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_{RS}) states,

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

with $\delta_{ij} = 0$ for parallel and $\delta_{ij} = 1$ 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_{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_{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	α2	r _{Fe-O}	Pair <i>i-j</i>	r _{ij}	J_{ij}
2A (3)	-	-	1.84	all		-132 ± 3
2B (4)	86	93	-	1-3 1-4	2.69	1 ± 1
				2-3 2-4		
	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 88	94 95	-	3-6 5-6	2.71 2.75	-37 ± 1 -22 ± 1		-	-	2.14 2.02	8-9 4-5	3.81 3.92	-22 ± 1 -98 ± 1
	85 83	102 101	-	1-2 4-8	2.84 2.84	-79 ± 1 -82 ± 1		-	-	2.04 2.16	3-7 1-6	4.00 4.12	-101 ± 1 -52 ± 1
	85 97	102	-	1-8	2.86	-106 ± 1	5R (56)	-	-	2.16	2-8	4.12	-50 ± 1
	91	95	-	2-5	2.80	-74 ± 1 25 ± 1	3D (30)	88	97 96	-	2-0 3-7	2.74	-91 ± 2 -6 ± 2
	93	94	-	4-5	2.89	22 ± 1		89	98	-	7-10	2.82	-13 ± 2
	87 88	97 96	-	2-4 4-7	2.90 2.91	-19 ± 1 -28 + 1		87 84	100	-	1-3 5-8	2.83	-52 ± 2 -75 + 2
	-	-	1.97	 5-7	3.19	-20 ± 1 -30 ± 1		91	94	-	6-10	2.87	25 ± 2
	-	-	1.96	6-7	3.33	-47 ± 1		87	95	-	6-8	2.88	6 ± 2
	-	-	1.83	1-3 3-7	3.35	-127 ± 1		93 87	97 98	-	8-10 3-9	2.91	0 ± 2 -10 + 2
	-	-	2.08	1-7	3.63	-24 ± 1		87	96	-	8-9	2.93	-7 ± 2
	-	-	1.92	2-6	3.68	-79 ± 1		87	96	-	1-9	2.96	-16 ± 2
	-	-	2.06 2.11	2-7 2-8	3.70 4.01	-55 ± 1 -49 + 1		85 86	99 99	-	5-9 9-10	2.96	-34 ± 2 -12 + 2
	-	-	2.14	1-4	4.08	-62 ± 1		-	-	1.93	7-9	3.00	-35 ± 2
	-	-	-	2-3	4.16	-2 ± 1		-	-	1.83	1-4	3.08	-143 ± 2
4B (37)	84 82	92 00	-	6-8 1 2	2.68	-57 ± 1		-	-	1.83 1.83	4-5 2-4	3.09	-144 ± 2 -150 + 2
	90	99 94	-	2-4	2.83	-32±3		95	98	-	6-9	3.18	9 ± 2
	86	100	-	5-7	2.84	-86 ± 1		96	101	-	2-9	3.19	-1 ± 2
	85 86	101	-	3-7 1-7	2.86 2.87	-76 ± 2 -80 + 1		-	-	2.01	1-2 1-5	3.39 3.47	-35 ± 2 -50 + 2
	92	94	-	3-4	2.88	2 ± 1		-	-	2.17	2-5	3.47	-9 ± 2
	85	97	-	2-3	2.91	-10 ± 2		-	-	2.01	2-3	3.92	-66 ± 2
	88	96	- 184	3-5 4-8	2.92 2.94	-22 ± 1 -125 + 1		-	-	2.13	6-7 2-8	3.93 4.22	-110 ± 2 -78 \pm 2
	-	-	1.97	4-5	3.06	-41 ± 1		-	-	2.13	5-6	4.22	-76 ± 2
	-	-	1.85	1-6 5.6	3.20	-139 ± 2							
	- -	- -	1.85 1.97 1.95	1-6 5-6 2-6	3.20 3.23 3.31	-139 ± 2 -33 ± 1 -53 ± 2	A singl	e Sl	ater	determi	nant of	a BS	state is
	- - -	- - -	1.85 1.97 1.95 2.00	1-6 5-6 2-6 4-6	3.20 3.23 3.31 3.38	-139 ± 2 -33 ± 1 -53 ± 2 -41 ± 1	A singl considera of higher	e SI bly s spin	ater pin co multi	determi ontamin plicities	nant of ated due into the	a BS e to the BS way	state is admixture vefunction.
