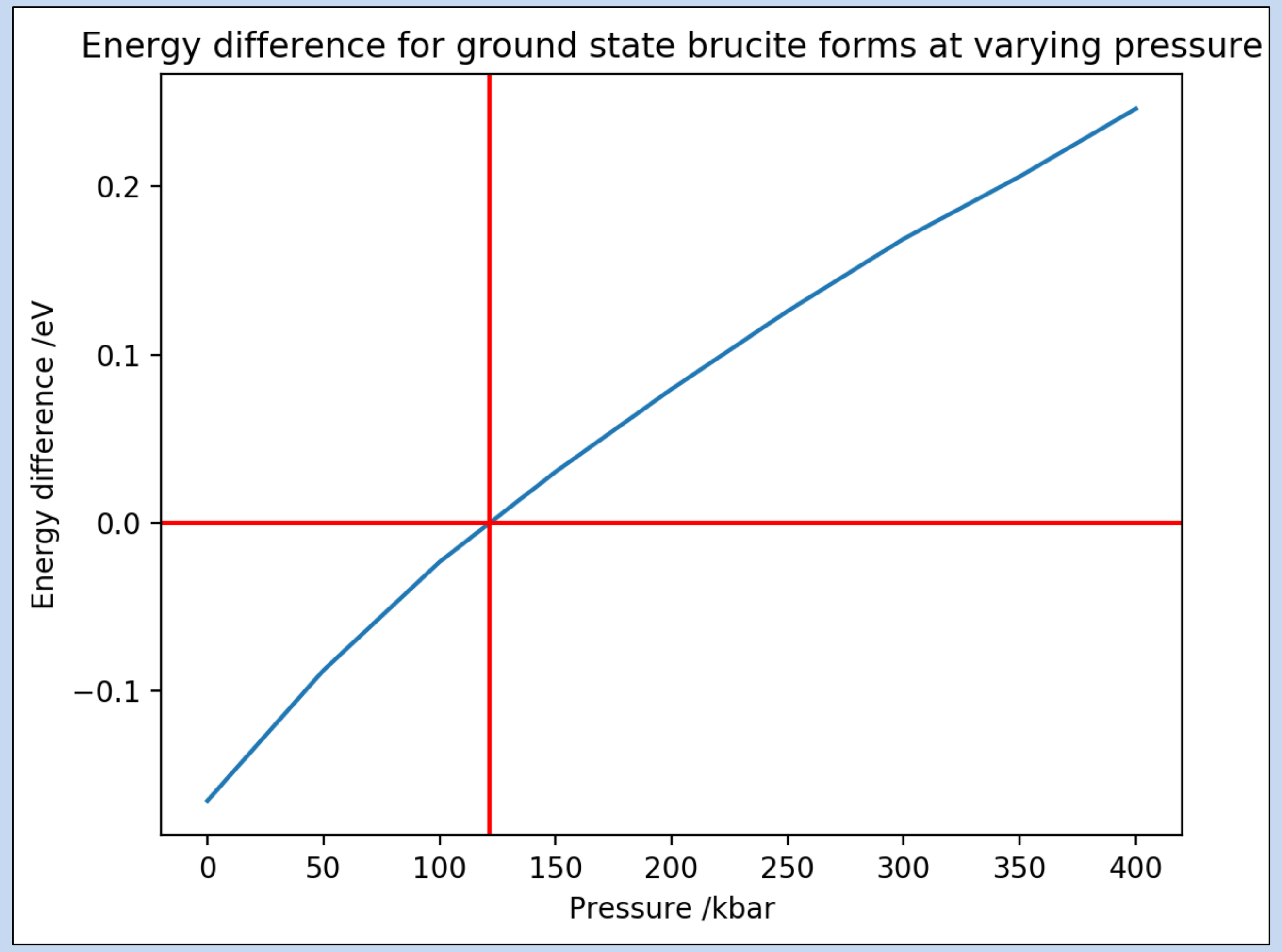

Figure 3: Energy difference of P$\bar{3}$m1 minus $P4_32_12_1$ for ground states

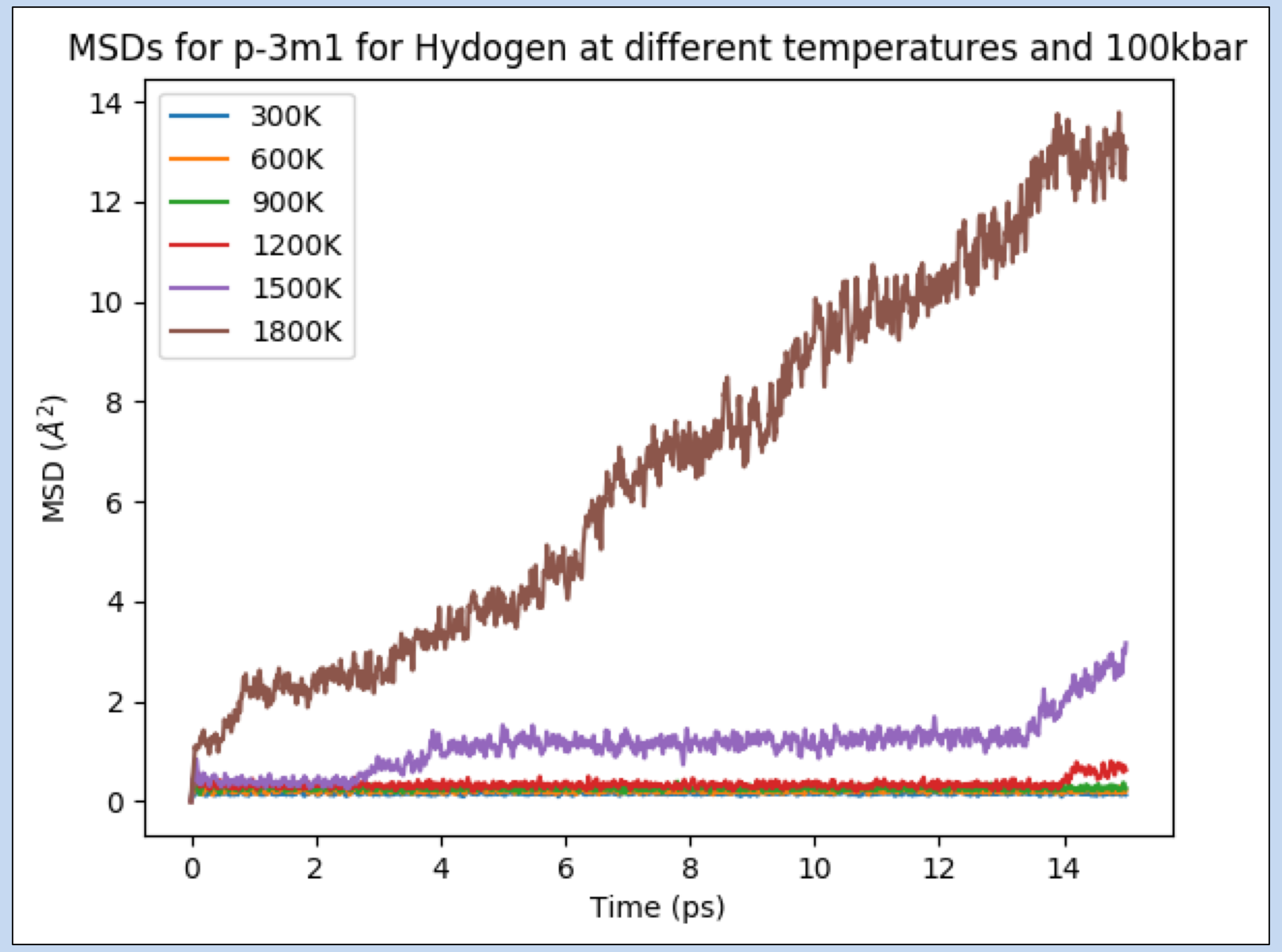

Figure 4: MSD for P$\bar{3}$m1 at 10 GPa for varying temperatures

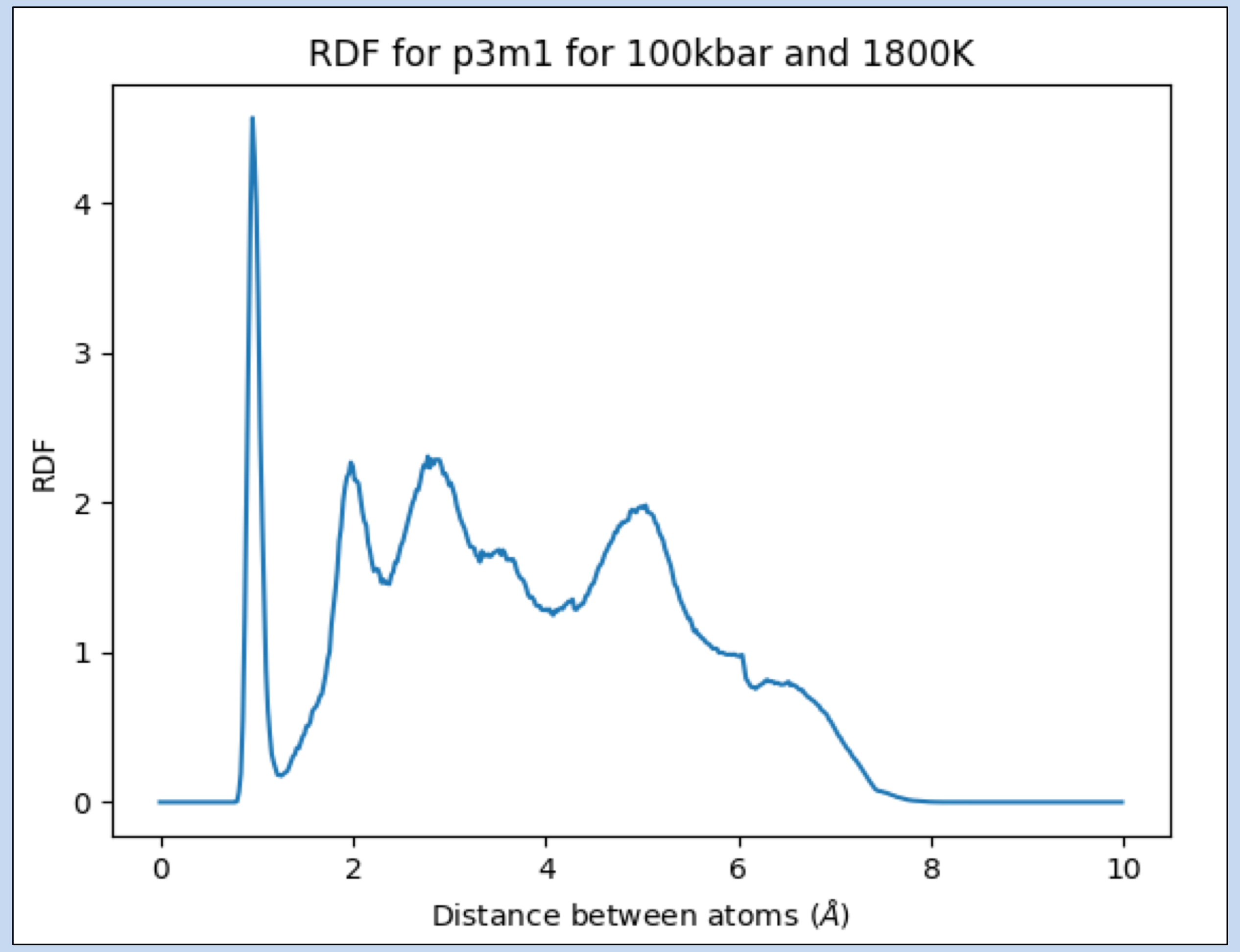

Figure 5: RDF for P$\bar{3}$m1 at 10 GPa 1800 K

Conclusions

The estimated pressure temperature (PT) graph is shown in Figure 6. This shows a rough approximation of the phase transition from P$\bar{3}$m1 to $P4_32_12$. The initial phase did turn superionic as expected when the pressure and temperature were increased to 10 GPa and 1800 K. The protons in this state had diffusion constant of the order 0.1 $Å^2ps^{-1}$. The second phase was more stable at higher pressures and temperatures and remained solid up to 40 GPa. This suggests Brucite is indeed stable deeper into the mantle of the Earth and therefore is likely much more prevalent in transportation of water than initially thought.

References

[1] Hermann & Mookherjee, High pressure phase of brucite stable at Earth's mantle transition zone and lower mantle conditions (2016)

Acknowledgements

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