Supplementary Information

Structure and magnetic properties of $(Fe_2O_3)_n$ clusters (n = 1-5)

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Determination of magnetic coupling constants

The exchange coupling constants J_{ij} between Fe atoms i and j in Eq. (1) were obtained using least square fits of energy differences ΔH between ferromagnetic (H_{FM}) and several broken symmetry (H_{BS}) states,

$$\Delta H = H_{FM} - H_{BS} = -\frac{25}{2}\sum_{i<j} J_{ij}\delta_{ij} \qquad \text{(S1)}$$

with δ_{ij} = 0 for parallel and δ_{ij} = 1 for antiparallel spin arrangements in the corresponding BS state, to the corresponding relative energies evaluated at the DFT level.

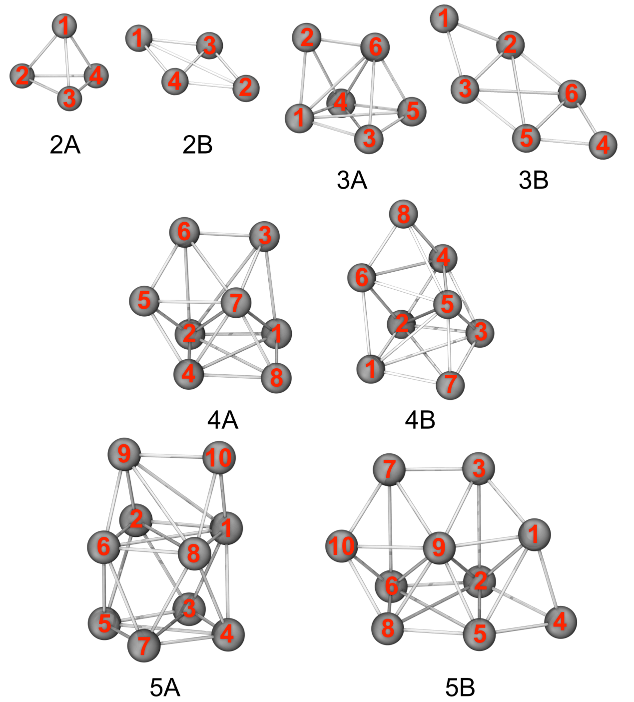


Fig. S1 Numbering of Fe atoms (grey) used in the calculation of magnetic coupling constants J_{ij} shown in Table S1. Sticks between atoms symbolize the calculated values of J_{ij}. O atoms are omitted for clarity.

For the two most stable isomers **2A** and **2B** of $(Fe_2O_3)_2$ all symmetry distinct Fe-Fe interactions were included in the fitting procedure. For $(Fe_2O_3)_n$ clusters with n = 3-5 an initial set of broken symmetry (BS) states and corresponding DFT relative energies were used employing all Fe-Fe interactions with Fe-Fe distance below 4.3 Å. Next, the most stable spin configurations predicted using the Ising Hamiltonian were refined at the DFT level and added to the fitting set. This procedure was repeated until relative energies of at least three most stable BS states computed according to Eq. S1 were sufficiently close to the corresponding DFT relative energies. The final least square fits of coupling constants J_{ij} used system of linear equations containing m energy differences ΔH between ferromagnetic (FM) H_{FM} and BS states H_{BS} (Table S1).

The final values of the coupling constants J_{ij} are summarized in Table S1 along with the corresponding Fe-Fe distances (r_{ij}) as well as mean Fe-O distances ($r_{\text{Fe-O}}$) and Fe-O-Fe bonding angels (α_1, α_2) for Fe-Fe pairs bridged by one and two O atoms, respectively. The numbering of Fe atoms is shown in Fig. S1. Fe-Fe pairs not directly connected by O atoms were also included in the fitting procedure. However, the resulting magnetic coupling constants turned out to be negligible.

Table S1 Coupling constants J_{ij} (cm^{-1}) for Fe atoms i and j (cf. Fig. S1) along with the corresponding Fe-Fe distances r_{ij} and the number of equations m included within the final least square fit. The mean Fe-O distances ($r_{\text{Fe-O}}$) and Fe-O-Fe angles (α_1, α_2) are given for Fe-Fe pairs bridged by one and two O atoms, respectively (cf. Fig. 2). Distances in Å, angles in degrees.

