Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Temperature and pressure-induced strains in anhydrous iron trifluoride polymorphs

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Convergence analysis of computational parameters

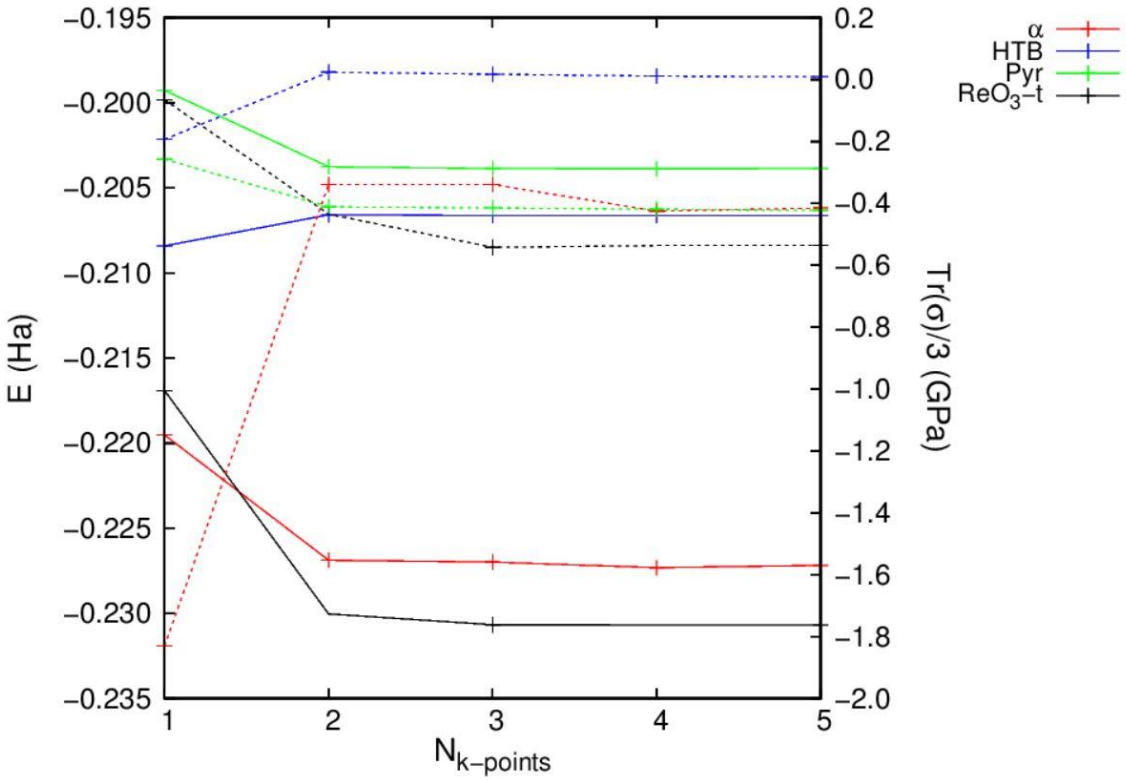

Fig. S1: Calculated hydrostatic pressure as a third of the stress tensor (σ) trace) and energy (E) for the four FeF3 polymorphs (α, HTB, *Pyr*, and ReO3-type) in terms of the *k*-points number, $N_{k\text{-points}}$, of the sampling grid. Solid and dashed lines stand for, respectively, total energy and stress tensor.

Table S1: Kinetic energy cutoff values and *k*-point grids ($N_{k\text{-points}}$x$N_{k\text{-points}}$x$N_{k\text{-points}}$) after convergence analysis. Using these values, energies and stress tensors are converged, respectively, to the order of 10^{-5} hartree and 0.5 GPa

