CompMatPhys Report

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July 10 2026

This report summarizes the results of the volume optimization project. Calculations were conducted using `Quantum ESPRESSO` via the `ASE` Python API package. The original crystal under study is an ideal HCP crystal of iron and aluminium, with an orthorombic unit cell of volume 56.050 Å^3 ($a = 2.7061$ Å, $b = 4.41901$ Å, $c = 4.6871$ Å). The crystal exists in space group 59 (P m m n), with Fe atoms at Wyckoff positions $2a$ and Al atoms at $2b$. The structure is shown in Figure 1.

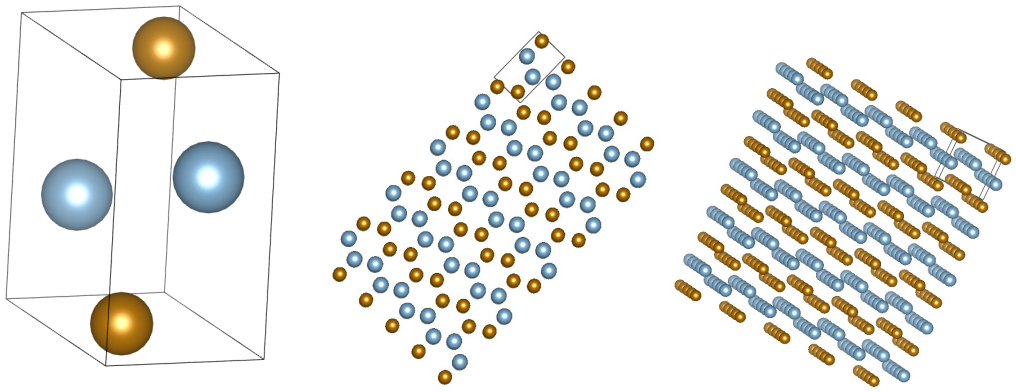

Figure 1: Views of the FeAl crystal and unit cell.

1 Volume Optimization

The unit cell was isotropically scaled to five volumes (0.80, 0.85, 0.90, 0.95, and 1.00 times the original 56.050 Å^3), and the total energy was computed at each volume with Quantum ESPRESSO (PBE PAW pseudopotentials, $E_{\text{cut}}^{\text{wfc}} = 70$ Ry, $E_{\text{cut}}^{\rho} = 700$ Ry, a $6 \times 4 \times 4$ k-mesh, Marzari-Vanderbilt smearing with $\sigma = 0.005$ Ry, and an SCF convergence threshold of 10^{-8}). The resulting E-V points were fit to a Birch-Murnaghan equation of state using ASE's `EquationOfState` module, giving

$$V_0 = 48.940 \text{Å}^3, \qquad E_0 = -10034.793 \text{ eV}, \qquad B_0 = 170.55 \text{ GPa}.$$

The optimized volume is about 12.7% smaller than the nominal (unrelaxed) cell volume, indicating the as-given structure was not volume-relaxed at this level of theory.

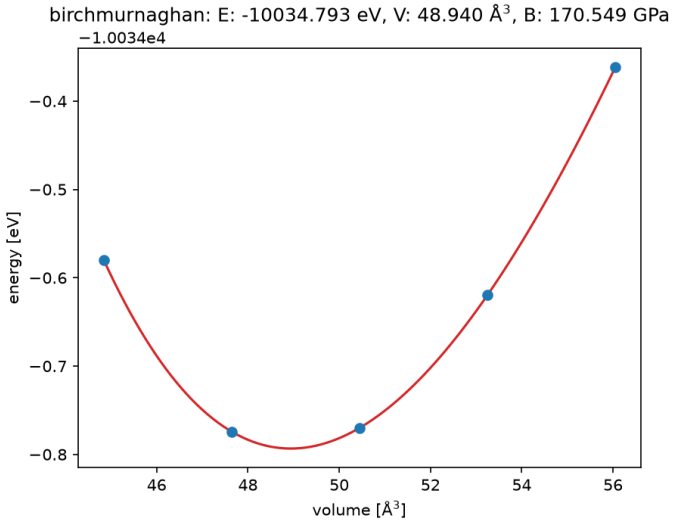

Figure 2: Birch-Murnaghan equation of state fit to the E-V data.

2 Cell Shape Optimization

Cell shape optimization was performed on the ratio $\frac{b}{a}$, keeping the ratio $\frac{c}{a}$ fixed at its original value, $c/a = 1.7320$, and the volume fixed at the optimized value from Section 1, $V_0 = 48.940$ Å^3. For each of eight target b/a ratios (the original ratio $b_0/a_0 = 1.6330$ scaled by factors of 0.97 to 1.04), a, b, and c were solved for analytically to satisfy $abc = V_0$ at the fixed c/a, and an SCF energy was computed at each point with the same medium-precision settings as Section 1.

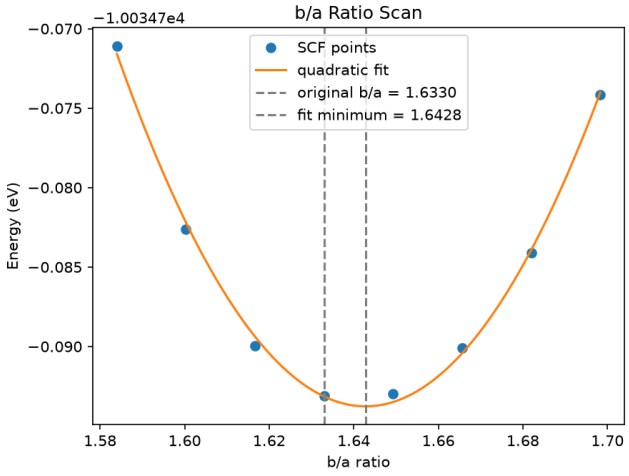

Figure 3: Energy versus b/a ratio at fixed volume V_0 and c/a.