Cluster (m)	α_1	α_2	$r_{\text{Fe-O}}$	Pair i-j	r_{ij}	J_{ij}
2A (3)	-	-	1.84	all		-132 ± 3
2B (4)	86	93	-	1-3 1-4 2-3 2-4	2.69	1 ± 1
	93	93	-	3-4	2.90	-11 ± 1
	-	-	-	1-2	4.54	5 ± 1
3A (33)	84	92	-	2-6	2.66	-57 ± 1
	80	100	-	1-4	2.81	-112 ± 1
	85	101	-	1-3	2.83	-50 ± 1
	83	101	-	3-5	2.84	-67 ± 1
	81	102	-	5-6	2.85	-100 ± 1
	80	104	-	4-5	2.88	-116 ± 1
	89	97	-	4-6	2.99	-21 ± 1
	-	-	1.83	1-2	3.06	-130 ± 1
	-	-	1.95	2-4	3.35	-63 ± 1
	-	-	2.08	3-4	3.73	-36 ± 1
	-	-	2.03	3-6	3.80	-64 ± 1
	-	-	2.15	1-6	3.84	-19 ± 1
	-	-	2.26	1-5	4.30	-32 ± 1
3B (26)	86	94	-	1-2	2.70	-23 ± 1
	86	94	-	1-3	2.70	-22 ± 1
	86	94	-	4-5	2.70	-22 ± 1
	86	94	-	4-6	2.70	-23 ± 1
	83	99	-	2-6	2.76	-74 ± 1
	83	99	-	3-5	2.76	-75 ± 1
	88	95	-	2-3	2.89	5 ± 1
	88	95	-	5-6	2.89	7 ± 1
	-	-	2.09	2-5	4.00	-77 ± 1
	-	-	2.09	3-6	4.00	-76 ± 1

