

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

King, D.J.M.; Middleburgh, S.C.; Burr, P. A.; Whiting, T.M.; Fossati, P.C.; Wenman, M.R.

### Physical Review B

DOI:

[10.1103/PhysRevB.98.024418](https://doi.org/10.1103/PhysRevB.98.024418)

Published: 20/07/2018

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

*Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):*

King, D. J. M., Middleburgh, S. C., Burr, P. A., Whiting, T. M., Fossati, P. C., & Wenman, M. R. (2018). Density functional theory study of the magnetic moment of solute Mn in bcc Fe. *Physical Review B*, 98(2), Article 024418. <https://doi.org/10.1103/PhysRevB.98.024418>

#### Hawliau Cyffredinol / General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

#### Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Supplementary Material for

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

D. J. M. King\*, S. C. Middleburgh, P. A. Burr, T. M. Whiting, P.C. Fossati, M. R. Wenman

\*Corresponding author. E-mail: [daniel.king@imperial.ac.uk](mailto:daniel.king@imperial.ac.uk)

**This PDF file includes:**

Methods

Equations S1-S5

Results

Table S1

Figure S1

Figure S2

## 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  $12 \times 13 \times 14$  Å. A non-self-consistent calculation at the  $\Gamma$  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  $\mu_B$ , respectively. The occupancies were found as follows:

Fe

Spin-up channel:  $3p^3 3d^5 4s^1$

Spin-down channel:  $3p^3 3d^1 4s^1$

Mn

Spin-up channel:  $3p^3 3d^5 4s^1$

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:

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

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:

$$H_{form} = E_{Fe,Mn} - (n_{Fe}E_{Fe}^{bulk} + n_{Mn}E_{Mn}^{bulk}) \quad (S2)$$

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:

$$E_{sub} = E_{Fe,Mn} - (n_{Fe}E_{Fe}^{bulk} + E_{Mn}^{bulk}) \quad (S2)$$

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

The binding energies between two defects were calculated as follows:

$$E_{bind} = (E_{D1,D2} + n_{Fe}E_{Fe}^{bulk}) - (E_{D1} + E_{D2}) \quad (S3)$$

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:

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

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

The interstitial formation enthalpy calculation was done as follows:

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

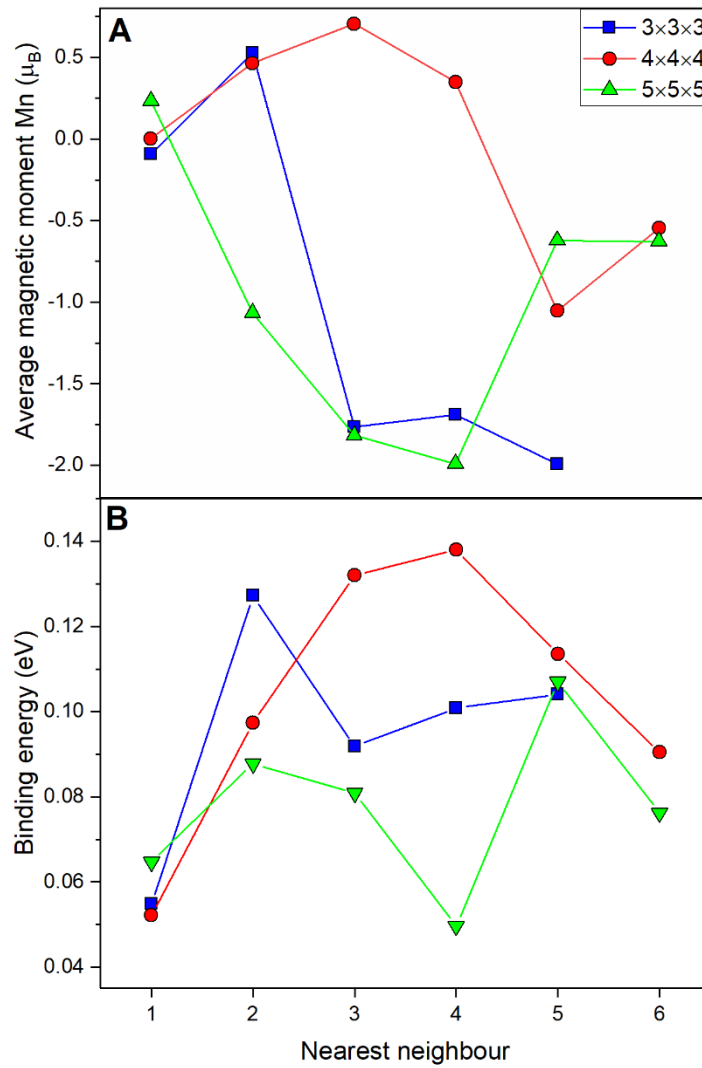
## 2. Supplementary results

Table S1. Magnetic moments of the allotropes of Mn.

