Supplementary information for article:

Magnetic Anisotropy and Exchange Coupling in a Family of Isostructural $Fe^{III}_2Ln^{III}_2$ Complexes

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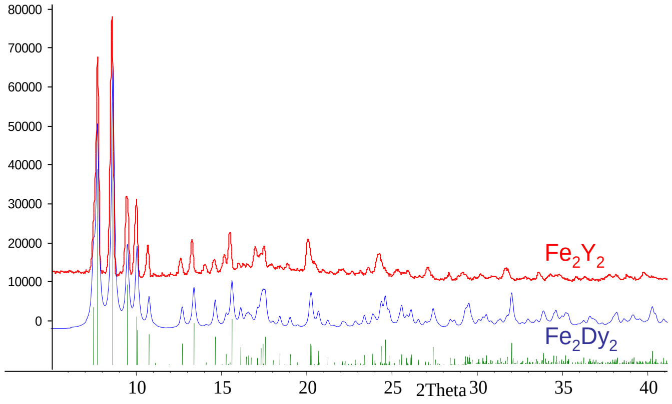


Figure S1. Powder diffraction X-ray data for Fe_2Y_2 (red line) theoretical powder diffraction for Fe_2Dy_2 (green line) and Lorentzian profile powder diffraction for Fe_2Dy_2 (blue line base width 8).

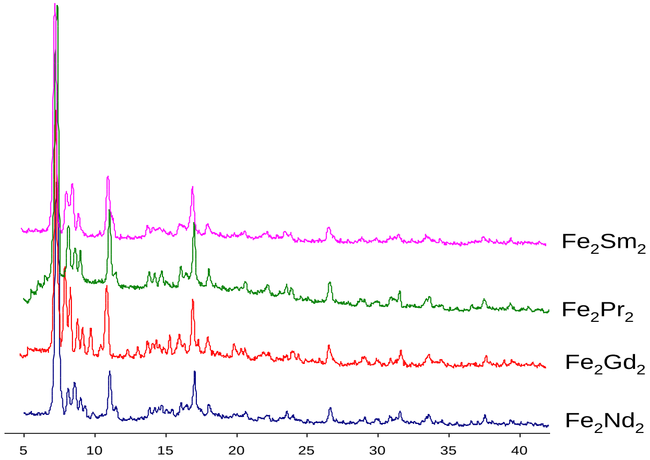
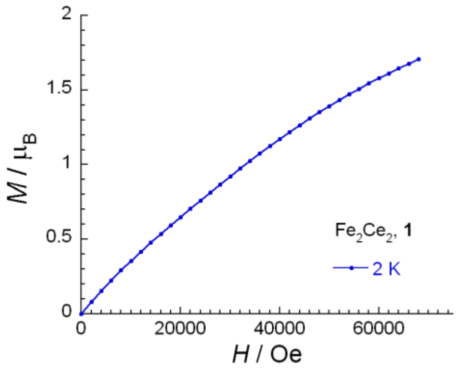
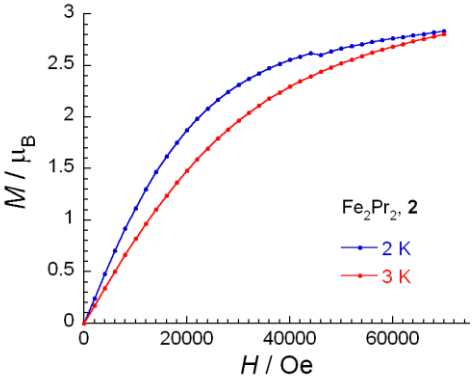
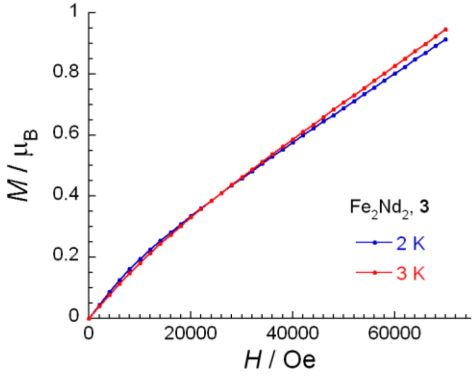


Figure S2. Powder diffraction of compounds Fe_2Sm_2, Fe_2Pr_2, Fe_2Gd_2 and Fe_2Nd_2.


