Electronic Supplementary Information

Influence of oxidation on the magnetism of small Co oxide clusters probed by Stern-Gerlach deflection

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The electronic supplementary information (ESI) contains:

- A schematic overview of the experimental setup (Fig. S1)
- A brief explanation about the determination of the magnetic field
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- Beam profiles of all identified Co_nO_m clusters (Fig. S3 - S5)

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1 Experimental setup

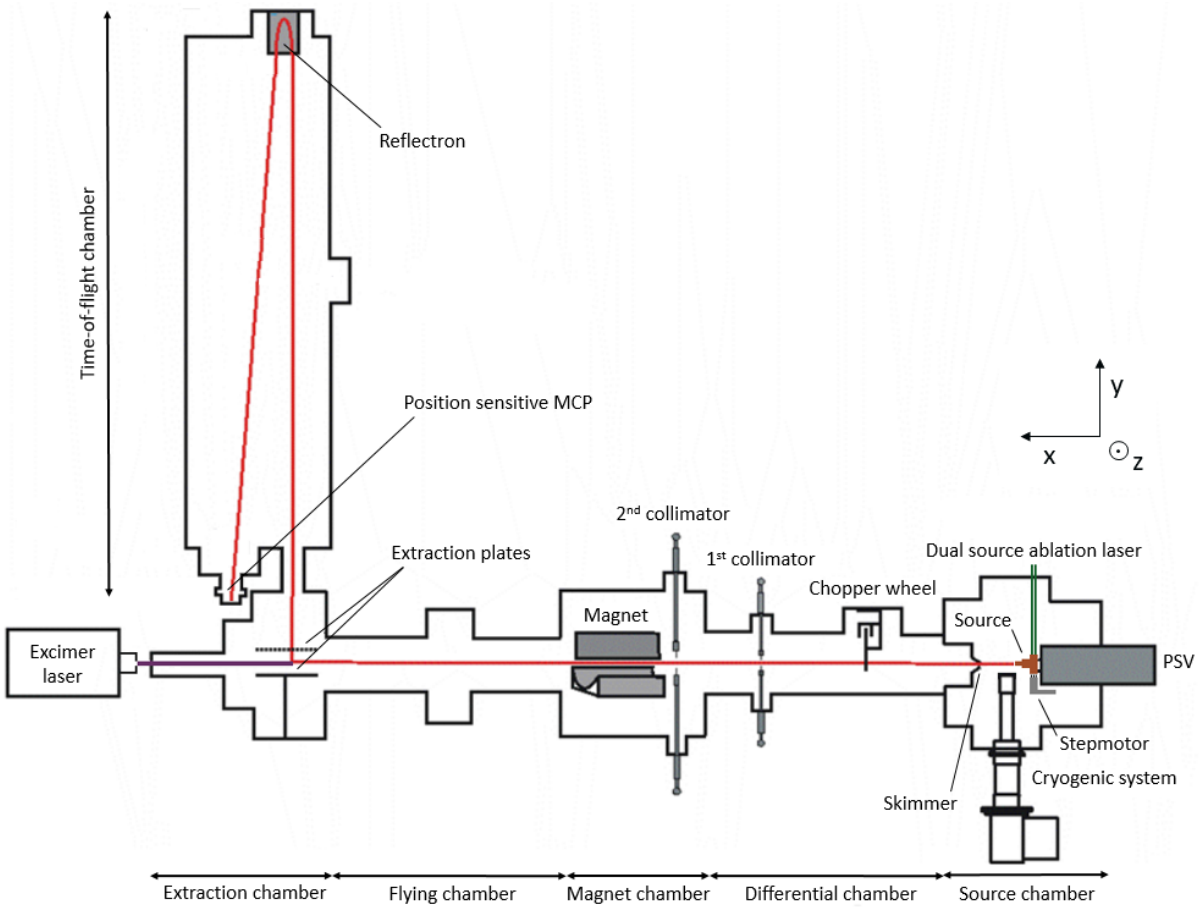

Fig. S1 Schematical top view of the magnetic deflection setup that was used to perform the velocity scan and Stern-Gerlach deflection experiments. The path of the molecular cluster beam is shown in red, emerging from the source chamber at the bottom right. The x, y and z directions are also defined.

2 Determination of the magnetic field

The magnetic field to which a cluster is subject during its trajectory inside the magnet is estimated as follows. The positional dependence of the magnetic field, $B(z)$, depends both on the geometry of the magnet and the applied current I. Because different positional dependences for different currents will only differ by a scaling factor $s(I)$, knowing the magnetic field gradient, $\delta_z B$, the value of the magnetic field at the high field pole, B_{max}, can be inferred from known reference values:

$$B_{max} = B_{max,ref} \frac{\delta_z B}{(\delta_z B)_{ref}}, \tag{1}$$

where quantities with index 'ref' refer to the respective reference values at a reference current I_{ref}. $B_{max,ref}$ was estimated from direct measurements with a Hall probe and the field gradient $(\delta_z B)_{ref}$ was determined by means of atomic deflection experiments. Between the poles of the magnet, a cluster follows a parabolic path that can be reconstructed from the measured total deflection d_{tot}. The deflection d_M at the end of the magnet, where the parabolic path ends and whereafter the clusters will follow a straight path, is given by:

$$d_M = \gamma_m d_{tot}, \tag{2}$$

with γ_m a proportionality constant that depends on the mass m of a cluster. Finally, the value of the magnetic field at a specific point on the cluster path can be calculated from the gradient and its distance from the point where B_{max} was determined.

