SUPPLEMENTARY INFORMATION
Magnetic Contributions to Corundum-Eskolaite and Corundum-Hematite Phase Equilibria: a DFT Cluster Expansion Study

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1 Lattice Parameters:

Input for the Alloy Theoretical Automated Toolkit (ATAT) used the following values in the 'lat.in' file to determine the initial lattice parameters. For corundum:hematite, the Cr+5 was replaced with Fe+8. For the purely magnetic systems, the metal alloy options were Cr+5 and Cr-5. For the 4-body configurational plus magnetic contribution calculations, the metal alloy options are Al1, Al2, Cr+5, Cr-5.

4.760600 0.000000 0.000000

-2.380300 4.122801 0.000000

0.000000 0.000000 12.994000

0.333330 -0.333330 -0.333330

-0.666670 -0.333330 -0.333330

0.333330 0.666670 -0.333330

-0.000010 0.000010 -0.647820 Al,Cr+5

-0.000010 0.000010 -0.352160 Al,Cr+5

-0.000010 0.000010 -0.852160 Al,Cr+5

-0.000010 0.000010 -0.147820 Al,Cr+5

0.360310 0.333340 -0.416660 O

-0.360330 -0.333320 -0.583320 O

-0.333340 0.026990 -0.416660 O

0.333320 -0.026970 -0.583320 O

-0.026990 -0.360310 -0.416660 O

0.026970 0.360330 -0.583320 O

2 Cross Validation:

The predictive ability of the cluster expansions were determined through cross validation scores as calculated from equation in SI EQ. 1, analagous to a root mean square error fit that allows estimation of energies for systems not included in the leas-squares fit. It was shown that the CV score was exceptionally well fit with values below suggested values of 0.025 eV. The following plots show the predicted per site energy vs. the calculated energy for each configuration and the associated CV score.

$$CV = \left(\frac{1}{n} \sum_{i=1}^{n} \left(E_i - \hat{E}_{(i)} \right)^2 \right)^{1/2} \tag{1}$$

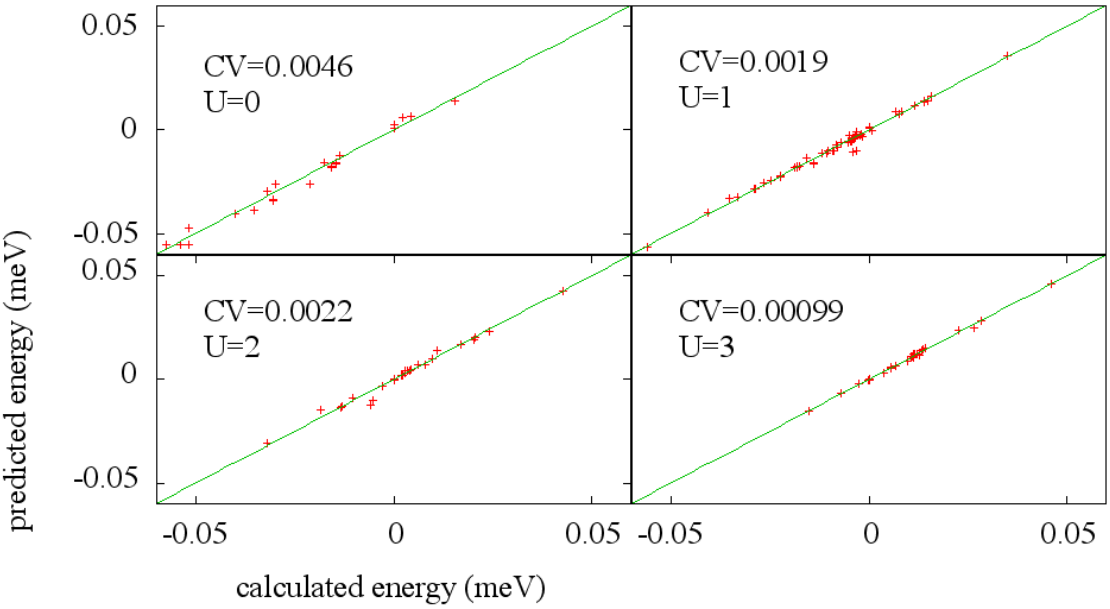

Figure 1: Predicted per site energies from Cluster Expansion vs. the calculated energies of eskolaite magnetic configurations across values of U.