Phase	α	HTB	*Pyr*	ReO_3
$N_{k\text{-points}}$	5	4	4	5
E_{cut}	70	70	70	70

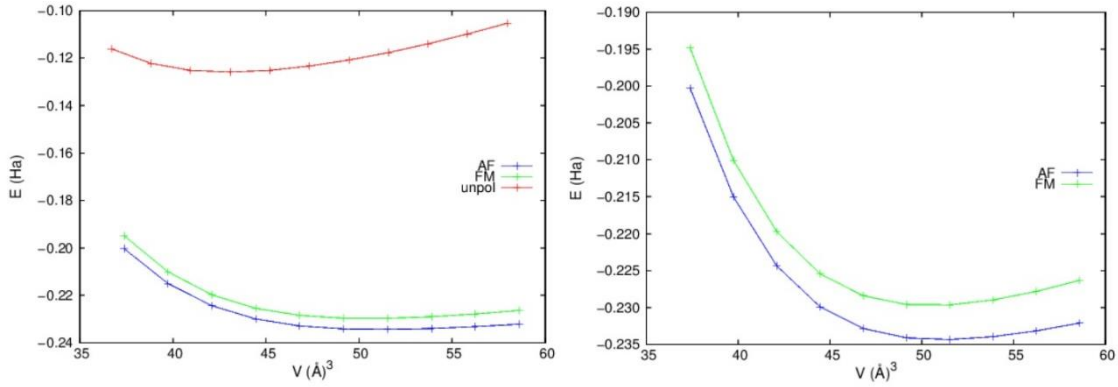

Fig. S2: Left: *V-E* plot for the α-FeF_3 phase considering the ferromagnetic, FM, antiferromagnetic, AF, and non-magnetic (unpol) orderings. Right: Zoom into the FM and AF cases.

E-a-c potential energy surface fitting

In order to fit the zero pressure potential energy surface as a function of the lattice parameters (*a,c*) of the rhombohedral phase, we have assumed that the energy can be analytically described by a Taylor expansion around the local minima (a_0,c_0):

$$\begin{aligned} E - E_0 = {} & p_1(a-a_0)^2 + p_2(a-a_0)(c-c_0) + p_3(c-c_0)^2 + p_4(a-a_0)^3 \\ & + p_5(a-a_0)^2(c-c_0) + p_6(c-c_0)^2(a-a_0) + p_7(c-c_0)^3 + p_8(a-a_0)^4 \\ & + p_9(a-a_0)^3(c-c_0) + p_{10}(c-c_0)^3(a-a_0) + p_{11}(a-a_0)^2(c-c_0)^2 \\ & + p_{12}(c-c_0)^4 + O(h^5) \end{aligned}$$

where p_i and E_0 are the coefficients of the expansion and the energy minima of the surface, respectively. The linear terms are set to zero in order to fulfill the condition of minima at (a_0,c_0).

This procedure is based on the energy expansion of the elastic constants. Indeed, it can be considered a particular case where only two strains are considered. To accurately calculate the Poisson ratio, cubic and quartic terms have been included to account for the anharmonic behavior of the surface out of the equilibrium point.

The fitting has been performed using the package *cftool* from MATLAB software. Both a_0 *and* c_0 have been fixed using the values obtained from DFT calculations (a_0 = 5.09 Å and c_0 = 13.67 Å). Least absolute residuals method with a trust region algorithm and a tolerance function of 10^{-6} was used to fit the potential energy surface. Obtained fitting parameters are summarized in **Table S2** and **Figure S3**. The goodness of fit (adjusted R-square value) is 0.991 with residuals lying between $-3{\cdot}10^{-4}$ and $3\ 10^{-4}$ hartree.

Table S2: Fitting parameters for the *E-a-c* PES (see analytical fitting equations above).

Parameter	Value	Parameter	Value
E_0	-257.2343 (hartree)	p_7	-0.002378 (hartree/Å^3)
p_1	0.02238 (hartree/Å^2)	p_8	0.03497 (hartree/Å^4)
p_2	0.01058 (hartree/Å^2)	p_9	0.01258 (hartree/Å^4)
p_3	0.002855 (hartree/Å^2)	p_{10}	-0.00314 (hartree/Å^4)
p_4	-0.03215 (hartree/Å^3)	p_{11}	0.00394 (hartree/Å^4)
p_5	-0.01103 (hartree/Å^3)	p_{12}	0.00310 (hartree/Å^4)
p_6	-0.00058 (hartree/Å^3)		