4A (49)	86	94	-	3-6	2.71	-37 ± 1
	88	95	-	5-6	2.75	-22 ± 1
	85	102	-	1-2	2.84	-79 ± 1
	83	101	-	4-8	2.84	-82 ± 1
	85	102	-	1-8	2.86	-106 ± 1
	87	102	-	7-8	2.86	-74 ± 1
	91	95	-	2-5	2.88	25 ± 1
	93	94	-	4-5	2.89	22 ± 1
	87	97	-	2-4	2.90	-19 ± 1
	88	96	-	4-7	2.91	-28 ± 1
	-	-	1.97	5-7	3.19	-30 ± 1
	-	-	1.96	6-7	3.33	-47 ± 1
	-	-	1.83	1-3	3.35	-127 ± 1
	-	-	1.92	3-7	3.39	-71 ± 1
	-	-	2.08	1-7	3.63	-24 ± 1
	-	-	1.92	2-6	3.68	-79 ± 1
	-	-	2.06	2-7	3.70	-55 ± 1
	-	-	2.11	2-8	4.01	-49 ± 1
	-	-	2.14	1-4	4.08	-62 ± 1
	-	-	-	2-3	4.16	-2 ± 1
4B (37)	84	92	-	6-8	2.68	-57 ± 1
	82	99	-	1-2	2.81	-92 ± 3
	90	94	-	2-4	2.83	-3 ± 1
	86	100	-	5-7	2.84	-86 ± 1
	85	101	-	3-7	2.86	-76 ± 2
	86	103	-	1-7	2.87	-80 ± 1
	92	94	-	3-4	2.88	2 ± 1
	85	97	-	2-3	2.91	-10 ± 2
	88	96	-	3-5	2.92	-22 ± 1
	-	-	1.84	4-8	2.94	-125 ± 1
	-	-	1.97	4-5	3.06	-41 ± 1
	-	-	1.85	1-6	3.20	-139 ± 2
	-	-	1.97	5-6	3.23	-33 ± 1
	-	-	1.95	2-6	3.31	-53 ± 2
	-	-	2.00	4-6	3.38	-41 ± 1
	-	-	1.92	5-8	3.60	-84 ± 2
	-	-	2.10	1-5	3.67	-15 ± 2
	-	-	2.11	2-5	3.86	-36 ± 1
	-	-	2.13	2-7	3.99	-41 ± 2
	-	-	2.14	1-3	4.09	-54 ± 2
5A (70)	87	98	-	3-4	2.79	-33 ± 1
	87	98	-	4-7	2.79	-32 ± 1
	87	98	-	3-5	2.81	-30 ± 1
	87	98	-	5-7	2.81	-30 ± 1
	84	96	-	1-8	2.86	-25 ± 1
	84	102	-	2-9	2.87	-110 ± 1
	84	102	-	6-9	2.87	-111 ± 1
	84	97	-	2-6	2.92	-27 ± 1
	86	98	-	1-2	2.93	-14 ± 1
	86	98	-	6-8	2.93	-11 ± 1
	-	-	1.83	9-10	2.95	-132 ± 1
	-	-	1.84	1-10	3.00	-145 ± 1
	-	-	1.84	8-10	3.00	-147 ± 1
	-	-	1.97	2-3	3.14	-26 ± 1
	-	-	1.97	6-7	3.14	-25 ± 1
	-	-	1.96	2-5	3.18	-30 ± 1
	-	-	1.96	5-6	3.18	-30 ± 1
	-	-	1.97	1-3	3.19	-30 ± 1
	-	-	1.97	7-8	3.19	-31 ± 1
	-	-	1.96	1-4	3.24	-34 ± 1
	-	-	1.96	4-8	3.24	-37 ± 1
	-	-	2.14	1-9	3.81	-24 ± 1
	-	-	2.14	8-9	3.81	-22 ± 1
	-	-	2.02	4-5	3.92	-98 ± 1
	-	-	2.04	3-7	4.00	-101 ± 1
	-	-	2.16	1-6	4.12	-52 ± 1
	-	-	2.16	2-8	4.12	-50 ± 1
5B (56)	81	97	-	2-6	2.74	-91 ± 2
	88	96	-	3-7	2.76	-6 ± 2
	89	98	-	7-10	2.82	-13 ± 2
	87	100	-	1-3	2.83	-52 ± 2
	84	102	-	5-8	2.85	-75 ± 2
	91	94	-	6-10	2.87	25 ± 2
	87	95	-	6-8	2.88	6 ± 2
	93	97	-	8-10	2.91	0 ± 2
	87	98	-	3-9	2.93	-19 ± 2
	87	96	-	8-9	2.93	-7 ± 2
	87	96	-	1-9	2.96	-16 ± 2
	85	99	-	5-9	2.96	-34 ± 2
	86	99	-	9-10	2.98	-12 ± 2
	-	-	1.93	7-9	3.00	-35 ± 2
	-	-	1.83	1-4	3.08	-143 ± 2
	-	-	1.83	4-5	3.09	-144 ± 2
	-	-	1.83	2-4	3.12	-150 ± 2
	95	98	-	6-9	3.18	9 ± 2
	96	101	-	2-9	3.19	-1 ± 2
	-	-	2.01	1-2	3.39	-35 ± 2
	-	-	2.00	1-5	3.47	-50 ± 2
	-	-	2.17	2-5	3.47	-9 ± 2
	-	-	2.01	2-3	3.92	-66 ± 2
	-	-	1.96	6-7	3.93	-110 ± 2
	-	-	2.13	2-8	4.22	-78 ± 2
	-	-	2.13	5-6	4.22	-76 ± 2