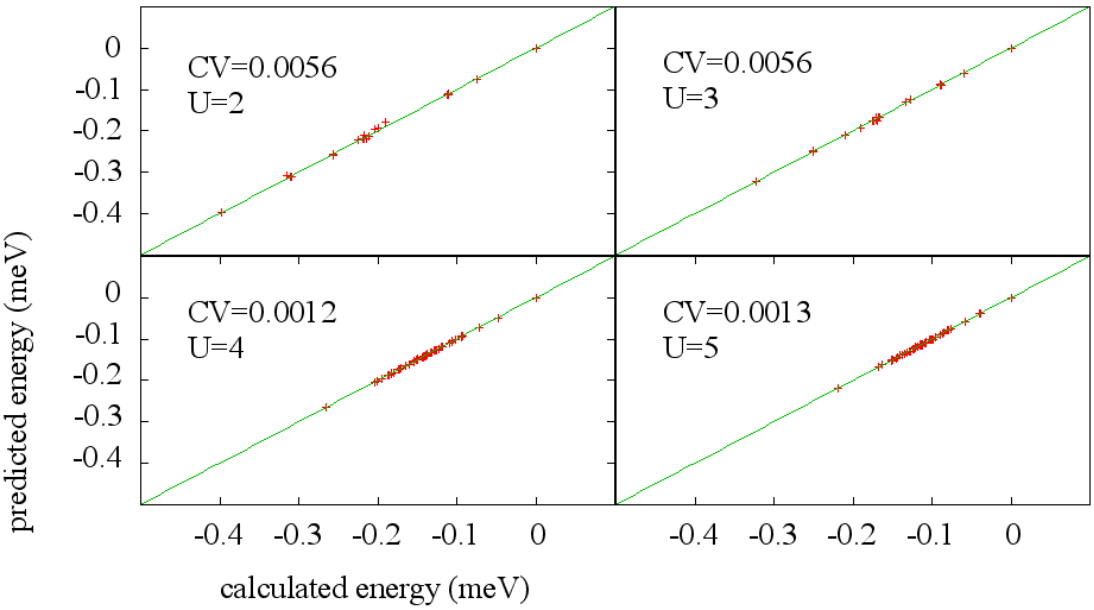

Figure 2: Predicted per site energies from Cluster Expansion vs. the calculated energies of hematite magnetic configurations across values of U.