M / μB
2
1.5
1
0.5
0
0
20000
40000
60000
H / Oe
Fe2Ce2, 1
2 K


M / μB
3
2.5
2
1.5
1
0.5
0
0
20000
40000
60000
H / Oe
Fe2Pr2, 2
2 K
3 K


M / μB
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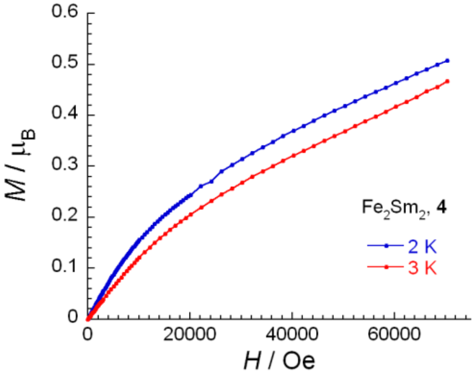
0.8
0.6
0.4
0.2
0
0
20000
40000
60000
H / Oe
Fe2Nd2, 3
2 K
3 K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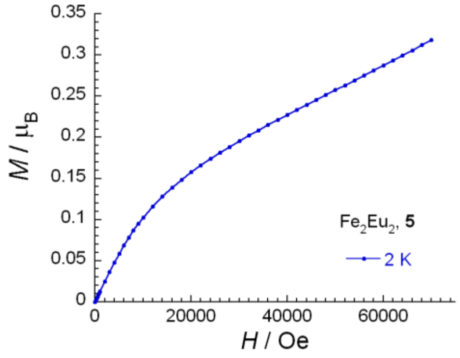
0.5
0.4
0.3
0.2
0.1
0
0
20000
40000
60000
H / Oe
Fe2Sm2, 4
2 K
3 K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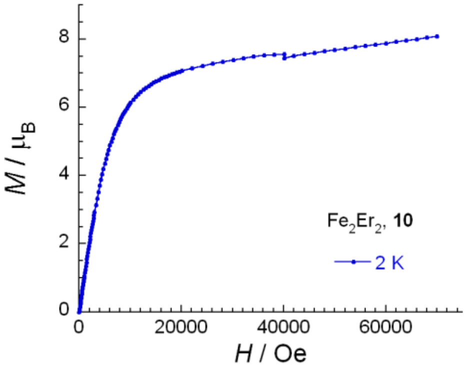
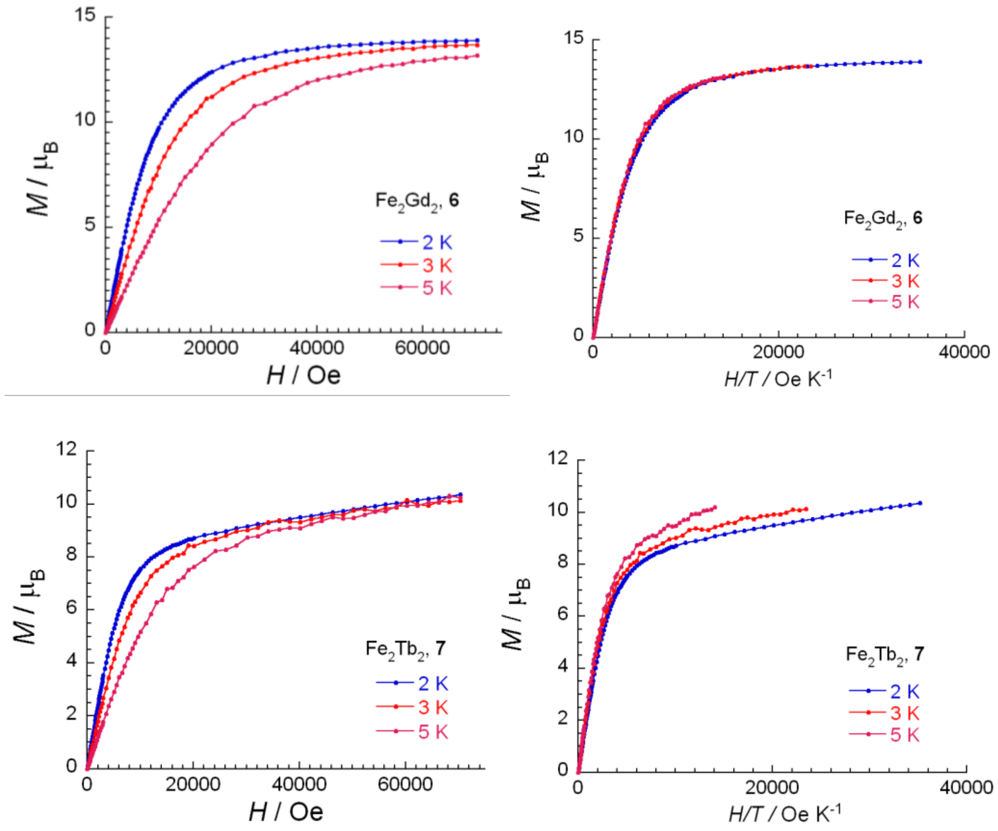
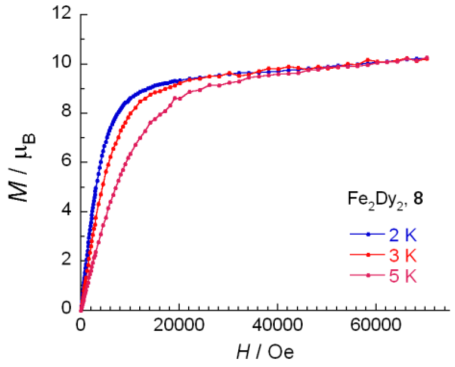
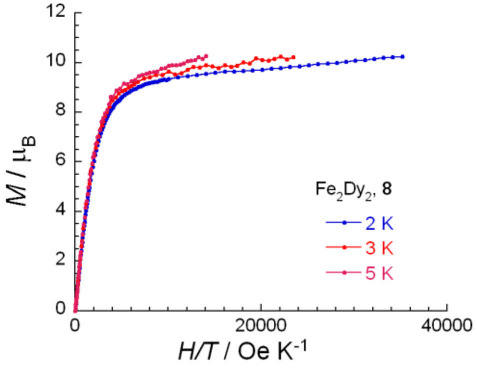
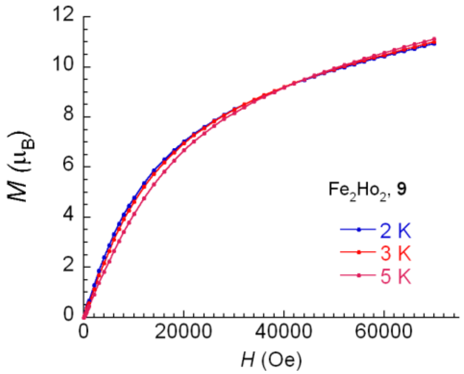
0.3
0.25
0.2
0.15
0.1
0.05
0
0
20000
40000
60000
H / Oe
Fe2Eu2, 5
2 K

