Phase Transition of Iron Calculated by Anharmonic Phonon Method Based on Machine Learning Force Field

Feng-ning Xue,[1] Yong-Chao Wu[1], Yong Lu [2]*, Jian-Li Shao[1]*

[1]State Key Laboratory of Explosion Science and Safety Protection, Beijing Institute of Technology,

Beijing, 100081, China

[2]College of Mathematics and Physics, Beijing University of Chemical Technology, Beijing 100029, China

Electronic Supporting Information

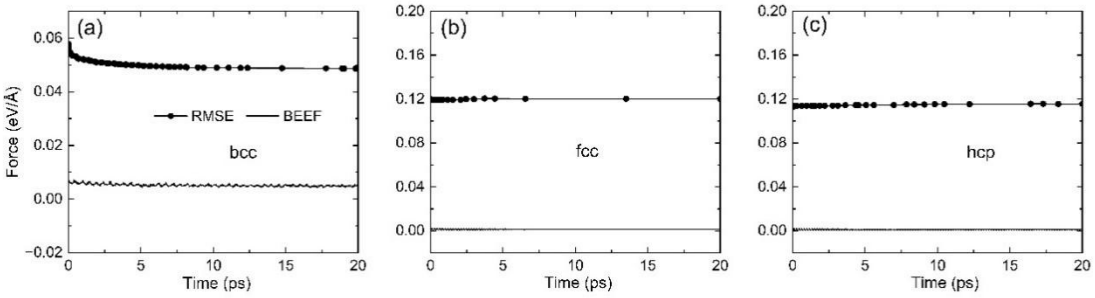

Figure S1 The root-mean-square error of force (RMSE) and the Bayesian error estimation of force (BEEF) (eV/Å^3) change over the last 20 ps of the force field prediction compared to the AIMD result for bcc(a), fcc(b) and hcp(c), respectively**.**

The BEEF is an estimate of the out-of-sample error, which is quantitatively closer to the true error and indicates the progress of the force field training, averaging the error that occurs when considering random new structures of the same coefficient. The out-of-sample error should be small for potential functions with high training accuracy. This is because if the Bayesian error of an atom is above the threshold, the structure will be added to the candidate list of new training structures to be used as a new training set for machine learning, thus reducing the Bayesian error. The RMSE is the in-sample error, an error analysis of the prediction results of the training data and the ab initio results. When the training accuracy of the potential function reaches the convergence threshold, the BEEF error of the force no longer has a large change and will converge to a small fluctuation around a constant with 10-4 eV/Å. The RMSE error converges to 0.04 eV/Å, 0.12 eV/Å, and 0.11 eV/Å for bcc, fcc, and hcp Fe, respectively.