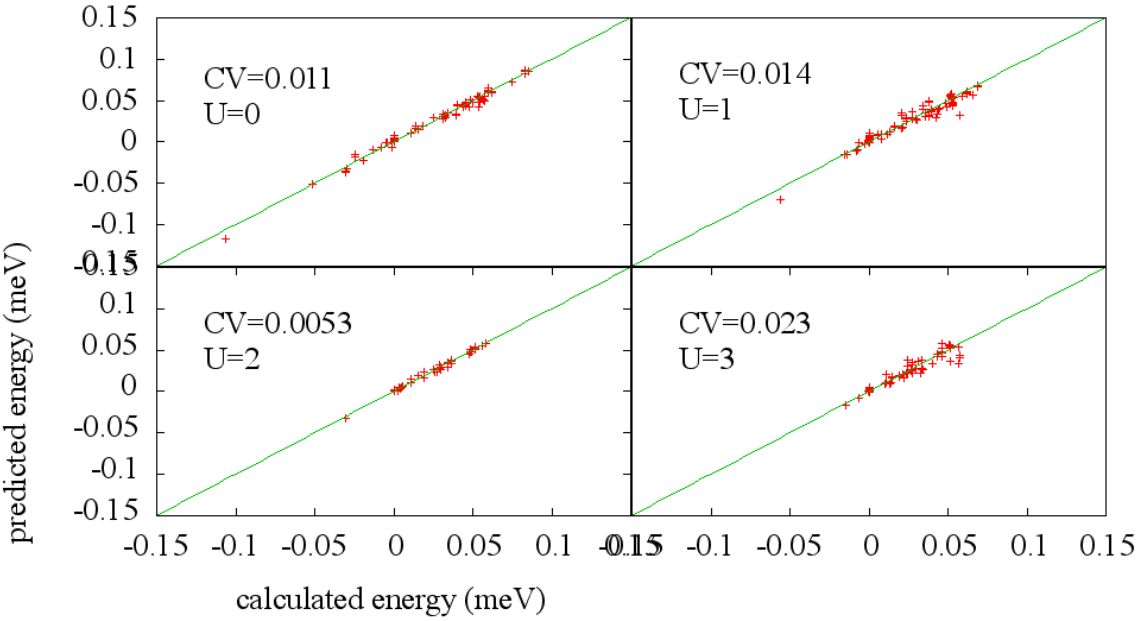

Figure 3: Predicted per site energies from Cluster Expansion vs. the calculated energies of corundum-eskolaite system across values of U.

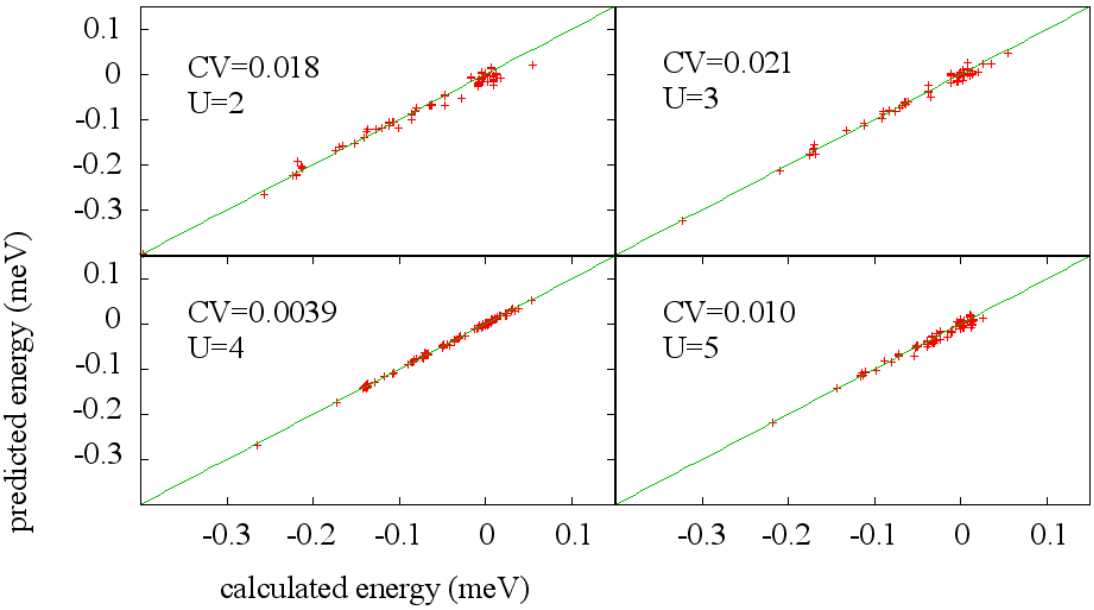

Figure 4: Predicted per site energies from Cluster Expansion vs. the calculated energies of corundum-hematite system across values of U.

3 Magnetic Disordering:

Magnetic disordering temperatures were determined from identifying peaks in energy variance vs. temperature plots from Monte Carlo simulations. Energy variance was normalized for all simulations for easier visualization. Magnetic disordering temperatures were taken as the peaks from these plots.

