Electronic Supplementary Information

Exceptionally high saturation magnetisation in Eu-doped magnetite stabilised by spin-orbit interaction

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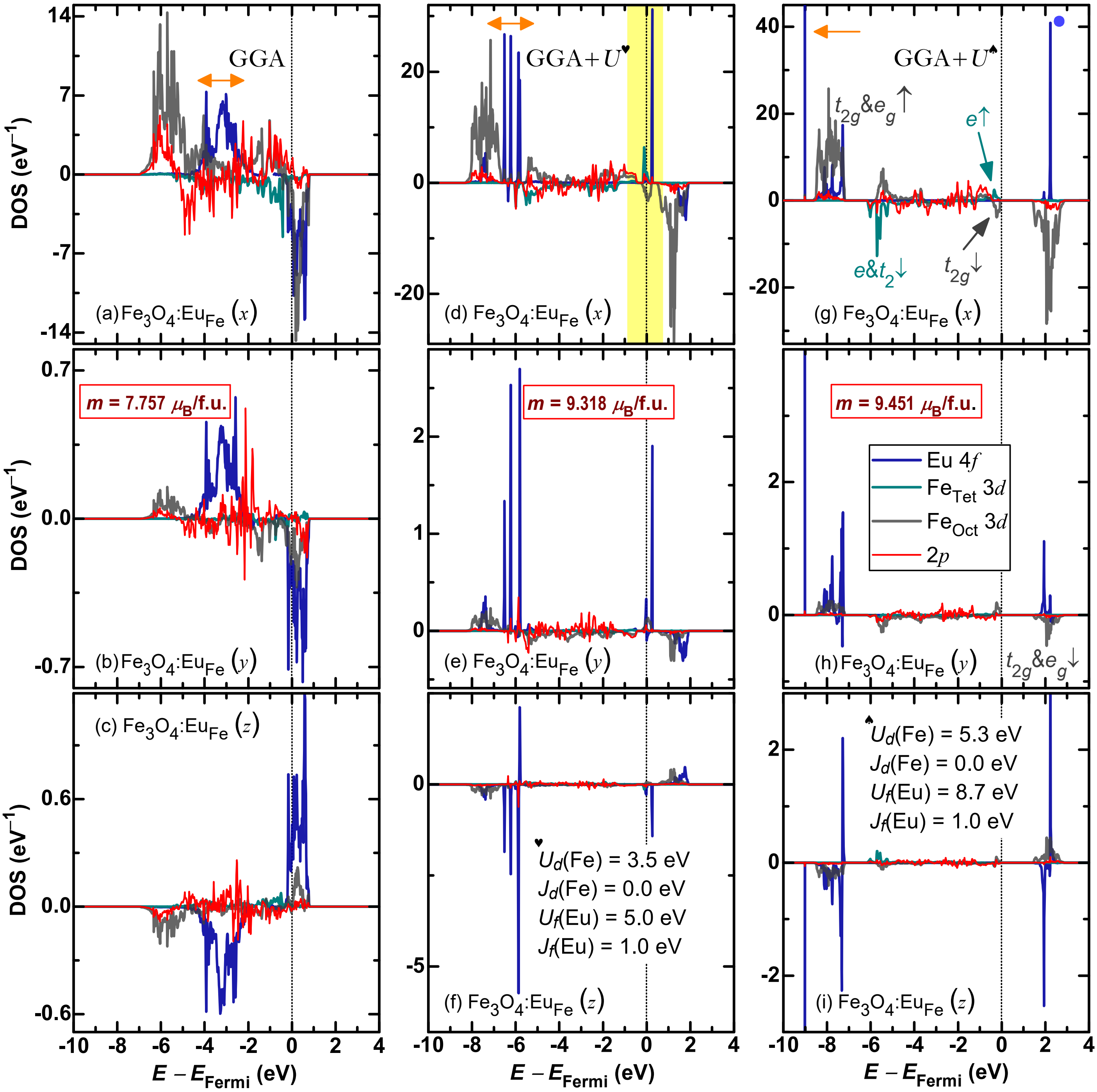

Figure S1. The partial density of states of Fe_3O_4 doped with tetrahedral Eu at the most stable configuration [configuration (b) of Figure 2] with spin-orbit interaction (SOI) considered. The first column [(a), (b), and (c)] corresponds to the calculation with GGA functional only. The second column [(d), (e), and (f)] corresponds to calculations with relatively smaller $U_{\rm eff}$ values; $U_{\rm eff}$(Eu) = 4 eV, and $U_{\rm eff}$(Fe) = 3.5 eV. The third column [(g), (h), and (i)] corresponds to calculations performed with larger $U_{\rm eff}$ values of 7.7 eV for Eu 4f electrons and 5.3 eV for Fe 3d electrons, reported in the article. The GGA calculations predict a metallic ground state and delocalise the 4f electron, marked with the orange arrow. The GGA+U implementation with the smaller $U_{\rm eff}$ values, although results in a slightly smaller spread of 4f states, still suffers from considerable delocalisation of the 4f states. Moreover, smaller $U_{\rm eff}$ values still predict a metallic state for the compound [shaded area in (d)]. Calculations with the larger $U_{\rm eff}$ values result in a sharp localisation of both filled 4f states [orange arrow in (g)] and empty 4f states (blue circle). The latter band description conforms with the sharp localisation of spacially confined 4f wavefunctions. The bandgap predicted by larger $U_{\rm eff}$ values also conforms with the Mott insulator nature of magnetite at low temperatures. The magnetisation per unit formula is also given for each simulation. The GGA method underestimates the total magnetisation.