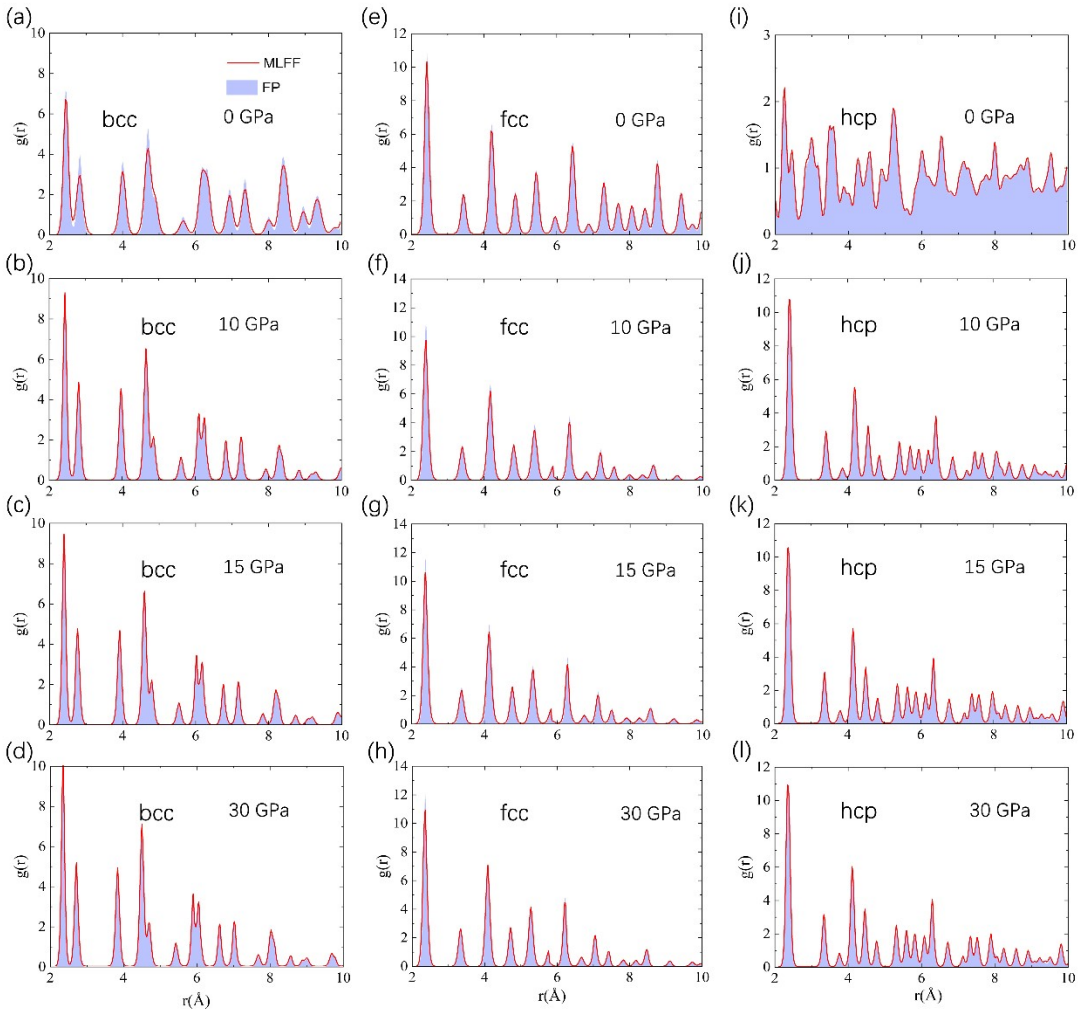

Figure S2 The pair correlation function of (a-d) bcc, (e-h) fcc, and (i-l) hcp phase of iron obtained by AIMD and FFMD. The purple area is the AIMD calculation results and the red line is the FFMD results.

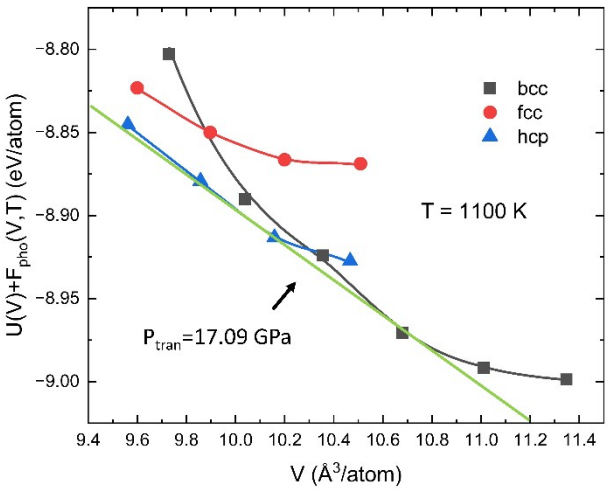

Figure S3 The phase transition threshold of Fe at 1000K calculated by AIMD.