3 Additional DFT results

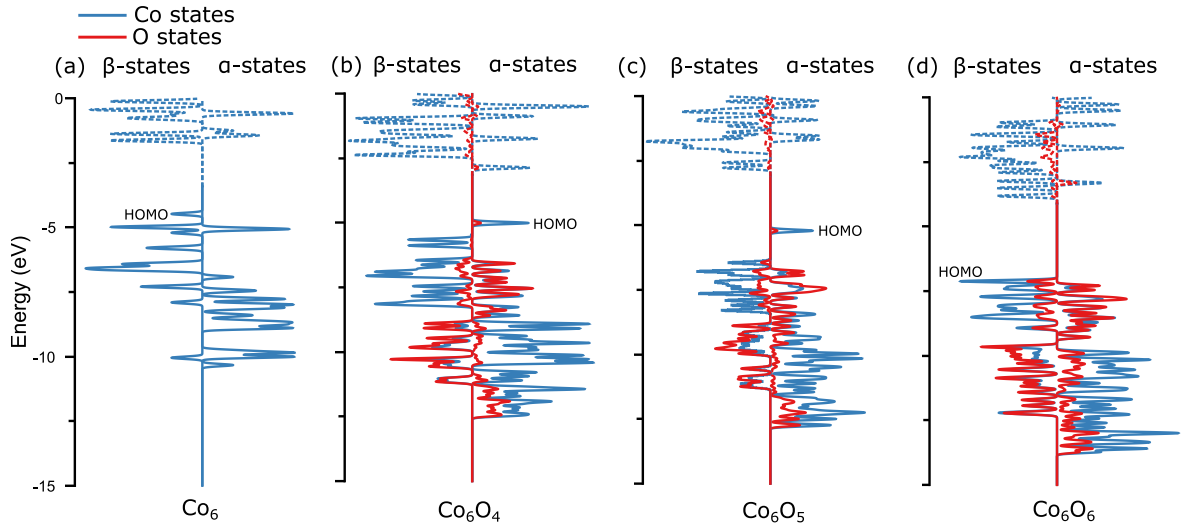

Fig. S2 Density of states of (a) Co_6, (b) Co_6O_4, (c) Co_6O_5 and (d) Co_6O_6, projected onto atomic orbitals of cobalt (blue) and oxygen (red). The occupied and empty states are depicted by continues and dotted lines, respectively. The left and right sides of each panel present the β- and α-states, respectively. The HOMO states are labeled. In Co_6, the valence d-band spans roughly between -4 and -10 eV. The addition of oxygen widens this band, with new states that result from hybridisation of Co 3d and O 2s and 2p contributions. The more oxygen is added, the more significant overlap between Co and O.

Table S1 Partial electron charges (in units of the elementary electric charge e) of the different atoms (labeled according to Fig. 5) in Co_6O_m (m = 0, 4 - 6) using the Löwdin, NPA and Bader schemes.

		Co(1)	Co(2)	Co(3)	Co(4)	Co(5)	Co(6)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
	Löwdin	-0.01	0.01	-0.01	0.00	0.00	0.01	-	-	-	-	-	-
Co_6	NPA	-0.01	0.01	-0.01	0.00	0.00	0.01	-	-	-	-	-	-
	Bader	-0.01	0.01	-0.01	0.00	0.00	0.01	-	-	-	-	-	-
	Löwdin	0.13	0.27	0.13	0.32	0.22	0.20	-0.31	-0.32	-0.32	-0.31	-	-
Co_6O_4	NPA	0.93	0.96	0.93	1.05	0.73	0.73	-1.32	-1.35	-1.35	-1.33	-	-
	Bader	0.83	0.84	0.83	0.91	0.66	0.65	-1.18	-1.18	-1.18	-1.18	-	-
	Löwdin	0.36	0.25	0.17	0.25	0.36	0.34	-0.35	-0.35	-0.33	-0.34	-0.35	-
Co_6O_5	NPA	1.40	0.86	0.98	0.85	1.39	1.39	-1.39	-1.38	-1.35	-1.36	-1.37	-
	Bader	1.22	0.77	0.88	0.76	1.21	1.21	-1.21	-1.21	-1.20	-1.21	-1.22	-
	Löwdin	0.28	0.36	0.28	0.13	0.24	0.36	-0.25	-0.25	-0.29	-0.29	-0.28	-0.28
Co_6O_6	NPA	1.26	1.22	1.29	1.07	1.18	1.20	-1.21	-1.20	-1.28	-1.26	-1.14	-1.26
	Bader	1.01	0.84	1.05	0.98	0.96	0.87	-0.96	-0.96	-1.00	-0.99	-0.92	-0.89

Table S2 Wiberg bond indices for the individual bonds between atoms (labeled according to Fig. 5) in Co_6O_m (m = 0, 4 - 6) with a minimal value of 0.05.