		-	1.85 1.97 1.95 2.00 1.92 2.10	1-6 5-6 2-6 4-6 5-8 1-5	3.20 3.23 3.31 3.38 3.60 3.67	-139 ± 2 -33 ± 1 -53 ± 2 -41 ± 1 -84 ± 2 -15 ± 2	A single considera of higher Several a	e SI bly s spin pproa	ater pin co multi aches	determi ontamina plicities were se	nant of ated due into the uggestee	a BS e to the BS way d for dete	state is admixture refunction. ermination
	- - - -		1.85 1.97 1.95 2.00 1.92 2.10 2.11	1-6 5-6 2-6 4-6 5-8 1-5 2-5	3.20 3.23 3.31 3.38 3.60 3.67 3.86	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \end{array}$	A singli considera of higher Several a of J _{ij} using BS form	e SI bly s spin pproa g spir alism	ater pin co multi aches n projo of	determi ontamina plicities were su ection o Noodle	nant of ated due into the uggested perators man ef	a BS e to the BS wav d for dete . Among	state is admixture refunction. ermination them, the a good
	- - - - -		1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13	1-6 5-6 2-6 4-6 5-8 1-5 2-5 2-7	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99	-139 ± 2 -33 ± 1 -53 ± 2 -41 ± 1 -84 ± 2 -15 ± 2 -36 ± 1 -41 ± 2 -36 ± 1	A single considera of higher Several a of <i>J_{ij}</i> using BS form approxima	e SI bly s spin pproa g spir alism ation	ater pin co multi aches n projo of whe	determi ontamin plicities were su ection o Noodle en ove	nant of ated due into the uggested perators man <i>et</i> rlap be	a BS e to the BS wav d for dete . Among <i>al.</i> is etween	state is admixture refunction. ermination them, the a good magnetic
54 (70)	- - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14	1-6 5-6 2-6 4-6 5-8 1-5 2-5 2-7 1-3	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79	$\begin{array}{r} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ \end{array}$	A single considera of higher Several a of <i>J_{ij}</i> using BS forma approxima orbitals is this condi	e SI bly s spin pproa g spir alism ation s suff	ater pin co multi aches projo of whe icient	determi ontamin plicities were su ection o Noodle en ove ly small	nant of ated due into the uggested perators man <i>et</i> rlap be . ¹⁻³ A go	a BS e to the BS way d for dete . Among <i>al.</i> is etween bod estin	state is admixture refunction. ermination them, the a good magnetic mation for
5A (70)	- - - - - - - - - - - 87 87	- - - - - - - - - - - - 98 98	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14	1-6 5-6 2-6 4-6 5-8 1-5 2-5 2-7 1-3 3-4 4-7	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79 2.79	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ -33 \pm 1 \\ -32 \pm 1 \end{array}$	A single considera of higher Several a of <i>J_{ij}</i> using BS forma orbitals is this condir spin expe	e SI bly s spin pproa g spir alism ation s suff tion c ectatio	ater pin co multi aches o projo of whe icient can be can be	determi ontamin plicities were su ection o Noodle en ove ly small e obtain lue of a	nant of ated due into the uggested perators man <i>et</i> rlap be . ¹⁻³ A go ed from single	a BS e to the BS wav d for dete . Among <i>al.</i> is etween bod estin comparia Slater de	state is admixture refunction. ermination them, the a good magnetic mation for son of the eterminant
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5A (70)	- - - - - - 87 87 87 87 87 87 84	- - - - - - - - - - - - - - - - - - -	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14 - - - - -	1-6 5-6 2-6 4-6 5-8 1-5 2-5 2-7 1-3 3-4 4-7 3-5 5-7 1-8	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79 2.79 2.79 2.81 2.81 2.86	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ \hline -33 \pm 1 \\ -32 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -25 \pm 1 \end{array}$	A single considera of higher Several a of <i>J_{ij}</i> using BS forma approxima orbitals is this condi spin expe built with with the determina	e SI bly s spin pproa g spir alism ation s suff tion c static spati one one	ater pin co multi aches of of whe icient can be on va ally o con 2). ⁴ F	determi ontamin plicities were su ection of Noodle en ove ly small e obtain lue of a rthogon nputed	nant of ated due into the uggested perators man <i>et</i> rlap be . ¹⁻³ A go ed from single s al α and for the total nu	a BS be to the BS way d for dete Among <i>al.