First-principles an-harmonic free energy calculation of iron up to core conditions: Implications for Earth inner core crystal structure

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Although it is now over 80 years since the discovery of the Earth's Fe-rich solid inner core (IC) by Lehmann, its crystal structure remains controversial. Experimentally, this can be attributed to the technical difficulty to reach the IC conditions in the lab (e.g., using DAC technique). Attempts to apply theory to predict stable phases requires free energy calculations, and for the current applications there are two main challenges: first, at such high temperatures (> 5000 K, near melting) an-harmonic effects are significant[(1)]; second, many-body effects (correlation) are important[(2)], such that standard *ab initio* methods (e.g., DFT) fail to reproduce experimental data for moderate temperature/pressure conditions[(3)]. However, treating both effects robustly is computationally expensive using standard methods, and has generally been considered inaccessible even with the advanced computing power available.

To tackle the first difficulty we utilized our recently introduced harmonically-mapped averaging (HMA) method[(4-5)] to measure an-harmonic free energy with orders of magnitude speedup in computation compared to conventional methods. As for the second complication, we went beyond the standard DFT model and used its combination with DMFT (dynamical mean-field theory), DFT+DMFT, to explicitly capture the many-body effects and their impact on the relative phase stability. However, since the DMFT is computationally demanding (cannot go beyond few atoms if local many-electron effects are treated exactly), and since the lattice (or static) energy is a zero-order term and quasi- and an-harmonic contributions are higher-order, we used DFT+DMFT to model only the former, applied standard DFT for the latter contribution. We employ a self-consistent in the charge-density DFT+DMFT scheme; the local many-electron problem on the Fe 3d shell is solved using a numerically-exact quantum Monte Carlo approach.

We start by applying this hybrid DFT+DMFT approach to the low pressure/temperature region of the phase diagram, where experimental data are available, and find excellent agreement in c/a-ratio, equation-of-state. Then, we apply this approach to the high pressure/temperature region using the most likely Earth's IC candidate structures (namely: hcp, bcc, and fcc). We report findings regarding the phase relation between these phases in the vicinity of the IC conditions.

References

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