Density functional theory study of the magnetic moment of solute Mn in bcc Fe

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Supplementary Material for

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1. Supplementary Methods

1.1 Cohesive enthalpy

Reference energies of isolated Fe and Mn were obtained by placing one atom of each element in separate supercells of dimensions 12×13×14 Å. A non-self-consistent calculation at the Γ point was performed without symmetry to determine the anisotropic orbital occupancies of the free atom. The magnetic moments for Fe and Mn were initialised as 4 and 4.4 μ_B, respectively. The occupancies were found as follows:

Fe	Mn
Spin-up channel: $3p^3\ 3d^5\ 4s^1$	Spin-up channel: $3p^3\ 3d^5\ 4s^1$
Spin-down channel: $3p^3\ 3d^1\ 4s^1$	Spin-down channel: $3p^3\ 4s^1$

Subsequent self-consistent energy calculations were performed until an electronic convergence of 10^{-6} eV was achieved. The cohesive enthalpy was then calculated using the following equation:

$$E_c = E^{bulk} - E^{free} \qquad \text{(S1)}$$

where E^{bulk} and E^{free} is the internal energy per atom of the element in its bulk and free state, respectively.

1.2 Formation, substitution, binding energy calculations

Calculations of the enthalpy of formation were performed as follows:

$$H_{form} = E_{Fe,Mn} - \left(n_{Fe}E_{Fe}^{bulk} + n_{Mn}E_{Mn}^{bulk}\right) \qquad \text{(S2)}$$

where $E_{Fe,Mn}$ is the internal energy of the Fe-Mn alloy and n is the number of atoms of the respective element in the alloy.

The calculations for the substitution energies were done using a similar method, however, $n_{Mn} = 1$ therefore:

$$E_{sub} = E_{Fe,Mn} - \left(n_{Fe}E'^{bulk}_{Fe} + E_{Mn}^{bulk}\right) \qquad \text{(S2)}$$

where E'^{bulk}_{Fe} is obtained from a supercell of consistent size and dimensions as $E_{Fe,Mn}$.

The binding energies between two defects were calculated as follows:

$$E_{bind} = \left(E_{D1,D2} + n_{Fe}E'^{bulk}_{Fe}\right) - (E_{D1} + E_{D2}) \qquad \text{(S3)}$$

where $E_{D1,D2}$ is the internal energy of the supercell containing both defects *D1* and *D2* and E_{D1} and E_{D2} is the internal energy of supercells (of consistent size and dimension with $E_{D1,D2}$) containing the respective defects.

1.3 Vacancy and interstitial formation enthalpy

In much the same method as calculating the substitution energy, the vacancy formation enthalpy is calculated as:

$$E_{vac} = \left(E_D + E_{Fe}^{bulk}\right) - E_P \quad \text{(S4)}$$

where E_D and E_P are the defected and pristine supercells, respectively.

The interstitial formation enthalpy calculation was done as follows:

$$E_{vac} = E_D - \left(E_P + E_{Fe}^{bulk}\right) \quad \text{(S5)}$$

2. Supplementary results

Table S1. Magnetic moments of the allotropes of Mn.

Crystal Structure	Magnetic Structure	Site	Spin vector		
			x	y	z
α-Mn	NCL	2a	0.00	0.00	2.90
		8c	0.00	0.00	–2.17
		24g	0.00	0.00	0.45
		24g'	0.00	0.00	–0.13
	AFM	2a	-	-	2.85
		8c	-	-	–2.3
		24g	-	-	1.20
		24g'	-	-	–0.01
β-Mn	AFM	8c	-	-	–0.12
		12d	-	-	0.45
γ-Mn	NM	4a	-	-	-
δ-Mn	FM	2a	-	-	0.90
α-Fe	FM	2a	-	-	2.20

When two Mn atoms were placed in 1st – 6th nearest neighbour (nn) from each other in a 3×3×3, 4×4×4 and 5×5×5 dimension supercell a stochastic behaviour was found in the resultant

magnetic moments of each Mn. Each adopted FM or AFM moments with varying magnitudes with no clear trend. The average magnetic moment and binding energies between the two Mn atoms are plotted below in Fig. S1.