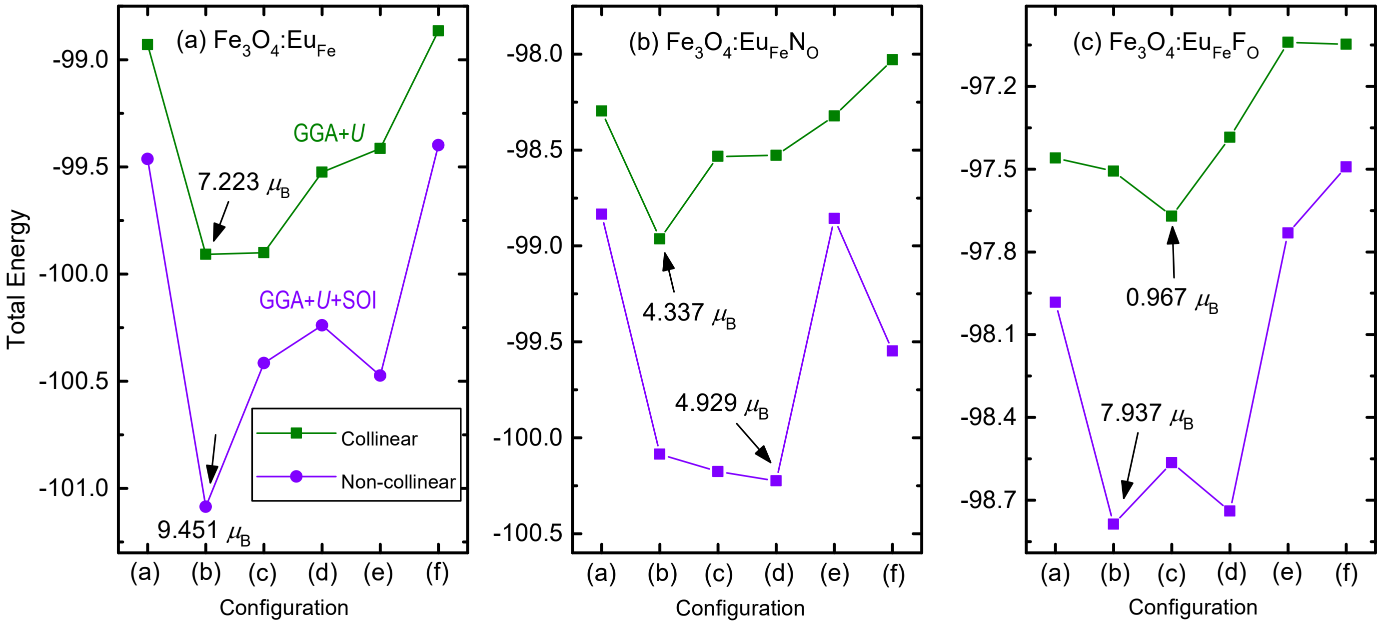

Figure S2. The total density functional energies for configuration (a)–(f) of Figure 2 with (purple) and without (green) spin-orbit interaction. The values with spin-orbit interactions were reported in Figure 3 with GGA+ *U*+SOI formalism. The U_{eff} values were 5.3 eV for Fe 3*d* electrons and 7.7 eV for Eu 4*f* electrons. The inclusion of the spin-orbit interaction lowers the total energy by about ~1 eV for the most stable configurations. Furthermore, the inclusion of the spin-orbit interaction enhances the total magnetisation of the compounds. SOI calculations, on average, consume 10 to 15 times more computational resources than non-SOI calculations.

Table S1. The lattice parameters, compound's total magnetisation and the density functional total energy of the pristine ferrimagnetic Fe_3O_4 in primitive unitcell, calculated without and with the spin-orbit interaction. In pristine Fe_3O_4, SOI plays a very minor role as it changes the lattice parameters by 0.006%, the total magnetisation by 0.01% and the total energy by 0.02%. The minor contribution of SOI in pristine Fe_3O_4 was anticipated as the compound contains only lighter elements.