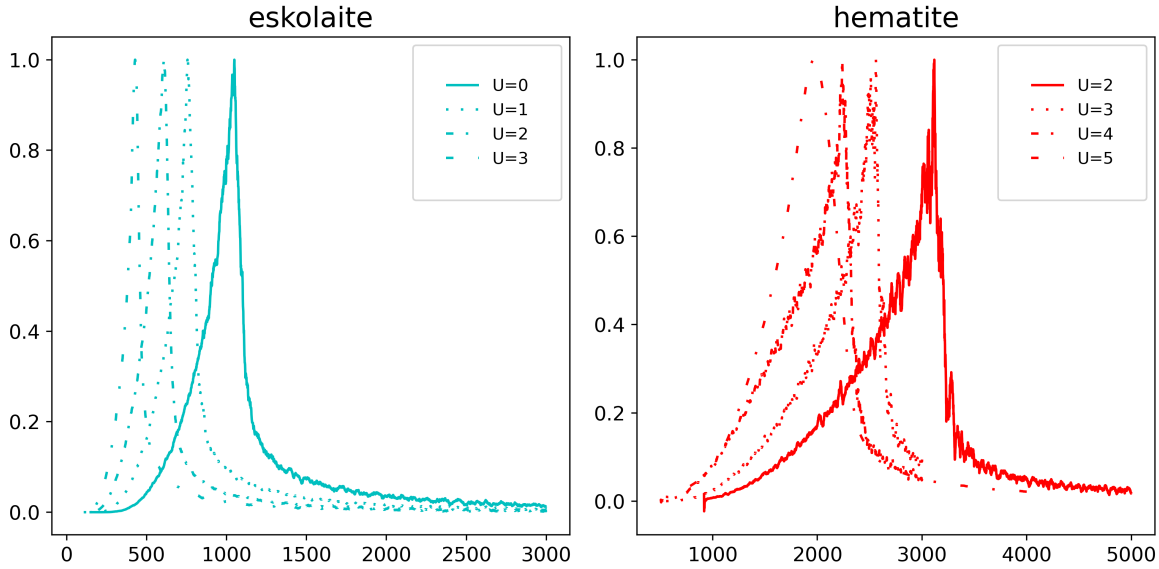

Figure 5: Normalized energy variance vs. temperature plots for eskolaite and hematite for each Hubbard parameter.

4 ECI to Exchange Parameter J Conversion:

ECIs and magnetic exchange parameters J are related by equating total energies of a Cluster Expansion and a quantum Heisenberg Hamiltonian. J values can then be determined under the following conditions.

1. CE is a two component system
2. CE is confined to pair interactions only
3. Atom site spin values are uniform, constant, and change by sign only

For two component systems, the cluster expansion giving the total energy of a configuration can be represented by an Ising like Hamiltonian as shown in SI Eq. 2. In this representation the ECIs are given by the ECI_0, the cell energy, ECI_1, the per site energies, and ECI_{ij}, the pair energies. The number of sites i is given by m_i and the number of neighbors j to site i is given by n_ij. In the two component cluster expansion, the cluster correlation functions are represented by the "spin" variable σ, which can take on values of 1 or -1 only.

$$E_{CE} = ECI_0 + \sum_i m_i ECI_i \sigma_i + \sum_i \sum_j m_i n_{ij} ECI_{ij} \sigma_i \sigma_j \tag{2}$$

The quantum Heisenberg Hamiltonian, in the absence of an external magnetic field is represented by equation SI Eq. 3, where E_0 is the reference energy, J is the magnetic interaction term, m_i is again the number of sites i, and n_{ij} is the number of neighbors to site i. The expectation value for $\langle \hat{S}_i \hat{S}_j \rangle$ is given by $S(S+1)$.

$$E_{mag} = E_0 - \frac{1}{2} \sum_{i,j} m_i n_{ij} J_{ij} \langle \hat{S}_i \hat{S}_j \rangle \tag{3}$$

As E_0 is a reference energy, it can be equated to ECI_0 plus the sum of ECI_i, and these terms can be removed from the equality of E_{CE} and E_{mag}. The resulting equation compares pair energies only.

$$\sum_i \sum_j m_i n_{ij} ECI_{ij} \sigma_i \sigma_j = -\frac{1}{2} \sum_{i,j} m_i n_{ij} J_{ij} \langle \hat{S}_i \hat{S}_j \rangle \tag{4}$$

If atom site spins are uniform across all pair interactions, this equation can be rearranged in terms of J giving the following.

$$\sum_{i,j} m_i n_{ij} J_{ij} = \frac{-2}{\langle \hat{S}_i \hat{S}_j \rangle} \sum_i \sum_j m_i n_{ij} ECI_{ij} \sigma_i \sigma_j \tag{5}$$

Under these constraints, Cluster Expansion ECIs are related to magnetic exchange energies by a scaling factor dependent on spin and can be directly compared to experimental values.