Co_6		Co_6O_4		Co_6O_5		Co_6O_6	
Co(1)-Co(2)	0.66	Co(1)-Co(2)	0.24	Co(1)-Co(2)	0.12	Co(1)-Co(2)	0.17
Co(1)-Co(3)	0.20	Co(1)-Co(3)	0.06	Co(1)-Co(4)	0.12	Co(1)-Co(4)	0.38
Co(1)-Co(4)	0.66	Co(1)-Co(4)	0.23	Co(1)-Co(5)	0.19	Co(1)-Co(5)	0.42
Co(1)-Co(5)	0.66	Co(1)-Co(5)	0.34	Co(1)-Co(6)	0.18	Co(1)-Co(6)	0.44
Co(1)-Co(6)	0.66	Co(1)-Co(6)	0.36	Co(1)-O(1)	0.85	Co(1)-O(1)	0.71
Co(2)-Co(3)	0.66	Co(1)-O(1)	1.02	Co(1)-O(2)	0.84	Co(1)-O(2)	0.69
Co(2)-Co(4)	0.65	Co(1)-O(2)	0.98	Co(1)-O(5)	0.68	Co(1)-O(5)	1.13
Co(2)-Co(5)	0.65	Co(2)-Co(3)	0.24	Co(2)-Co(3)	0.38	Co(2)-Co(3)	0.41
Co(2)-Co(6)	0.20	Co(2)-Co(4)	0.31	Co(2)-Co(4)	0.50	Co(2)-Co(4)	0.43
Co(3)-Co(4)	0.66	Co(2)-Co(5)	0.25	Co(2)-Co(5)	0.20	Co(2)-Co(5)	0.43
Co(3)-Co(5)	0.66	Co(2)-Co(6)	0.06	Co(2)-O(1)	0.84	Co(2)-Co(6)	0.07
Co(3)-Co(6)	0.66	Co(2)-O(1)	0.88	Co(2)-O(4)	0.67	Co(2)-O(1)	0.97
Co(4)-Co(5)	0.20	Co(2)-O(4)	0.88	Co(3)-Co(4)	0.38	Co(2)-O(4)	1.02
Co(4)-Co(6)	0.65	Co(3)-Co(4)	0.23	Co(3)-Co(5)	0.18	Co(2)-O(6)	0.14
Co(5)-Co(6)	0.65	Co(3)-Co(5)	0.34	Co(3)-Co(6)	0.19	Co(3)-Co(4)	0.42
		Co(3)-Co(6)	0.36	Co(3)-O(3)	1.03	Co(3)-Co(5)	0.32
		Co(3)-O(3)	0.99	Co(3)-O(4)	0.99	Co(3)-Co(6)	0.20
		Co(3)-O(4)	1.02	Co(4)-Co(6)	0.19	Co(3)-O(3)	0.77
		Co(4)-Co(5)	0.05	Co(4)-O(2)	0.86	Co(3)-O(4)	0.71
		Co(4)-Co(6)	0.22	Co(4)-O(3)	0.60	Co(3)-O(6)	1.09
		Co(4)-O(2)	0.87	Co(5)-Co(6)	0.11	Co(4)-Co(5)	0.11
		Co(4)-O(3)	0.87	Co(5)-O(1)	0.69	Co(4)-Co(6)	0.42
		Co(5)-Co(6)	0.56	Co(5)-O(4)	0.80	Co(4)-O(1)	0.88
		Co(5)-O(1)	0.61	Co(5)-O(5)	0.86	Co(4)-O(2)	0.88
		Co(5)-O(4)	0.60	Co(6)-O(2)	0.68	Co(4)-O(3)	0.07
		Co(6)-O(2)	0.64	Co(6)-O(3)	0.83	Co(4)-O(6)	1.21
		Co(6)-O(3)	0.64	Co(6)-O(5)	0.85	Co(5)-Co(6)	0.38
						Co(5)-O(1)	0.06
						Co(5)-O(3)	0.59
						Co(5)-O(4)	0.73
						Co(5)-O(5)	1.04
						Co(6)-O(2)	0.96
						Co(6)-O(3)	1.01
						Co(6)-O(5)	0.14
						O(2)-O(6)	0.06

Table S3 Partial electron charges (in units of the elementary electric charge e) of the different atoms (labeled according to Fig. 5) in Co_7O_m (m = 0, 3 - 5) using the Löwdin, NPA and Bader schemes.

		Co(1)	Co(2)	Co(3)	Co(4)	Co(5)	Co(6)	Co(7)	O(1)	O(2)	O(3)	O(4)	O(5)
Co_7	Löwdin	-0.09	0.00	0.12	0.02	-0.07	0.11	-0.09	-	-	-	-	-
	NPA	-0.08	-0.03	0.13	-0.04	-0.01	0.08	-0.06	-	-	-	-	-
	Bader	0.01	-0.01	-0.00	-0.01	-0.02	0.02	0.02	-	-	-	-	-
Co_7O_3	Löwdin	0.06	0.15	0.07	0.22	0.14	0.09	0.10	-0.26	-0.29	-0.29	-	-
	NPA	0.44	0.79	0.49	0.94	0.78	0.53	-0.08	-1.27	-1.31	-1.29	-	-
	Bader	0.40	0.69	0.46	0.82	0.71	0.49	-0.11	-1.15	-1.16	-1.17	-	-
Co_7O_4	Löwdin	0.13	0.16	0.18	0.19	0.12	0.18	0.19	-0.28	-0.29	-0.27	-0.29	-
	NPA	0.81	0.81	0.79	0.89	0.51	0.48	0.93	-1.28	-1.32	-1.27	-1.35	-
	Bader	0.76	0.73	0.70	0.79	0.53	0.34	0.86	-1.17	-1.17	-1.16	-1.20	-
Co_7O_5	Löwdin	0.16	0.17	0.23	0.16	0.16	0.24	0.30	-0.30	-0.28	-0.29	-0.28	-0.27
	NPA	0.82	0.80	0.95	0.77	0.82	0.95	1.25	-1.33	-1.27	-1.29	-1.25	-1.24
	Bader	0.77	0.75	0.84	0.71	0.77	0.85	1.15	-1.19	-1.18	-1.18	-1.16	-1.13

Table S4 Wiberg bond indices for the individual bonds between atoms (labeled according to Fig. 5) in Co_7O_m (m = 0, 3 - 5) with a minimal value of 0.05.