A single Slater determinant of a BS state is considerably spin contaminated due to the admixture of higher spin multiplicities into the BS wavefunction. Several approaches were suggested for determination of J_{ij} using spin projection operators. Among them, the BS formalism of Noodleman *et al.* is a good approximation when overlap between magnetic orbitals is sufficiently small.[1-3] A good estimation for this condition can be obtained from comparison of the spin expectation value of a single Slater determinant built with spatially orthogonal α and β orbitals, $\langle S^2\rangle_{SD}$, with the one computed for the unrestricted BS determinant $\langle S^2\rangle$.[4] For the total number of α and β electrons n_α and n_β $(n_\alpha \geq n_\beta)$, respectively, $\langle S^2\rangle_{SD}$ is given by

$$\langle S^2\rangle_{SD} = \left(\frac{n_\alpha - n_\beta}{2}\right)^2 + \left(\frac{n_\alpha + n_\beta}{2}\right). \qquad \text{(S2)}$$

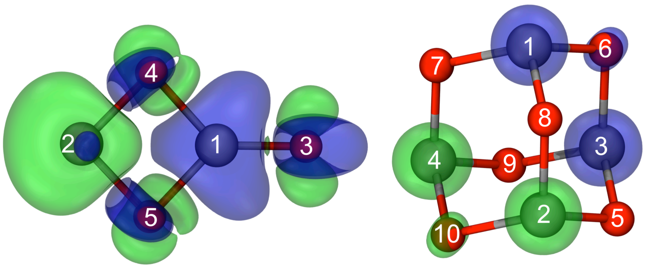
Calculated $\langle S^2\rangle_{SD}$ and $\langle S^2\rangle$ values are summarized in Table S2 for the two most stable $(Fe_2O_3)_n$ clusters with n = 2-5 along with corresponding spin multiplicities. It is apparent that in all cases the spin contamination of FM state, which is usually well described by a single Slater determinant, is negligible. Computed values of $\langle S^2\rangle$ are very close to the corresponding $\langle S^2\rangle_{SD}$ ones indicating a weak overlap of magnetic orbitals. This supports the approach used for calculation of magnetic coupling constants.

Table S2 Expectation values $\langle S^2\rangle_{SD}$ (Eq. S2) and computed $\langle S^2\rangle$ values for different states of $(Fe_2O_3)_n$ clusters with n = 2-5.

Cluster	Multiplicity	$<S^2>_{SD}$	$<S^2>$
2A	1	10	9.43
	11	35	34.57
	21	110	110.07
2B	1	10	9.73
	11	35	34.82
	21	110	110.07
3A	1	15	14.48
	11	40	39.55
	21	115	114.68
	31	240	240.09
3B	1	15	14.71
	11	40	39.72
	21	115	114.82
	31	240	240.10
4A	1	20	19.25
	11	45	44.30
	21	120	119.59
	31	245	244.66
	41	420	420.12
4B	1	20	19.09
	11	45	44.32
	21	120	119.30
	31	245	244.65
	41	420	420.12
5A	1	25	24.53
	11	50	49.36
	21	125	124.24
	31	250	249.60
	41	425	424.77
	51	650	650.15
5B	1	25	24.27
	11	50	49.04
	21	125	124.48
	31	250	249.68
	41	425	424.91
	51	650	650.15

Electronic structure of Fe_2O_3

Results of natural population analysis[5] for the ground states of the most stable $(Fe_2O_3)_n$ clusters with n = 1-5 are summarized in Table S3. The spin density isosurfaces of **1A** and **2A** are shown in Fig. S2.



1A

2A

Fig. S2 Spin density isosurfaces for the $^1B_1$ state of **1A** and $^1A_2$ state of **2A**. (Fe: grey, O: red, α-spin: green, β-spin: blue).

In **1A** the spin density isosurface plot (Fig. S2) indicates presence of both α and β spin density at the twofold coordinated Fe2 atom. In contrast, exclusively β-spin density is found at the threefold coordinated Fe1 atom. The natural population analysis (Table S3) yields a higher positive charge and a lower occupation of 3d states in Fe1 compared to Fe2. Comparison of the charges and natural electron configurations of O atoms in **1A** suggests that the lower positive charge at Fe2 results from less pronounced electron transfer to the terminal O3 atom. Indeed, the occupation of 2p states of O3 is 0.35 electrons lower than the 2p occupation of twofold coordinated O1 and O2.