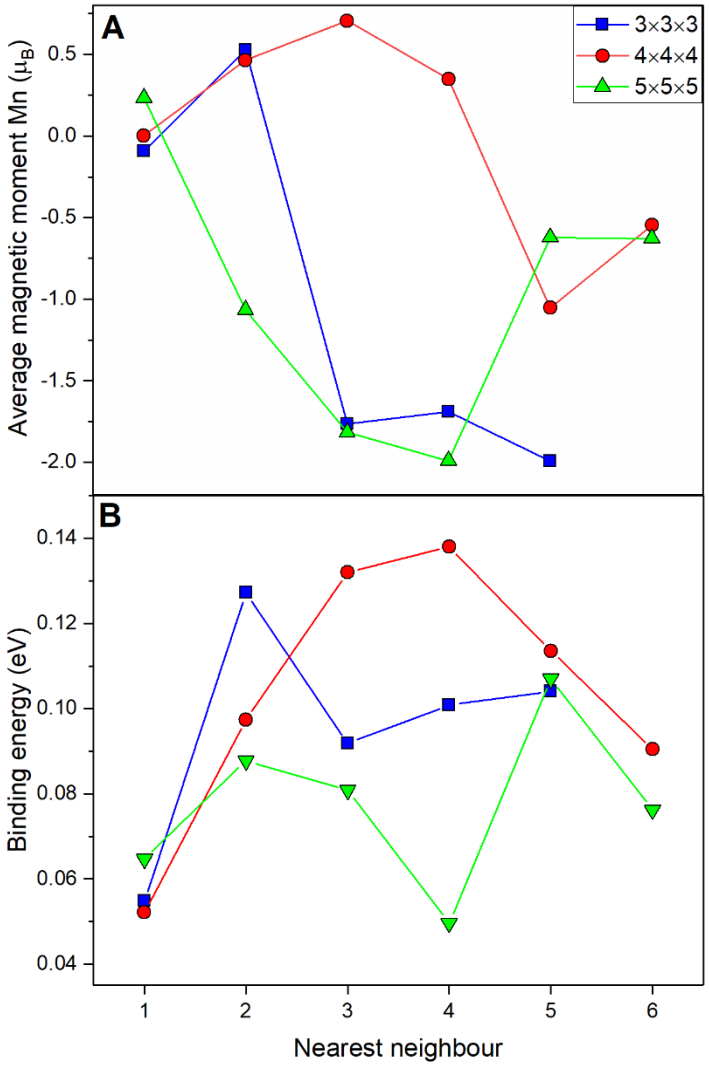

Fig. S1. (A) Average magnetic moment and (B) binding energy for Mn-Mn nearest neighbours in α-Fe.

No correlation was found between spin on Mn atom and the location of the remaining five Mn atoms in the cell, as illustrated in Figure S2. Mn substitutions were found to retain

both FM and AFM ordering (with respect to Fe), irrespective of the distance from other Mn atoms. However, a general trend is observed whereby the spin on Mn atoms decreases with increasing distance from neighbouring Mn atoms.

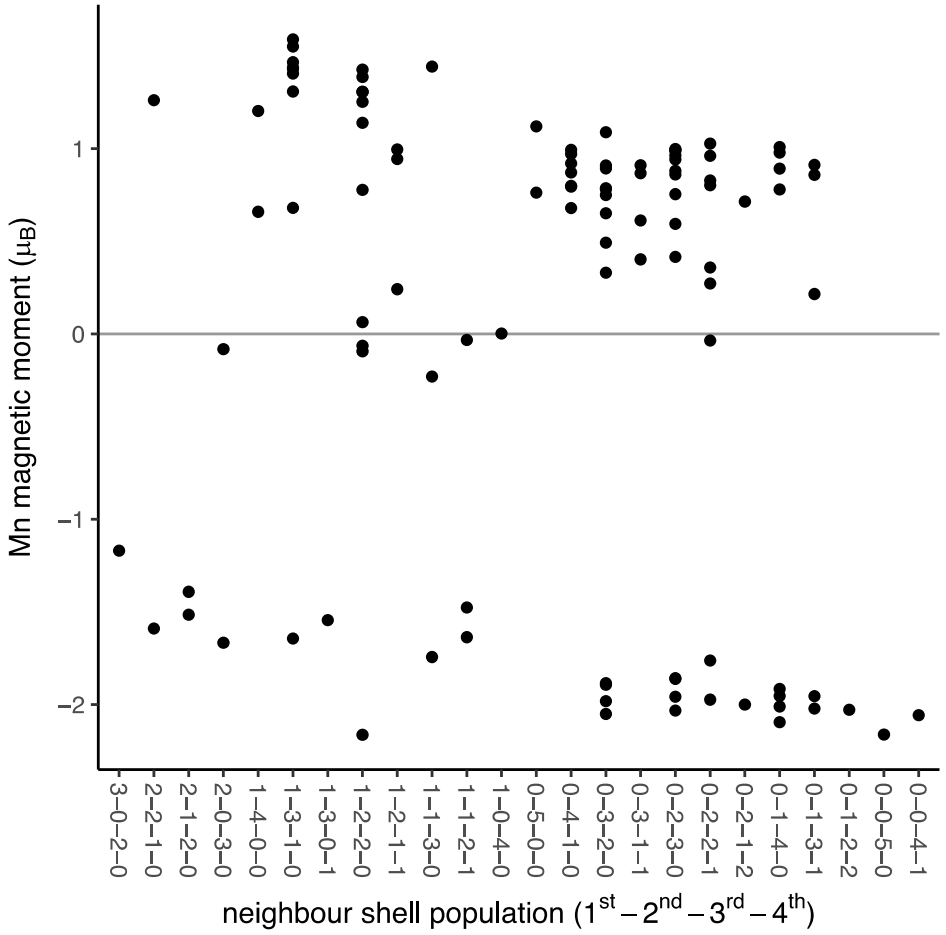

Fig. S2. Magnetic moment of each Mn atoms for different configuration of the remaining 5 Mn atoms in supercell (located in shells 1 to 4). Configurations ordered from closes cumulative distance ("3-0-2-0" being 3 in the first shell, 0 in the second, 2 in the third and 0 in the fourth), to furthest ("0-0-4-1": no Mn atoms in the first two shells, 4 in the third and one in the fourth).