</i> is etween comparia Slater de Slater de unresti mber of	state is admixture refunction. ermination them, the a good magnetic mation for son of the eterminant als, $\langle S^2 \rangle_{SD}$, ricted BS
5A (70)	- - - - - - 87 87 87 87 87 87 84 84	- - - - - - - - - - - - - - - - - - -	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14 - - - - - - - - -	1-6 5-6 2-6 4-6 5-8 1-5 2-5 2-7 1-3 3-4 4-7 3-5 5-7 1-8 2-9	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79 2.79 2.81 2.81 2.81 2.86 2.87	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ -33 \pm 1 \\ -32 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -25 \pm 1 \\ -110 \pm 1 \end{array}$	A single considera of higher Several a of <i>J_{ij}</i> using BS forma orbitals is this condir spin exper built with with the determina electrons	e SI bly s spin pproa g spir alism ation s suff tion c spati one spati n_{α} an	ater pin co multipaches of of whe icient can be on val ally o con 2 $^{.4}$ F nd n_{β}	determine ontamine plicities were sup- ection of Noodle on over ly small e obtain lue of a rthogon puted for the $(n_{\alpha} \geq 1)$	nant of ated due into the uggested perators man <i>et</i> rlap be . ¹⁻³ A go ed from single s al α and for the total nu n_{β}), res	a BS e to the BS wav d for dete Among <i>al.</i> is etween compari- Slater de Unresti mber of pectively	state is admixture refunction. ermination them, the a good magnetic mation for son of the eterminant als, $\langle S^2 \rangle_{SD}$, ricted BS α and β $\langle S^2 \rangle_{SD}$ is
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5A (70)	- - - - - - - - - - 87 87 87 87 87 87 87 87 87 84 84 84 84 84 86 86 - - - - - - - - - - - - - - - - -	- - - - - - - - - - - - - - - - - - -	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14 - - - - - - - - - - - - - - - - - - -	$\begin{array}{c} 1-6\\ 5-6\\ 2-6\\ 4-6\\ 5-8\\ 1-5\\ 2-7\\ 1-3\\ 3-4\\ 4-7\\ 3-5\\ 5-7\\ 1-8\\ 2-9\\ 6-9\\ 2-6\\ 1-2\\ 6-8\\ 9-10\\ 1-10\\ 8-10\\ 2-3\\ 6-7\\ 2-5\\ 5-6\\ 1-3\\ 7-8\\ 1-4\\ \end{array}$	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79 2.79 2.81 2.81 2.81 2.81 2.86 2.87 2.92 2.93 2.93 2.93 2.93 2.95 3.00 3.00 3.14 3.18 3.18 3.19 3.19 3.24	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ \hline -33 \pm 1 \\ -32 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -111 \pm 1 \\ -112 \pm 1 \\ -142 \pm 1 \\ -145 \pm 1 \\ -145 \pm 1 \\ -26 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -31 \pm 1 \\ -34 \pm 1 \\ \end{array}$	A single considera of higher Several a of J_{ij} using BS form: approxima orbitals is this condi spin expe- built with with the determina electrons given by $\langle S$ Calculated Table S2 n = 2-5 a is apparent FM state, Slater det $\langle S^2 \rangle$ are windicating supports t	e SI bly s spin pproa g spir alism ation c spati- tion c spati- one n_{α} an $2^{SD} =$ d $\langle S^{2} \rangle$ for th long nt that whice termin very c a w the ap	ater pin co multipaches aches proje of whe icient can be pon val ally o con con con 2). ⁴ F nd n_β = $\left(\frac{n_\alpha}{m_\beta}\right)^{-2}$ so are chose con con con con con con con con	determine plicities were supervised ection of Noodle en over ly small e obtain lue of a rthogon puted for the $(n_{\alpha} \ge \frac{-n_{\beta}}{2})^2$ and $\langle S^2 \rangle$ we correspond all cases usually is negliging to the poverlap ch used	nant of ated due into the uggested perators man <i>et</i> rlap be al α and for the total nu n_{β}), res $+\left(\frac{n_{\alpha}+}{2}\right)$ values a table (Fe onding spin well des gible. Co correspondent for calcular	a BS be to the BS wave d for dete Among al. is between bod estin comparia Slater de bod estin comparia Slater de l β orbita unrestri mber of pectively $\frac{n_{\beta}}{2}$). re summ $c_2O_3)_n$ clup pin multi n contan cribed b bomputed boding (S netic orb ulation of	state is admixture vefunction. ermination them, the a good magnetic mation for son of the eterminant als, $\langle S^2 \rangle_{SD}$, ricted BS α and β $\langle S^2 \rangle_{SD}$ is (S2) marized in usters with plicities. It nination of y a single values of $\langle S^2 \rangle_{SD}$ ones itals. This f magnetic
5A (70)	- - - - - - - - - - 87 87 87 87 87 87 87 87 87 87 87 87 87	- - - - - - - - - - - - - - - - - - -	1.85 1.97 1.95 2.00 1.92 2.10 2.11 2.13 2.14 - - - - - - - - - - - - - - - - - - -	$\begin{array}{c} 1-6\\ 5-6\\ 2-6\\ 4-6\\ 5-8\\ 1-5\\ 2-7\\ 1-3\\ 3-4\\ 4-7\\ 3-5\\ 5-7\\ 1-8\\ 2-9\\ 6-9\\ 2-6\\ 1-2\\ 6-8\\ 9-10\\ 1-10\\ 8-10\\ 2-3\\ 6-7\\ 2-5\\ 5-6\\ 1-3\\ 7-8\\ 4-8\\ 4-8\\ 4-8\\ 4-8\\ 4-8\\ 4-8\\ 4-8\\ 4$	3.20 3.23 3.31 3.38 3.60 3.67 3.86 3.99 4.09 2.79 2.79 2.81 2.81 2.81 2.86 2.87 2.87 2.92 2.93 2.93 2.93 2.95 3.00 3.00 3.14 3.18 3.18 3.19 3.24 3.24	$\begin{array}{c} -139 \pm 2 \\ -33 \pm 1 \\ -53 \pm 2 \\ -41 \pm 1 \\ -84 \pm 2 \\ -15 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -36 \pm 1 \\ -41 \pm 2 \\ -54 \pm 2 \\ \hline -33 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -110 \pm 1 \\ -111 \pm 1 \\ -125 \pm 1 \\ -144 \pm 1 \\ -145 \pm 1 \\ -145 \pm 1 \\ -26 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -30 \pm 1 \\ -31 \pm 1 \\ -34 \pm 1 \\ $	A single considera of higher Several a of J_{ij} using BS forms approxima orbitals is this condi spin exper- built with with the determina electrons given by $\langle S$ Calculated Table S2 n = 2-5 a is apparent FM state, Slater det $\langle S^2 \rangle$ are w indicating supports t coupling of	e SI bly s spin pproa g spir alism ation c sctatic spati- ctatic spati- na an $^{2}\rangle_{SD} =$ d $\langle S^{2}\rangle$ for th long nt that whick remini- very of a with the ap-	ater pin co multiplications projection of where icient can be con value ally on con con con con con con con c	determining plicities were supervised ection of Noodle e obtain lue of a rthogon for the $(n_{\alpha} \ge \frac{-n_{\beta}}{2})^2$ and $\langle S^2 \rangle =$ most sic correspond all cases usually to the poverlap ch used	nant of ated due into the uggested perators man <i>et</i> rlap be . ¹⁻³ A go ed from single and for the total nu n_{β} , res + $\left(\frac{n_{\alpha} + +}{2}\right)$ values a table (Fe onding spin well des gible. Co corresponding for calcu	a BS to the BS way d for dete Among <i>al.</i> is etween bod estin comparia Slater de unrestri- mber of pectively $\frac{n_{\beta}}{2}$. re summ $c_2O_3)_n$ clup pin multin n contant cribed b bomputed bomputed bod orbitant cribed not and a statement onding (S	state is admixture refunction. ermination them, the a good magnetic mation for son of the eterminant als, $\langle S^2 \rangle_{SD}$, ricted BS α and β r, $\langle S^2 \rangle_{SD}$ is (S2) narized in usters with plicities. It nination of y a single values of $S^2 \rangle_{SD}$ ones itals. This f magnetic

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	<s²>_{SD}</s²>	<\$ 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 Fe₂O₃

Results of natural population analysis⁵ 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.