Crystal Structure	Magnetic Structure	Site	Spin vector		
			x	y	z
$\alpha$ -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
$\beta$ -Mn	AFM	8c	-	-	-0.12
		12d	-	-	0.45
$\gamma$ -Mn	NM	4a	-	-	-
$\delta$ -Mn	FM	2a	-	-	0.90
$\alpha$ -Fe	FM	2a	-	-	2.20

When two Mn atoms were placed in 1<sup>st</sup> – 6<sup>th</sup> 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

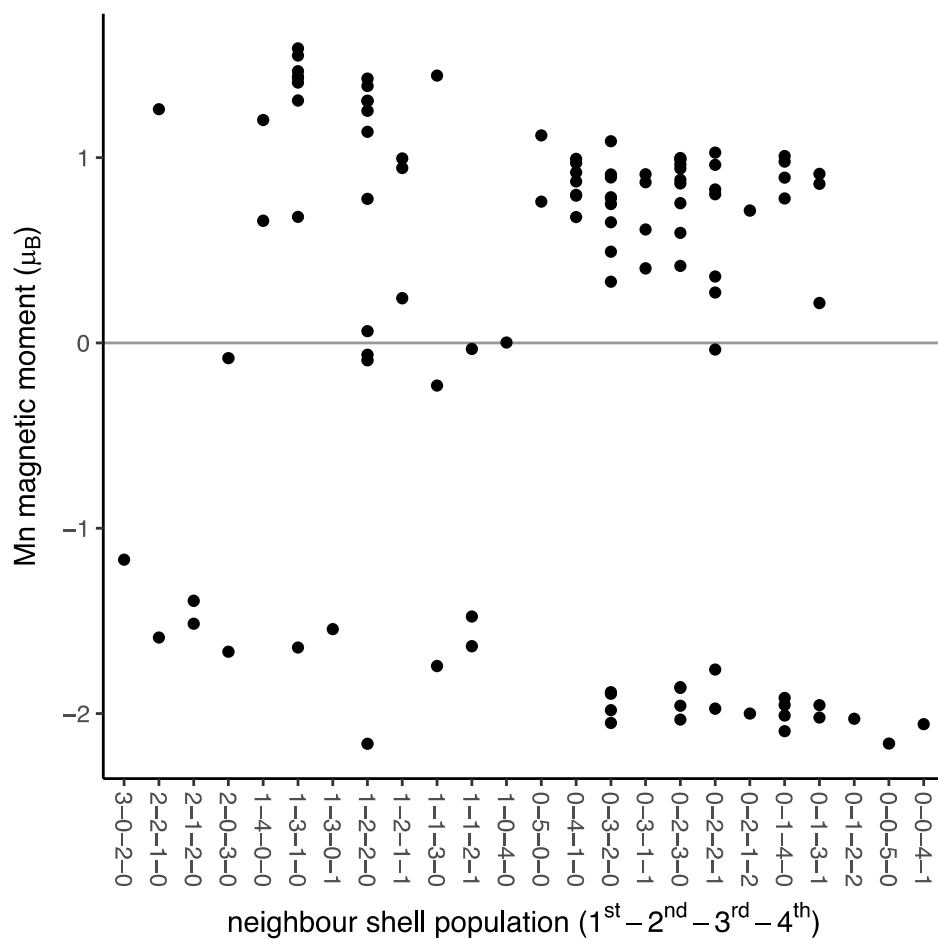
magnetic moments of each Mn. Each adopted FM or AFM moments with varying magnitudes with no clear trend. The average magnetic moment and binding energies between the two Mn atoms are plotted below in Fig. S1.



**Fig. S1.** (A) Average magnetic moment and (B) binding energy for Mn-Mn nearest neighbours in  $\alpha$ -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).