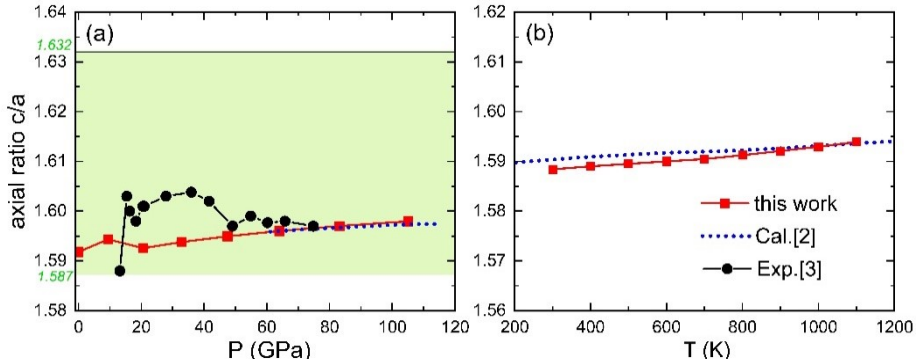

Figure S4 The c/a ratio of hcp Fe at different pressures and temperatures. The green shaded area in (a) was obtained from [1]. The red lines are the results of the calculations in this paper, the blue dotted line is the reference of the theoretical calculations [2], and the red data is the experimental values [3]. Note that (a) was calculated at 300 K and 0 GPa.

There are conflicting findings in theoretical and experimental studies regarding the pressure dependence of the c/a ratio in the hcp phase. Some studies report a trend of the c/a ratio of hcp iron decreasing with increasing pressure, while others report seemingly no trend, a very weak trend, or a trend that changes with pressure [1]. Sha et al. [2] reported that the c/a ratio of hcp Fe increases with increasing pressure in theoretical calculation. We considered the c/a ratio of hcp Fe at different pressures and temperatures in Fig. S4. The range of c/a ratio of hcp Fe are all within the range reported in [1]. The relationship between c/a ratio of hcp Fe and pressure in Fig. S4 is in agreement with Sha et al. [2]

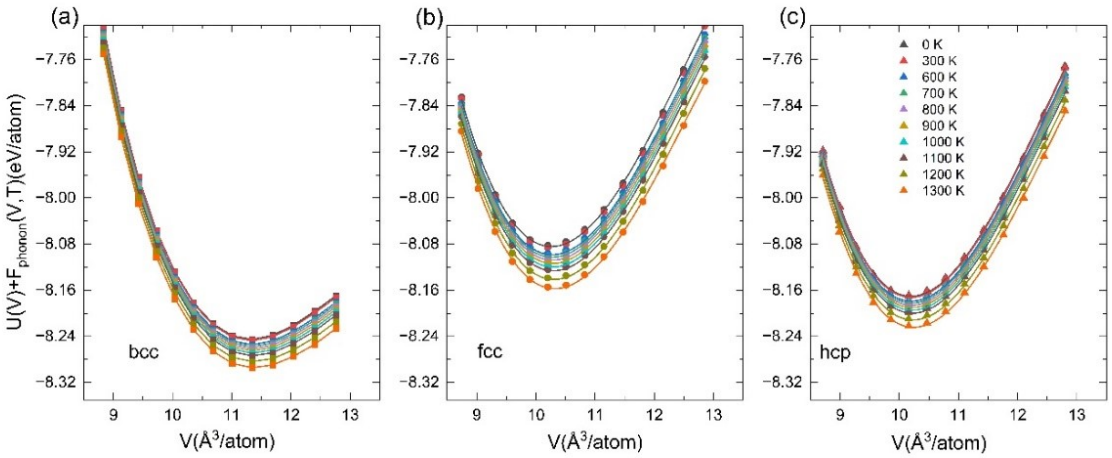

Figure S5 Free energy F (V, T) versus volumes of Fe for bcc (solid line), fcc (dotted line), and hcp (dashed line) phases at different temperatures through the QHA method.