Co_7		Co_7O_3		Co_7O_4		Co_7O_5	
Co(1)-Co(2)	0.50	Co(1)-Co(2)	0.29	Co(1)-Co(2)	0.26	Co(1)-Co(2)	0.23
Co(1)-Co(3)	0.13	Co(1)-Co(3)	0.49	Co(1)-Co(3)	0.27	Co(1)-Co(3)	0.38
Co(1)-Co(4)	0.13	Co(1)-Co(4)	0.08	Co(1)-Co(4)	0.08	Co(1)-Co(5)	0.07
Co(1)-Co(5)	0.52	Co(1)-Co(5)	0.30	Co(1)-Co(5)	0.32	Co(1)-Co(6)	0.22
Co(1)-Co(6)	0.47	Co(1)-Co(6)	0.48	Co(1)-Co(6)	0.23	Co(1)-Co(7)	0.24
Co(1)-Co(7)	0.52	Co(1)-Co(7)	0.53	Co(1)-Co(7)	0.31	Co(1)-O(3)	0.94
Co(2)-Co(3)	0.49	Co(1)-O(1)	0.84	Co(1)-O(3)	0.88	Co(1)-O(4)	0.98
Co(2)-Co(4)	0.13	Co(2)-Co(3)	0.08	Co(1)-O(4)	0.84	Co(2)-Co(3)	0.36
Co(2)-Co(5)	0.13	Co(2)-Co(4)	0.29	Co(2)-Co(3)	0.27	Co(2)-Co(4)	0.30
Co(2)-Co(6)	0.51	Co(2)-Co(5)	0.28	Co(2)-Co(4)	0.27	Co(2)-Co(5)	0.21
Co(2)-Co(7)	0.50	Co(2)-Co(6)	0.34	Co(2)-Co(5)	0.39	Co(2)-Co(6)	0.06
Co(3)-Co(4)	0.52	Co(2)-O(1)	0.88	Co(2)-Co(7)	0.07	Co(2)-Co(7)	0.06
Co(3)-Co(5)	0.13	Co(2)-O(2)	0.85	Co(2)-O(2)	0.87	Co(2)-O(2)	0.90
Co(3)-Co(6)	0.50	Co(3)-Co(4)	0.34	Co(2)-O(3)	0.92	Co(2)-O(3)	0.84
Co(3)-Co(7)	0.50	Co(3)-Co(5)	0.36	Co(3)-Co(4)	0.29	Co(3)-Co(4)	0.34
Co(4)-Co(5)	0.49	Co(3)-Co(6)	0.53	Co(3)-Co(5)	0.06	Co(3)-Co(7)	0.22
Co(4)-Co(6)	0.49	Co(3)-Co(7)	0.66	Co(3)-Co(7)	0.31	Co(3)-O(1)	0.90
Co(4)-Co(7)	0.50	Co(3)-O(3)	0.79	Co(3)-O(1)	0.79	Co(3)-O(3)	0.85
Co(5)-Co(6)	0.53	Co(4)-Co(5)	0.28	Co(3)-O(3)	0.83	Co(4)-Co(5)	0.32
Co(5)-Co(7)	0.50	Co(4)-Co(6)	0.33	Co(4)-Co(5)	0.35	Co(4)-Co(7)	0.24
Co(6)-Co(7)	0.43	Co(4)-O(2)	0.90	Co(4)-Co(7)	0.28	Co(4)-O(1)	0.87
		Co(4)-O(3)	0.90	Co(4)-O(1)	0.92	Co(4)-O(2)	0.84
		Co(5)-Co(6)	0.09	Co(4)-O(2)	0.90	Co(5)-Co(6)	0.43
		Co(5)-O(1)	0.89	Co(5)-Co(6)	0.69	Co(5)-Co(7)	0.20
		Co(5)-O(3)	0.87	Co(5)-Co(7)	0.27	Co(5)-O(2)	0.91
		Co(6)-Co(7)	0.62	Co(5)-O(2)	0.82	Co(5)-O(5)	0.98
		Co(6)-O(2)	0.83	Co(5)-O(4)	0.10	Co(6)-Co(7)	0.21
				Co(6)-Co(7)	0.20	Co(6)-O(4)	1.02
				Co(6)-O(4)	0.90	Co(6)-O(5)	1.04
				Co(7)-O(1)	0.91	Co(7)-O(1)	0.78
				Co(7)-O(4)	0.84	Co(7)-O(4)	0.60
						Co(7)-O(5)	0.60

Table S5 Natural electron configuration per atom (labeled according to Fig. 5) in Co_6 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.82}4p^{0.09}4d^{0.01}$
Co(2)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.81}4p^{0.09}4d^{0.01}$
Co(3)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.82}4p^{0.09}4d^{0.01}$
Co(4)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.81}4p^{0.09}4d^{0.01}$
Co(5)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.81}4p^{0.09}4d^{0.01}$
Co(6)	[Ar]$4s^{0.65}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.42}3d^{2.81}4p^{0.09}4d^{0.01}$

Table S6 Natural electron configuration per atom (labeled according to Fig. 5) in Co_6O_4 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.24}3d^{4.91}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.24}3d^{2.63}4p^{0.02}4d^{0.01}$
Co(2)	[Ar]$4s^{0.16}3d^{4.96}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.32}3d^{2.52}4p^{0.04}4d^{0.01}$
Co(3)	[Ar]$4s^{0.24}3d^{4.91}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.24}3d^{2.63}4p^{0.02}4d^{0.01}$
Co(4)	[Ar]$4s^{0.15}3d^{4.96}4p^{0.02}$	[Ar]$4s^{0.29}3d^{2.46}4p^{0.04}4d^{0.01}$
Co(5)	[Ar]$4s^{0.48}3d^{4.98}4p^{0.05}4d^{0.01}$	[Ar]$4s^{0.24}3d^{2.46}4p^{0.04}4d^{0.01}$
Co(6)	[Ar]$4s^{0.48}3d^{4.98}4p^{0.05}4d^{0.01}$	[Ar]$4s^{0.23}3d^{2.46}4p^{0.05}4d^{0.01}$
O(1)	[He]$2s^{0.97}2p^{2.84}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.54}3d^{0.01}$
O(2)	[He]$2s^{0.97}2p^{2.84}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.56}3d^{0.01}$
O(3)	[He]$2s^{0.97}2p^{2.84}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.56}3d^{0.01}$
O(4)	[He]$2s^{0.97}2p^{2.85}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.54}3d^{0.01}$