Fig. S2 Spin density isosurfaces for the ${}^{1}B_{1}$ state of **1A** and ${}^{1}A_{2}$ 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 Fe²⁺ (Fe2, Fig. S2), threefold coordinated Fe³⁺ (Fe1), two twofold coordinated O²⁻ (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 Fe³⁺, Fe²⁺ and O⁻, respectively. In contrast, the remaining clusters can be interpreted exclusively in terms of Fe³⁺ and O²⁻ 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 o	configuration
1 A	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}
	07	-1.09	[core]	2s ^{1.94}	2p ^{5.15}
	08	-1.09	[core]	2s ^{1.94}	2p ^{5.15}
	09	-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}	
	07	-1.07	[core]	2s ^{1.92}	2p ^{5.15}	
	08	-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}	
	011	-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}	
	014	-1.06	[core]	2s ^{1.93}	2p ^{5.13}	
	015	-1.07	[core]	2s ^{1.92}	2p ^{5.15}	
44	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]	$4 e^{0.26}$	3d ^{6.05}	
	Fo5	1.00	[core]	40 ^{0.26}	3d ^{6.05}	
	Fe6	1.03	[core]	40 ^{0.26}	3d ^{6.04}	
	Fo7	1.70	[core]	40 ^{0.24}	3d ^{6.05}	
		1.71	[coro]	45 40 ^{0.24}	3d ^{6.05}	
		1.71	[core]	45 20 ^{1.92}	20 ^{5.38}	
	09	-1.30	[core]	25 2e ^{1.92}	2p 2m ^{5.14}	
	010	-1.06	[core]	2S	2p	
	011	-1.07	[core]	2S	2p 2,5,21	
	012	-1.13	[core]	25 ¹⁹²	2p ^{5.15}	
	013	-1.07	[core]	2s ^{1.02}	2p ^{5.16}	
	014	-1.06	[core]	2s ¹	2p ⁵¹⁷	
	O15	-1.04	[core]	2s ^{1.92}	2p_12	
	O16	-1.20	[core]	2s ^{1.92}	2p ^{5.28}	
	017	-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]	49 ^{0.24}	3d ^{6.04}	
	F_Q	1.72	[core]	$1e^{0.22}$	3d ^{6.05}	
	Fo10	1.70	[core]	40 ^{0.22}	3d ^{6.06}	
		1.72	[coro]	45 2c ^{1.91}	2n ^{5.31}	
	011	-1.22	[core]	25 20 ^{1.92}	2p 2p ^{5.37}	
	012	-1.29	[core]	25 2e ^{1.92}	2p 2p ^{5.28}	
	013	-1.20	[core]	2S 0=1.91	2p	
	014	-1.21	[core]	2S	2p	
	015	-1.13	[core]	2S ¹ 91	2p	
	016	-1.25	[core]	2s ^{1.0}	2p ^{5.01}	
	017	-1.03	[core]	2s ¹ ³²	2p ⁵ 18	
	O18	-1.10	[core]	2s ^{1.92}	2p	
	O19	-1.13	[core]	2s ^{1.92}	2p ^{5.2}	
	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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