A quadratic fit to the eight points gives a minimum at $b/a \approx 1.6428$, only 0.6 meV below the energy at $b_0/a_0 = 1.6330$, itself the lowest-energy point sampled. The original b/a and c/a ratios are thus already close to optimal once the volume is relaxed, and the energy scale here is ≈ 1 order of magnitude smaller than for the volume optimization—the shape dependence is much weaker.

Rebuilding the cell at this ratio (again fixing $c/a = 1.7320$ and $abc = V_0$) gives the optimized lattice lengths

$$a = 2.5813\text{Å}, \qquad b = 4.2406\text{Å}, \qquad c = 4.4709\text{Å} \qquad (V = 48.940\text{Å}^3),$$

which, with atoms still at their original fractional coordinates, is carried into the position relaxation in Section 3.

3 Atomic Position Relaxation

Every calculation so far used a rigid `scf` run, so Fe (Wyckoff $2a$) and Al ($2b$) remained at their ideal, as-given free-parameter values, $z_{\mathrm{Fe}} = 0.91667$ and $z_{\mathrm{Al}} = 0.41667$. A `relax` calculation (fixed cell, `ion_dynamics = bfgs`) was run on the Section 2 cell to find the true equilibrium positions, using $E_{\mathrm{cut}}^{\mathrm{wfc}} = 70$ Ry, $E_{\mathrm{cut}}^{\rho} = 700$ Ry, a $6\times4\times4$ k-mesh, Marzari-Vanderbilt smearing with $\sigma = 0.005$ Ry, and a 10^{-9} SCF threshold.

BFGS converged in 7 ionic steps (8 SCF cycles), lowering the total force from 0.034 to 0.001 Ry/bohr and the total energy from -10034.793766 eV to -10034.876663 eV, a further 82.9 meV.

Site symmetry pins the x and y coordinates of all four atoms; only the free z parameter relaxed:

$$z_{\mathrm{Fe}}:\ 0.91667 \to 0.90248\ (\Delta z = -0.0142,\ -0.063\text{Å}),$$

$$z_{\mathrm{Al}}:\ 0.41667 \to 0.39418\ (\Delta z = -0.0225,\ -0.101\text{Å}).$$

Each symmetry-related partner site shifts by the same amount in the opposite direction, being fixed at $1 - z$. Al displaces about 60% further than Fe.

4 Full Optimization (vc-relax)

Sections 1–3 optimized volume, shape, and positions one at a time, each holding the other degrees of freedom fixed. To relax all of them simultaneously, a `vc-relax` calculation was run starting from the Section 3 relaxed structure, at higher precision ($E_{\mathrm{cut}}^{\mathrm{wfc}} = 90$ Ry, $E_{\mathrm{cut}}^{\rho} = 900$ Ry, a $14\times8\times8$ k-mesh, 10^{-9} SCF threshold).

BFGS converged in 10 ionic steps (11 SCF cycles), meeting all three criteria: energy change $< 10^{-4}$ Ry, max. force $< 10^{-3}$ Ry/bohr, and cell gradient error < 0.5 kbar (reached 0.44 kbar, with the trajectory pressure at that step $P = 0.14$ kbar, down from -3.2 kbar initially). A separate, higher-accuracy static recalculation at the converged geometry—not itself subject to the convergence check—reports $P = 1.07$ kbar; given $B_0 = 170.55$ GPa, this residual corresponds to a further volume change of only $\Delta V/V \approx P/B_0 \approx 6\times10^{-4}$, well below other sources of numerical error in the calculation. The total energy dropped further, from -10034.876663 eV to -10035.141158 eV (-264.5 meV). The cell remained orthorhombic (no shear developed), but its shape changed substantially even though the volume barely moved:

$$a: 2.5813 \to 2.7416\text{Å}\ (+6.2\%),\quad b: 4.2406 \to 4.2420\text{Å}\ (\approx 0\%),\quad c: 4.4709 \to 4.1890\text{Å}\ (-6.3\%),$$

$$V: 48.940 \to 48.718\text{Å}^3\ (-0.45\%),\qquad b/a: 1.6428 \to 1.5473,\qquad c/a: 1.7320 \to 1.5279.$$

So the $c/a = 1.7320$ constraint held fixed throughout Sections 2–3 was, in fact, far from the true equilibrium—only the volume and b/a ratio had actually been optimized.

The x and y coordinates remained pinned by symmetry. Notably, the z parameters relaxed back toward their original, ideal values once the cell was free to move with them:

$$z_{\mathrm{Fe}}:\ 0.90248 \to 0.91984\ (\text{original: } 0.91667),\qquad z_{\mathrm{Al}}:\ 0.39418 \to 0.41550\ (\text{original: } 0.41667).$$

This suggests the sizable z-shifts found in Section 3 were largely an artifact of relaxing positions inside a cell shape that was not itself at equilibrium, rather than a real deviation from the ideal HCP structure.