Table S7 Natural electron configuration per atom (labeled according to Fig. 5) in Co_6O_5 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.14}3d^{4.97}4p^{0.01}$	[Ar]$4s^{0.12}3d^{2.34}4p^{0.01}$
Co(2)	[Ar]$4s^{0.47}3d^{4.98}4p^{0.05}4d^{0.01}$	[Ar]$4s^{0.24}3d^{2.35}4p^{0.03}4d^{0.01}$
Co(3)	[Ar]$4s^{0.23}3d^{4.93}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.23}3d^{2.57}4p^{0.02}4d^{0.01}$
Co(4)	[Ar]$4s^{0.49}3d^{4.98}4p^{0.05}4d^{0.01}$	[Ar]$4s^{0.23}3d^{2.35}4p^{0.03}$
Co(5)	[Ar]$4s^{0.15}3d^{4.96}4p^{0.01}$	[Ar]$4s^{0.12}3d^{2.34}4p^{0.01}$
Co(6)	[Ar]$4s^{0.15}3d^{4.96}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.13}3d^{2.36}4p^{0.01}$
O(1)	[He]$2s^{0.98}2p^{2.90}3s^{0.02}3p^{0.01}$	[He]$2s^{0.95}2p^{2.52}$
O(2)	[He]$2s^{0.98}2p^{2.90}3s^{0.02}3p^{0.01}$	[He]$2s^{0.95}2p^{2.52}$
O(3)	[He]$2s^{0.97}2p^{2.86}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.54}3d^{0.01}$
O(4)	[He]$2s^{0.97}2p^{2.86}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.56}3d^{0.01}$
O(5)	[He]$2s^{0.97}2p^{2.88}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.54}$

Table S8 Natural electron configuration per atom (labeled according to Fig. 5) in Co_6O_6 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.17}3d^{4.95}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.18}3d^{2.38}4p^{0.02}4d^{0.01}$
Co(2)	[Ar]$4s^{0.21}3d^{4.93}4p^{0.01}$	[Ar]$4s^{0.10}3d^{2.51}4p^{0.01}$
Co(3)	[Ar]$4s^{0.16}3d^{4.96}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.13}3d^{2.42}4p^{0.01}4d^{0.01}$
Co(4)	[Ar]$4s^{0.17}3d^{4.35}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.18}3d^{3.16}4p^{0.02}4d^{0.01}$
Co(5)	[Ar]$4s^{0.18}3d^{4.95}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.19}3d^{2.42}4p^{0.03}4d^{0.01}$
Co(6)	[Ar]$4s^{0.21}3d^{4.93}4p^{0.01}$	[Ar]$4s^{0.12}3d^{2.50}4p^{0.02}$
O(1)	[He]$2s^{0.96}2p^{2.76}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.52}3d^{0.01}$
O(2)	[He]$2s^{0.96}2p^{2.77}3s^{0.01}3d^{0.01}$	[He]$2s^{0.95}2p^{2.49}3d^{0.01}$
O(3)	[He]$2s^{0.97}2p^{2.86}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.48}3d^{0.01}$
O(4)	[He]$2s^{0.97}2p^{2.84}3s^{0.01}3p^{0.01}3d^{0.01}$	[He]$2s^{0.95}2p^{2.47}3d^{0.01}$
O(5)	[He]$2s^{0.97}2p^{2.87}3s^{0.01}3p^{0.01}3d^{0.01}$	[He]$2s^{0.95}2p^{2.33}3d^{0.01}$
O(6)	[He]$2s^{0.96}2p^{2.71}3s^{0.01}3p^{0.01}3d^{0.01}$	[He]$2s^{0.95}2p^{2.47}3d^{0.01}$

Table S9 Natural electron configuration per atom (labeled according to Fig. 5) in Co_7 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.55}3d^{4.98}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.49}3d^{2.96}4p^{0.06}4d^{0.01}$
Co(2)	[Ar]$4s^{0.58}3d^{4.98}4p^{0.02}$	[Ar]$4s^{0.44}3d^{2.95}4p^{0.04}$
Co(3)	[Ar]$4s^{0.65}3d^{4.99}4p^{0.02}$	[Ar]$4s^{0.47}3d^{2.66}4p^{0.06}4d^{0.01}$
Co(4)	[Ar]$4s^{0.60}3d^{4.98}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.49}3d^{2.87}4p^{0.05}4d^{0.01}$
Co(5)	[Ar]$4s^{0.53}3d^{4.98}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.39}3d^{3.00}4p^{0.05}$
Co(6)	[Ar]$4s^{0.45}3d^{4.98}4p^{0.01}$	[Ar]$4s^{0.50}3d^{2.96}4p^{0.01}$
Co(7)	[Ar]$4s^{0.54}3d^{4.98}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.47}3d^{2.96}4p^{0.06}4d^{0.01}$

Table S10 Natural electron configuration per atom (labeled according to Fig. 5) in Co_7O_3 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.27}3d^{4.94}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.33}3d^{2.90}4p^{0.07}4d^{0.01}$
Co(2)	[Ar]$4s^{0.22}3d^{4.89}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.27}3d^{2.77}4p^{0.02}4d^{0.01}$
Co(3)	[Ar]$4s^{0.28}3d^{4.95}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.34}3d^{2.79}4p^{0.08}4d^{0.02}$
Co(4)	[Ar]$4s^{0.23}3d^{4.91}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.22}3d^{2.64}4p^{0.03}4d^{0.01}$
Co(5)	[Ar]$4s^{0.23}3d^{4.89}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.26}3d^{2.78}4p^{0.02}4d^{0.01}$
Co(6)	[Ar]$4s^{0.28}3d^{4.95}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.33}3d^{2.77}4p^{0.08}4d^{0.01}$
Co(7)	[Ar]$4s^{0.46}3d^{4.96}4p^{0.01}$	[Ar]$4s^{0.61}3d^{2.99}4p^{0.02}$
O(1)	[He]$2s^{0.95}2p^{2.81}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.55}3d^{0.01}$
O(2)	[He]$2s^{0.95}2p^{2.80}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.60}3d^{0.01}$
O(3)	[He]$2s^{0.95}2p^{2.79}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.59}3d^{0.01}$