	GGA + *U*	GGA + *U* + SOI
a_p (Å)	6.0320	6.0324
b_p (Å)	6.0320	6.0324
c_p (Å)	6.0320	6.0324
α_p Å)	60.000	60.000
β_p (Å)	60.000	60.000
γ_p (Å)	60.000	60.000
m (μ_B/f.u.)	3.933	3.929
E^t (eV)	−93.5395	−93.5170

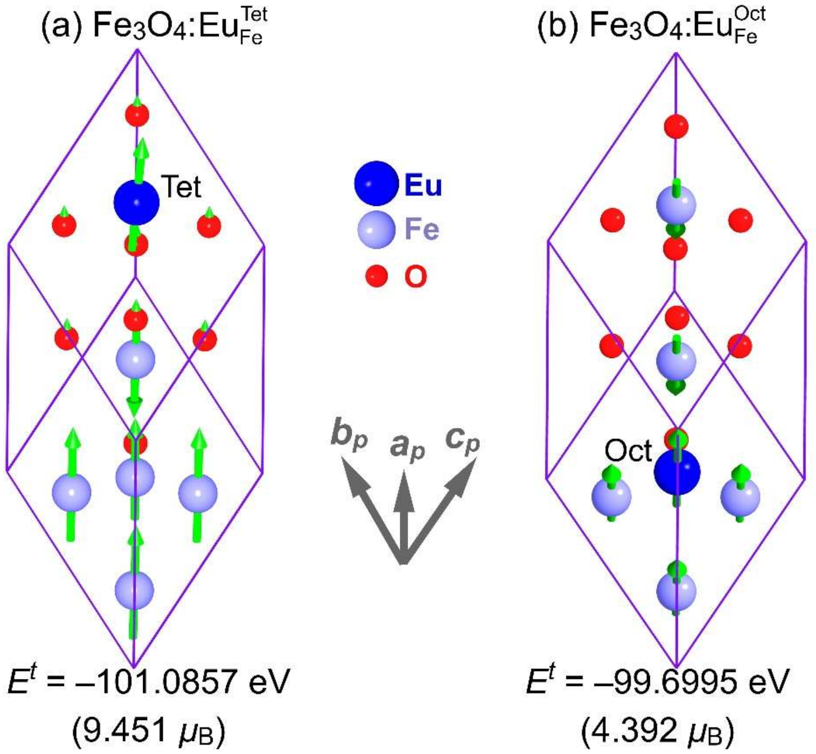

Figure S3. The schematic structures, spin alignments, density functional total energy (E^t), and the total magnetisation of Fe_3O_4 doped with tetrahedral Eu (a) and octahedral Eu (b). Both structures correspond to the most stable spin configurations obtained with the GGA+U+SOI formalism. The tetrahedral Eu doping was more stable by 1.3862 eV.

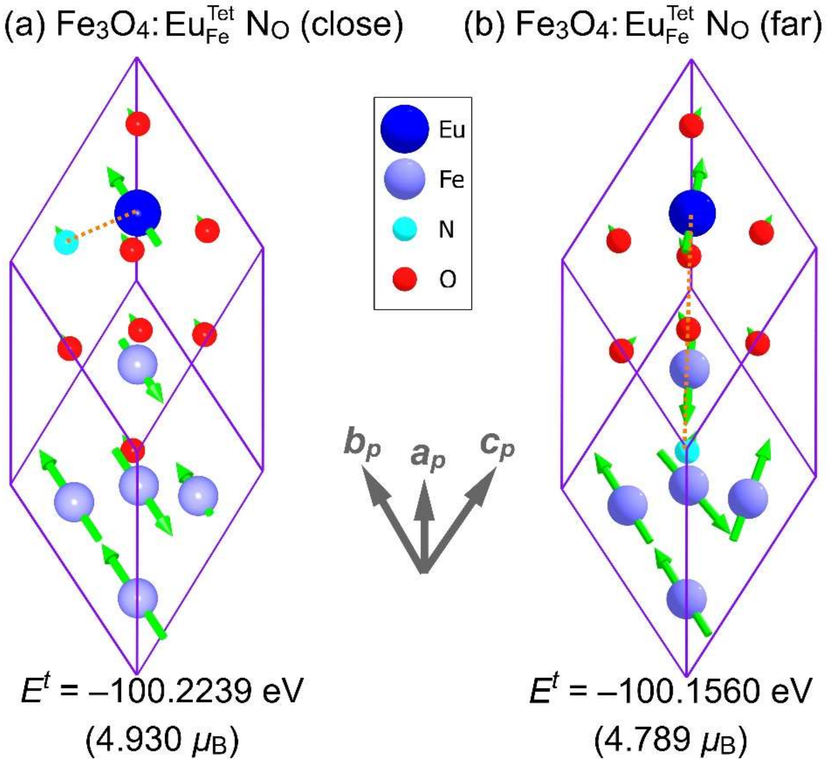

Figure S4. The effect of anionic co-dopant's placement on the total energy and saturation magnetisation is examined here for the case of N codopant simulating hole doping. Among two possibilities for N placements, the site coordinating Eu in (a), *i.e.*, the closest site to Eu, was slightly more stable than the site further away from Eu in (b).