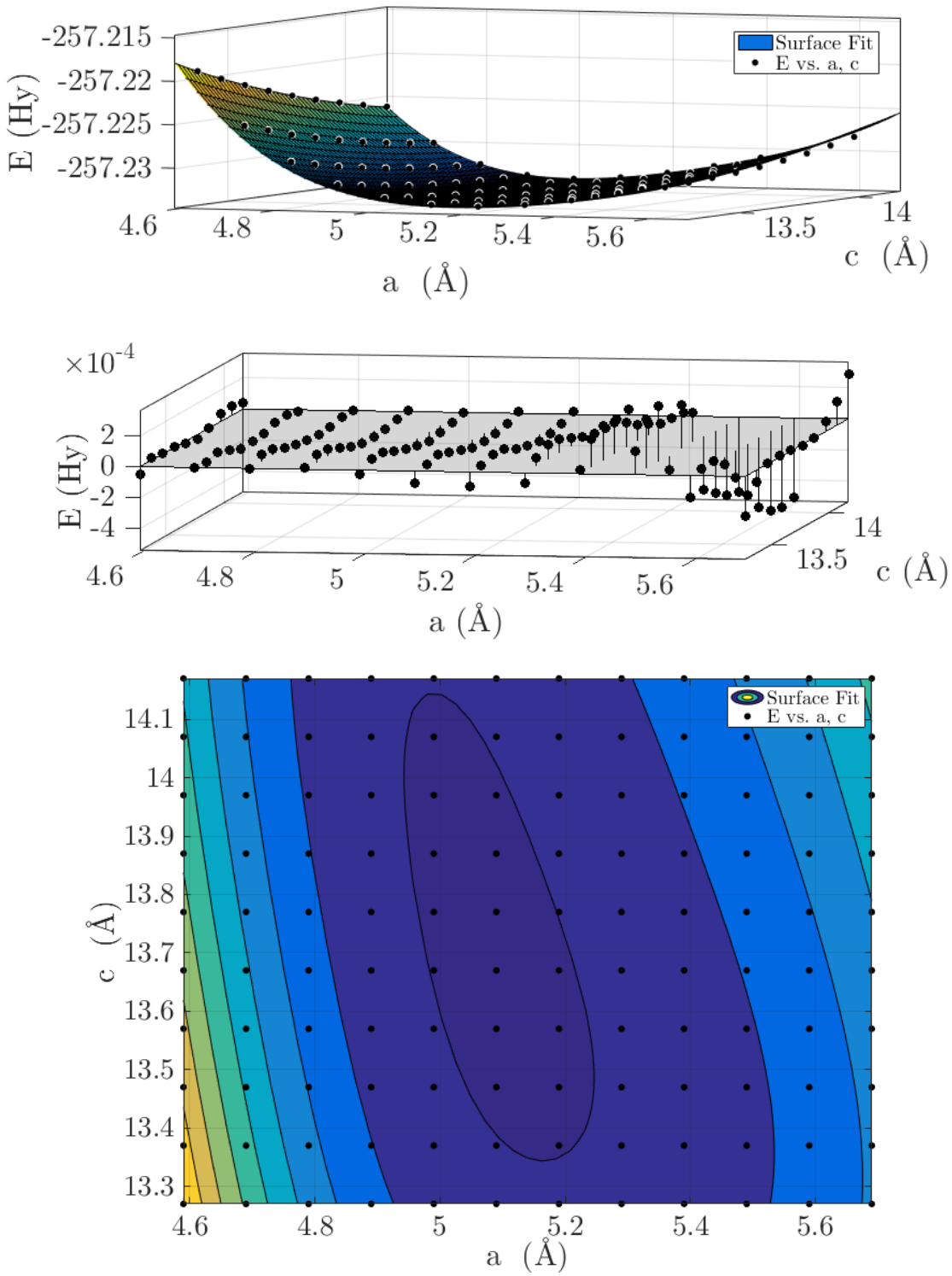

Fig. S3: Top: *E-a-c* data (black dots) and surface fit for the α-FeF_3 phase. Middle: Residual plot from the surface fitting. Down: Contour map of the fitted surface