Table S11 Natural electron configuration per atom (labeled according to Fig. 5) in Co_7O_4 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.22}3d^{4.91}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.26}3d^{2.73}4p^{0.03}4d^{0.01}$
Co(2)	[Ar]$4s^{0.23}3d^{4.90}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.27}3d^{2.73}4p^{0.02}4d^{0.01}$
Co(3)	[Ar]$4s^{0.21}3d^{4.91}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.26}3d^{2.79}4p^{0.02}4d^{0.01}$
Co(4)	[Ar]$4s^{0.23}3d^{4.91}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.25}3d^{2.66}4p^{0.03}4d^{0.01}$
Co(5)	[Ar]$4s^{0.48}3d^{4.97}4p^{0.04}4d^{0.01}$	[Ar]$4s^{0.34}3d^{2.55}4p^{0.08}4d^{0.01}$
Co(6)	[Ar]$4s^{0.55}3d^{4.98}4p^{0.03}4d^{0.01}$	[Ar]$4s^{0.40}3d^{2.55}4p^{0.01}$
Co(7)	[Ar]$4s^{0.22}3d^{4.92}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.23}3d^{2.63}4p^{0.04}4d^{0.01}$
O(1)	[He]$2s^{0.95}2p^{2.80}3p^{0.01}$	[He]$2s^{0.94}2p^{2.57}3d^{0.01}$
O(2)	[He]$2s^{0.95}2p^{2.80}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.59}3d^{0.01}$
O(3)	[He]$2s^{0.95}2p^{2.82}3p^{0.01}$	[He]$2s^{0.93}2p^{2.55}3d^{0.01}$
O(4)	[He]$2s^{0.96}2p^{2.85}3s^{0.01}3p^{0.01}$	[He]$2s^{0.93}2p^{2.57}$

Table S12 Natural electron configuration per atom (labeled according to Fig. 5) in Co_7O_5 for α-spin (left) and β-spin (right).

	α	β
Co(1)	[Ar]$4s^{0.26}3d^{4.88}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.27}3d^{2.71}4p^{0.02}4d^{0.01}$
Co(2)	[Ar]$4s^{0.23}3d^{4.89}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.28}3d^{2.74}4p^{0.02}4d^{0.01}$
Co(3)	[Ar]$4s^{0.22}3d^{4.93}4p^{0.02}4d^{0.01}$	[Ar]$4s^{0.22}3d^{2.61}4p^{0.04}4d^{0.01}$
Co(4)	[Ar]$4s^{0.22}3d^{4.90}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.26}3d^{2.78}4p^{0.02}4d^{0.01}$
Co(5)	[Ar]$4s^{0.24}3d^{4.90}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.31}3d^{2.65}4p^{0.04}4d^{0.01}$
Co(6)	[Ar]$4s^{0.16}3d^{4.20}4p^{0.01}$	[Ar]$4s^{0.24}3d^{3.40}4p^{0.03}4d^{0.01}$
Co(7)	[Ar]$4s^{0.15}3d^{4.96}4p^{0.01}4d^{0.01}$	[Ar]$4s^{0.15}3d^{2.42}4p^{0.02}4d^{0.01}$
O(1)	[He]$2s^{0.95}2p^{2.80}3s^{0.01}3p^{0.01}$	[He]$2s^{0.94}2p^{2.60}3d^{0.01}$
O(2)	[He]$2s^{0.94}2p^{2.81}3s^{0.01}3p^{0.01}$	[He]$2s^{0.93}2p^{2.56}3d^{0.01}$
O(3)	[He]$2s^{0.94}2p^{2.79}3p^{0.01}3d^{0.01}$	[He]$2s^{0.94}2p^{2.59}3d^{0.01}$
O(4)	[He]$2s^{0.95}2p^{2.72}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.61}$
O(5)	[He]$2s^{0.95}2p^{2.74}3s^{0.01}3p^{0.01}$	[He]$2s^{0.95}2p^{2.57}3d^{0.01}$