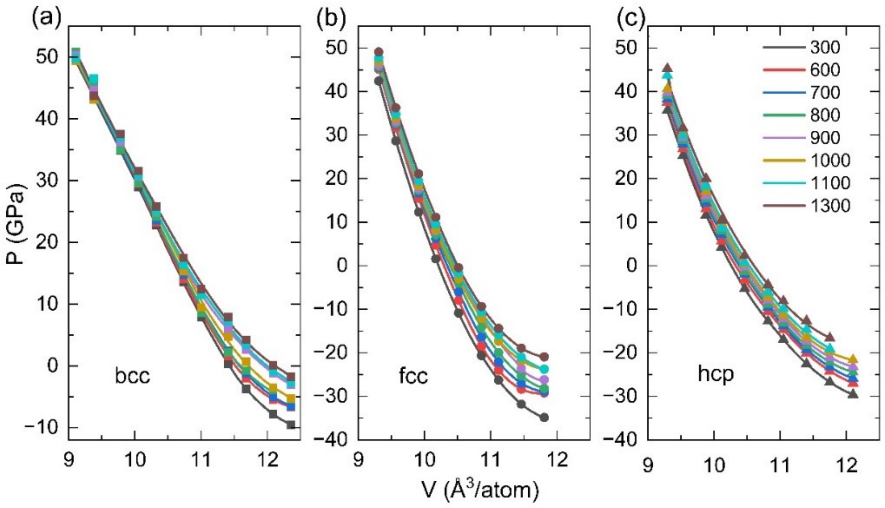

Figure S6 Pressure-volume relation obtained from FFMD of Fe for bcc phase (a), fcc phase (b), and hcp phase (c), respectively.

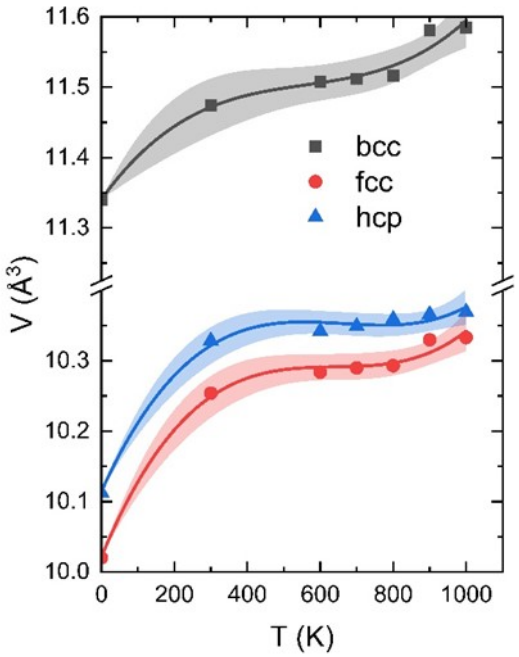

Figure S7 Volume-temperature relation obtained from FFMD of Fe for bcc phase, fcc phase, and hcp phase, respectively.

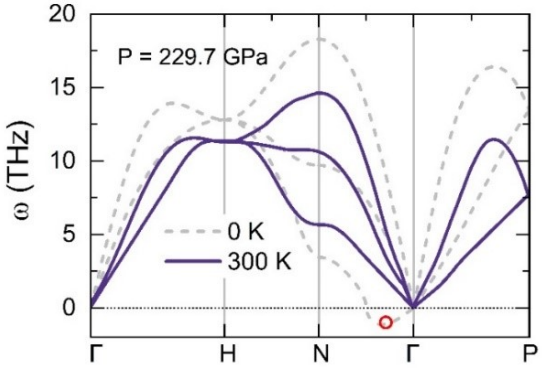

Figure S8 The anharmonic phonon dispersion curve of bcc Fe at 229.7 GPa. The grey dot is obtained at 0 K, and the purple line is calculated at 300 K. The **q** = (1/8, 0, 0) is marked in (a) with a circle.