In **2A** the spin density isosurface plot shows exclusively either α or β spin density well localized at the four Fe atoms. Natural population analysis yields virtually the same charge and natural electron configuration for the different Fe and O atoms. The charge and natural electron configuration of Fe atoms in **2A** is very close to ones obtained for the threefold coordinated Fe1 in **1A**. The oxygen atoms in **2A** show similar charge and natural electron configuration as the twofold coordinated O4 and O5 atoms in **1A**.

The comparison of the spin density plots (Fig. S2 and Fig. 1) and the results of natural population analysis for **1A** and larger clusters (Table S3) points to a distinct character of the twofold coordinated Fe2 and terminal O3 atom in **1A**. This suggests a formal interpretation of the electronic structure of **1A** in terms of a twofold coordinated Fe^{2+} (Fe2, Fig. S2), threefold coordinated Fe^{3+} (Fe1), two twofold coordinated O^{2-} (O4 and O5) as well as the terminal O^- radical (O3). This simplified picture is consistent with the singlet ground state of **1A** with spin states S = -5/2, S = 4/2 and S = 1/2 for Fe^{3+}, Fe^{2+} and O^-, respectively. In contrast, the remaining clusters can be interpreted exclusively in terms of Fe^{3+} and O^{2-} species.

Table S3 Natural charges and natural electron configuration of Fe and O atoms in the ground states of $(Fe_2O_3)_n$ clusters with n = 1-5.

	Atom	Charge	Natural electron configuration		
1A	Fe1	1.51	[core]	$4s^{0.27}$	$3d^{6.22}$
	Fe2	1.25	[core]	$4s^{0.32}$	$3d^{6.41}$
	O3	-0.69	[core]	$2s^{1.95}$	$2p^{4.74}$
	O4	-1.04	[core]	$2s^{1.94}$	$2p^{5.10}$
	O5	-1.04	[core]	$2s^{1.94}$	$2p^{5.10}$
2A	Fe1	1.66	[core]	$4s^{0.23}$	$3d^{6.11}$
	Fe2	1.66	[core]	$4s^{0.23}$	$3d^{6.11}$
	Fe3	1.66	[core]	$4s^{0.23}$	$3d^{6.11}$
	Fe4	1.66	[core]	$4s^{0.23}$	$3d^{6.11}$
	O5	-1.09	[core]	$2s^{1.94}$	$2p^{5.15}$
	O6	-1.14	[core]	$2s^{1.94}$	$2p^{5.20}$
	O7	-1.09	[core]	$2s^{1.94}$	$2p^{5.15}$
	O8	-1.09	[core]	$2s^{1.94}$	$2p^{5.15}$
	O9	-1.09	[core]	$2s^{1.94}$	$2p^{5.15}$
	O10	-1.14	[core]	$2s^{1.94}$	$2p^{5.20}$
3A	Fe1	1.73	[core]	$4s^{0.24}$	$3d^{6.03}$
	Fe2	1.67	[core]	$4s^{0.23}$	$3d^{6.10}$
	Fe3	1.69	[core]	$4s^{0.27}$	$3d^{6.04}$