4 Beam profiles

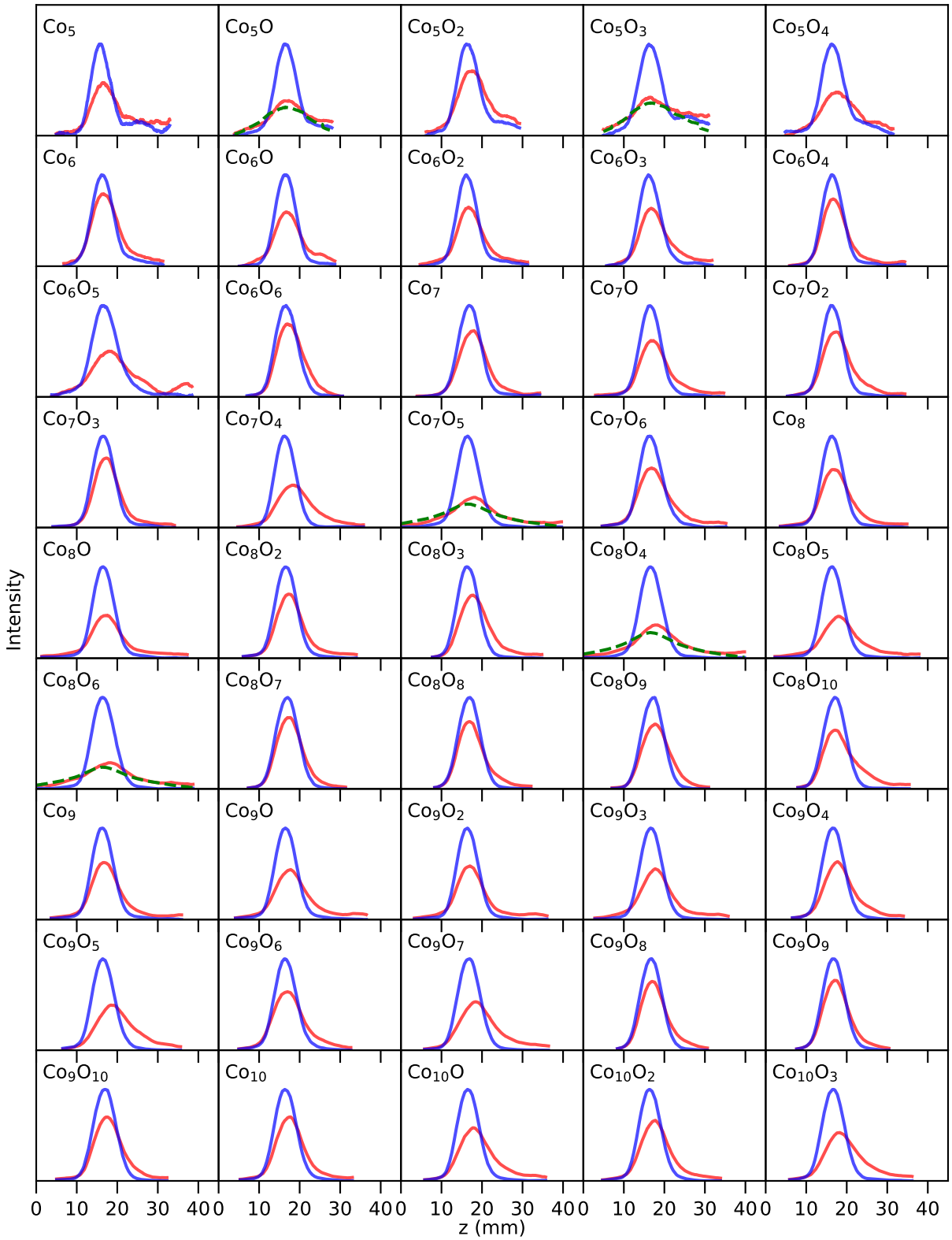

Fig. S3 Beam profiles of all identified Co_nO_m clusters (part one of three). The red and blue solid lines correspond to the Gaussian smoothened (FWHM = 5 mm) intensities at detector positions z with and without magnetic field, respectively. The data has been corrected for the non-uniform ionization profile, after background subtraction. The background was estimated to correspond to the zero-intensity offset of the Gaussian smoothed off profile. The green dashed curves represent the best suiting ARRM (if applicable).