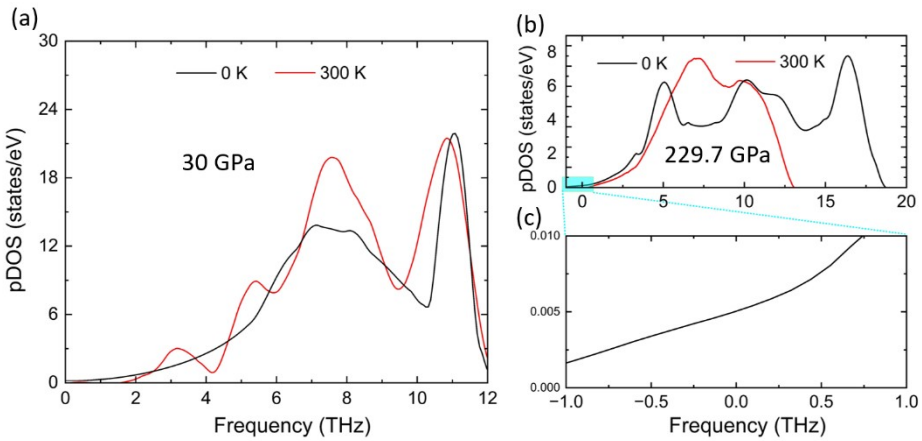

Figure S9 The calculated phonon density of states (pDOS) of bcc at 30 GPa and 229.7GPa, respectively. The black line and red line were calculated at 0 K and 300 K, respectively.

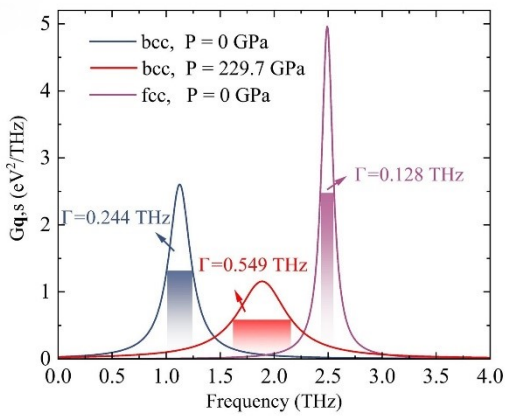

Figure S10 The power spectrum $G_{\mathbf{q},s}$ and linewidth Γ. Note that the blue, red, and purple lines are for 0 GPa bcc, 229.7 GPa bcc, and 0 GPa fcc Fe, respectively. The calculation temperature is 300 K.

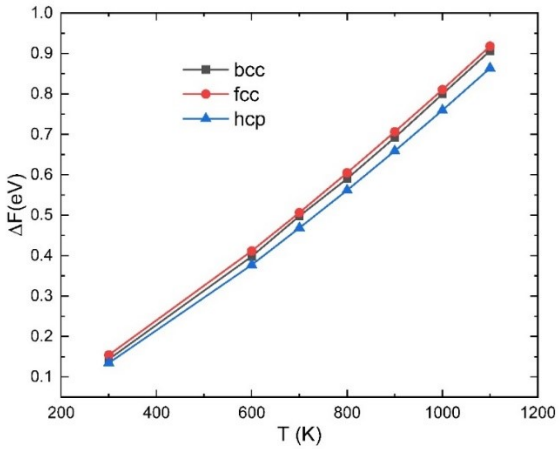

Figure S11 The energy difference $\Delta F=-T(S_{anharm}-S_{harm})$ of bcc, fcc, and hcp phase of Fe as a function of temperature at V_{eq} (T=0K).

Table S1 The harmonic (0 K) and anharmonic (300 K) phonon frequencies (THz) of the transverse acoustic branch (TA) and longitudinal acoustic branch (LA) for bcc, fcc, and hcp at phases **q** = (1/8, 0, 0), respectively.

Branch	T(K)	bcc(0 GPa)	bcc (30 GPa)	fcc	hcp
TA1	0	1.625	2.978	2.579	2.679
	300	1.125	1.258	2.489	2.237
TA2	0	1.801	4.258	2.589	2.741
	300	1.626	5.072	2.493	1.964
LA	0	3.173	7.830	4.860	4.656
	300	2.909	6.065	5.053	4.238

Reference：

[1] Fischer and Campbell, The axial ratio of hcp Fe and Fe–Ni–Si alloys to the conditions of Earth's inner core, American Mineralogist (2015) 100: 2718–2724

[2] X. Sha and R.E. Cohen, Thermal effects on lattice strain in ε-Fe under pressure, Phys.Rev.B **74**, 2006, 064103.

[3] A. P. Jephcoat, H. K. Mao, and P. M. Bell, Static compression of iron to 78 GPa with rare gas solids as pressure-transmitting media, J. Geophys. Res, **91**, 1986, 4677–4684.