	Fe4	1.71	[core]	$4s^{0.24}$	$3d^{6.05}$
	Fe5	1.71	[core]	$4s^{0.24}$	$3d^{6.05}$
	Fe6	1.67	[core]	$4s^{0.26}$	$3d^{6.07}$
	O7	-1.07	[core]	$2s^{1.92}$	$2p^{5.15}$
	O8	-1.22	[core]	$2s^{1.93}$	$2p^{5.29}$
	O9	-1.29	[core]	$2s^{1.93}$	$2p^{5.36}$
	O10	-1.11	[core]	$2s^{1.92}$	$2p^{5.19}$
	O11	-1.10	[core]	$2s^{1.92}$	$2p^{5.18}$
	O12	-1.10	[core]	$2s^{1.93}$	$2p^{5.17}$
	O13	-1.14	[core]	$2s^{1.93}$	$2p^{5.21}$
	O14	-1.06	[core]	$2s^{1.93}$	$2p^{5.13}$
	O15	-1.07	[core]	$2s^{1.92}$	$2p^{5.15}$
4A	Fe1	1.75	[core]	$4s^{0.23}$	$3d^{6.02}$
	Fe2	1.70	[core]	$4s^{0.25}$	$3d^{6.05}$
	Fe3	1.70	[core]	$4s^{0.23}$	$3d^{6.07}$
	Fe4	1.69	[core]	$4s^{0.26}$	$3d^{6.05}$
	Fe5	1.69	[core]	$4s^{0.26}$	$3d^{6.05}$
	Fe6	1.70	[core]	$4s^{0.26}$	$3d^{6.04}$
	Fe7	1.71	[core]	$4s^{0.24}$	$3d^{6.05}$
	Fe8	1.71	[core]	$4s^{0.24}$	$3d^{6.05}$
	O9	-1.30	[core]	$2s^{1.92}$	$2p^{5.38}$
	O10	-1.06	[core]	$2s^{1.92}$	$2p^{5.14}$
	O11	-1.07	[core]	$2s^{1.93}$	$2p^{5.14}$
	O12	-1.13	[core]	$2s^{1.92}$	$2p^{5.21}$
	O13	-1.07	[core]	$2s^{1.92}$	$2p^{5.15}$
	O14	-1.06	[core]	$2s^{1.92}$	$2p^{5.14}$
	O15	-1.04	[core]	$2s^{1.92}$	$2p^{5.12}$
	O16	-1.20	[core]	$2s^{1.92}$	$2p^{5.28}$
	O17	-1.15	[core]	$2s^{1.92}$	$2p^{5.23}$
	O18	-1.26	[core]	$2s^{1.92}$	$2p^{5.34}$
	O19	-1.23	[core]	$2s^{1.92}$	$2p^{5.31}$
	O20	-1.09	[core]	$2s^{1.92}$	$2p^{5.17}$
5A	Fe1	1.73	[core]	$4s^{0.24}$	$3d^{6.03}$
	Fe2	1.71	[core]	$4s^{0.24}$	$3d^{6.05}$
	Fe3	1.71	[core]	$4s^{0.25}$	$3d^{6.04}$
	Fe4	1.71	[core]	$4s^{0.25}$	$3d^{6.04}$
	Fe5	1.71	[core]	$4s^{0.25}$	$3d^{6.04}$
	Fe6	1.72	[core]	$4s^{0.24}$	$3d^{6.04}$
	Fe7	1.71	[core]	$4s^{0.25}$	$3d^{6.04}$
	Fe8	1.72	[core]	$4s^{0.24}$	$3d^{6.04}$
	Fe9	1.73	[core]	$4s^{0.22}$	$3d^{6.05}$
	Fe10	1.72	[core]	$4s^{0.22}$	$3d^{6.06}$
	O11	-1.22	[core]	$2s^{1.91}$	$2p^{5.31}$
	O12	-1.29	[core]	$2s^{1.92}$	$2p^{5.37}$
	O13	-1.20	[core]	$2s^{1.92}$	$2p^{5.28}$
	O14	-1.21	[core]	$2s^{1.91}$	$2p^{5.30}$
	O15	-1.13	[core]	$2s^{1.92}$	$2p^{5.21}$
	O16	-1.25	[core]	$2s^{1.91}$	$2p^{5.34}$
	O17	-1.03	[core]	$2s^{1.92}$	$2p^{5.11}$
	O18	-1.10	[core]	$2s^{1.92}$	$2p^{5.18}$
	O19	-1.13	[core]	$2s^{1.92}$	$2p^{5.21}$
	O20	-1.06	[core]	$2s^{1.92}$	$2p^{5.14}$
	O21	-1.26	[core]	$2s^{1.91}$	$2p^{5.35}$
	O22	-1.10	[core]	$2s^{1.92}$	$2p^{5.18}$
	O23	-1.04	[core]	$2s^{1.92}$	$2p^{5.12}$
	O24	-1.09	[core]	$2s^{1.92}$	$2p^{5.17}$
	O25	-1.05	[core]	$2s^{1.92}$	$2p^{5.13}$

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