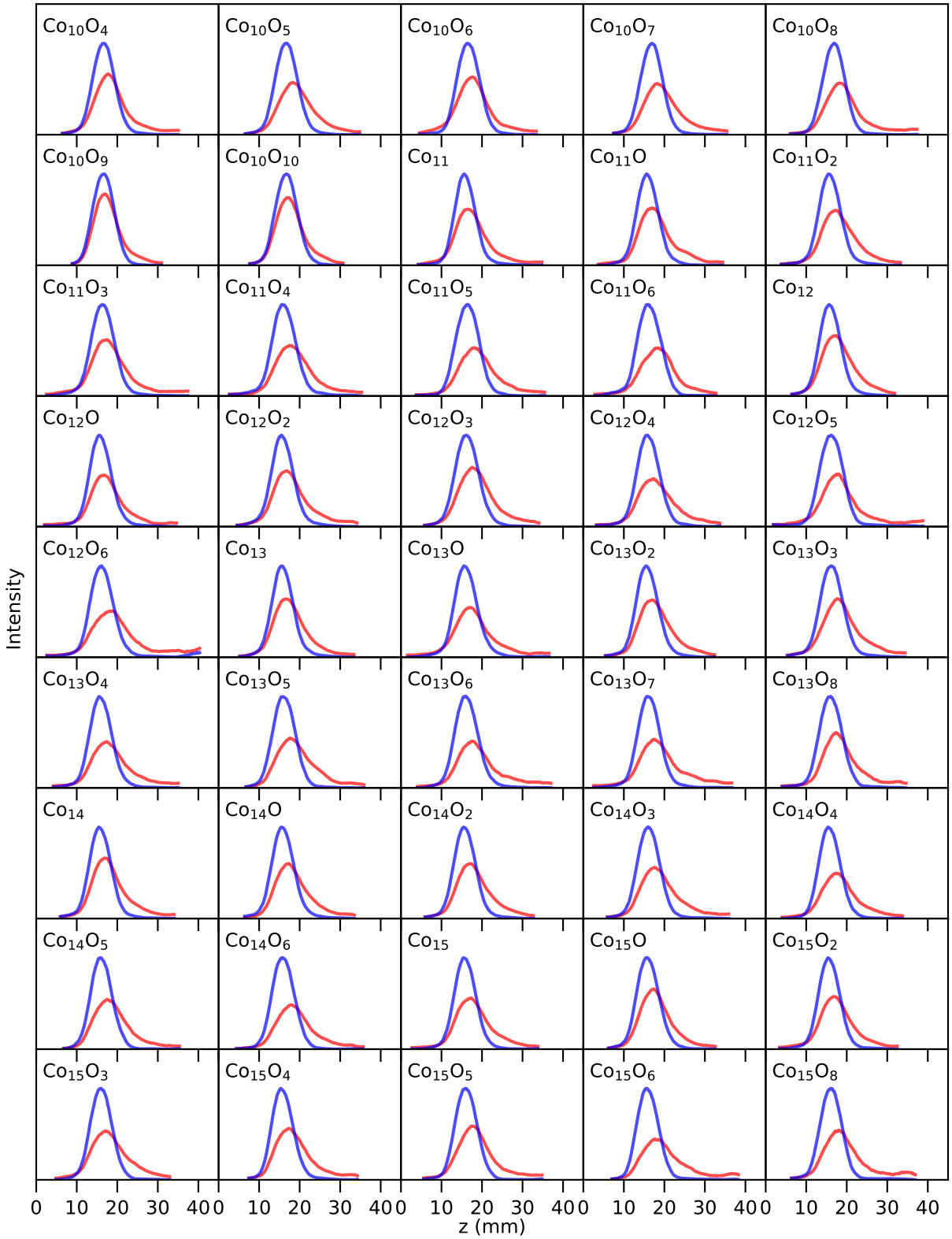

Fig. S4 Beam profiles of all identified Co_nO_m clusters (part two of three). The red and blue solid lines correspond to the Gaussian smoothened (FWHM = 5 mm) intensities at detector positions z with and without magnetic field, respectively. The data has been corrected for the non-uniform ionization profile, after background subtraction. The background was estimated to correspond to the zero-intensity offset of the Gaussian smoothed off profile.

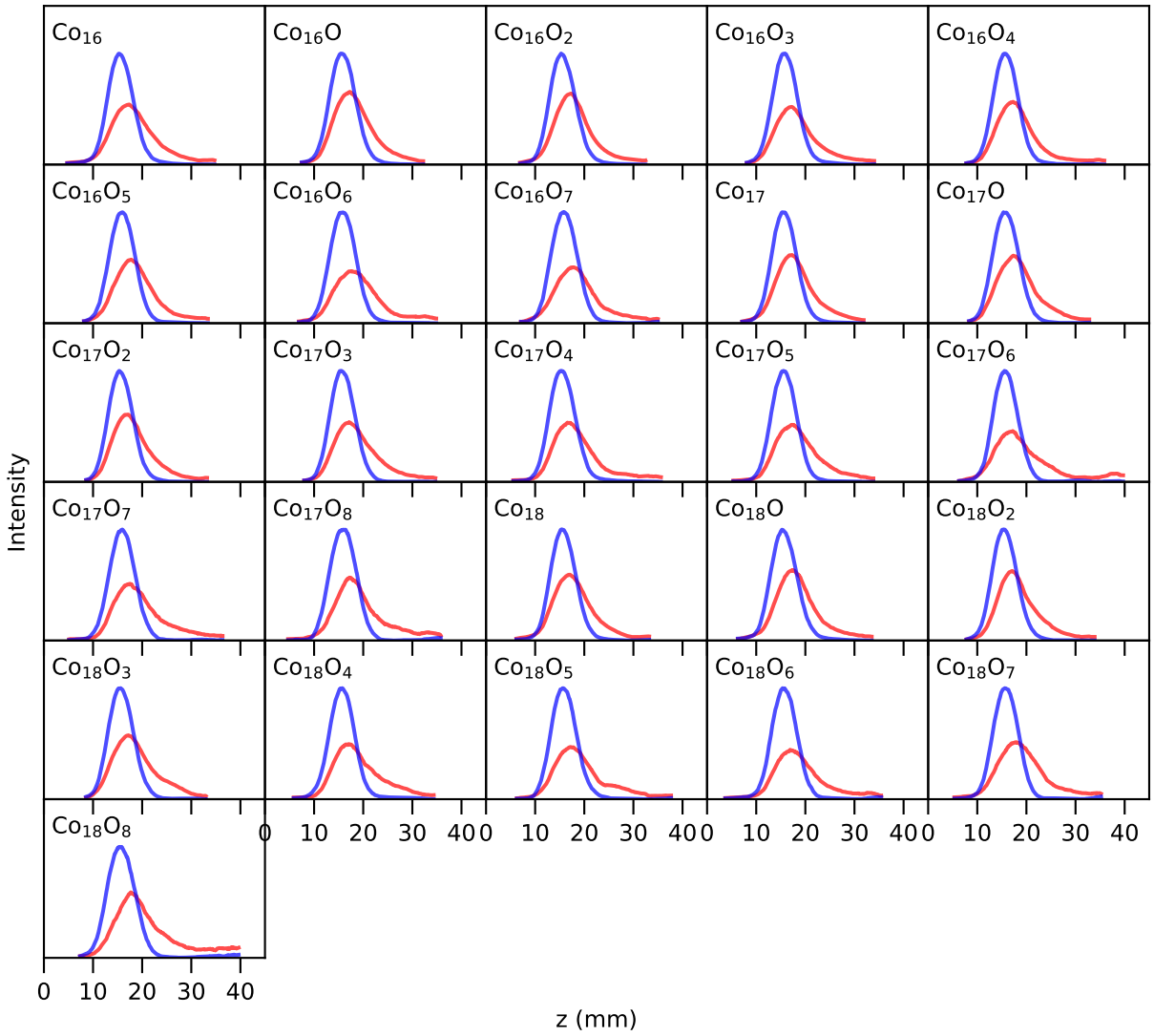

Fig. S5 Beam profiles of all identified Co_nO_m clusters (part three of three). The red and blue solid lines correspond to the Gaussian smoothened (FWHM = 5 mm) intensities at detector positions z with and without magnetic field, respectively. The data has been corrected for the non-uniform ionization profile, after background subtraction. The background was estimated to correspond to the zero-intensity offset of the Gaussian smoothed off profile.