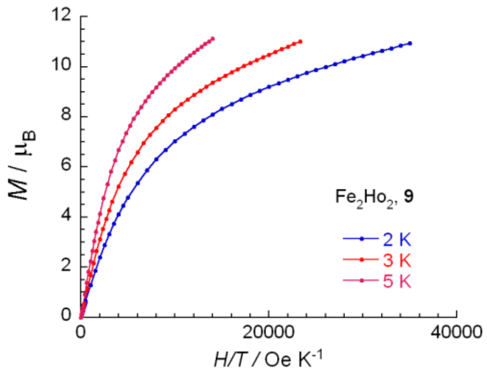

M / μB
8
6
4
2
0
0
20000
40000
60000
H / Oe
Fe2Er2, 10
2 K

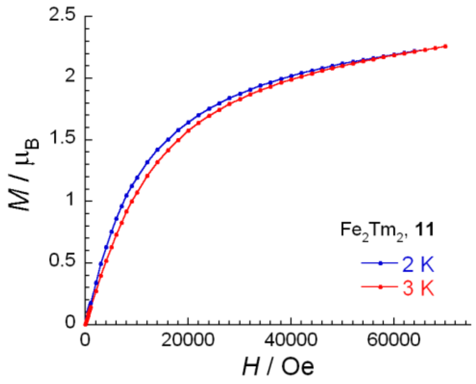

M / μ_B
H / Oe
H/T / Oe K^{-1}
0
5
10
15
20000
40000
60000
Fe_2Gd_2, **6**
2 K
3 K
5 K
0
2
4
6
8
10
12
Fe_2Tb_2, **7**

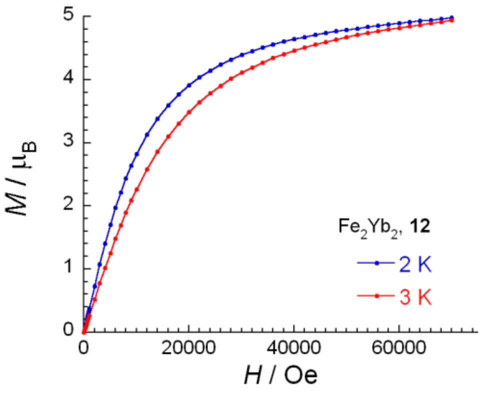

12
10
8
6
4
2
0
M / μ_B
0
20000
40000
60000
H / Oe
Fe_2Dy_2, **8**
2 K
3 K
5 K


12
10
8
6
4
2
0
M / μ_B
0
20000
40000
H/T / Oe K^{-1}
Fe_2Dy_2, **8**
2 K
3 K
5 K


12
10
8
6
4
2
0
M (μ_B)
0
20000
40000
60000
H (Oe)
Fe_2Ho_2, **9**
2 K
3 K
5 K


12
10
8
6
4
2
0
M / μ_B
0
20000
40000
H/T / Oe K^{-1}
Fe_2Ho_2, **9**
2 K
3 K
5 K


2.5
2
1.5
1
0.5
0
M / μ_B
0
20000
40000
60000
H / Oe
Fe_2Tm_2, **11**
2 K
3 K


5
4
3
2
1
0
M / μ_B
0
20000
40000
60000
H / Oe
Fe_2Yb_2, **12**
2 K
3 K

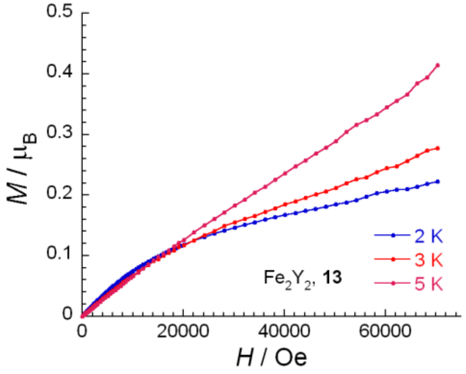


Figure S3. Field dependence of magnetization at low temperatures for all compounds. Compound codes are indicated in the inset of figures.

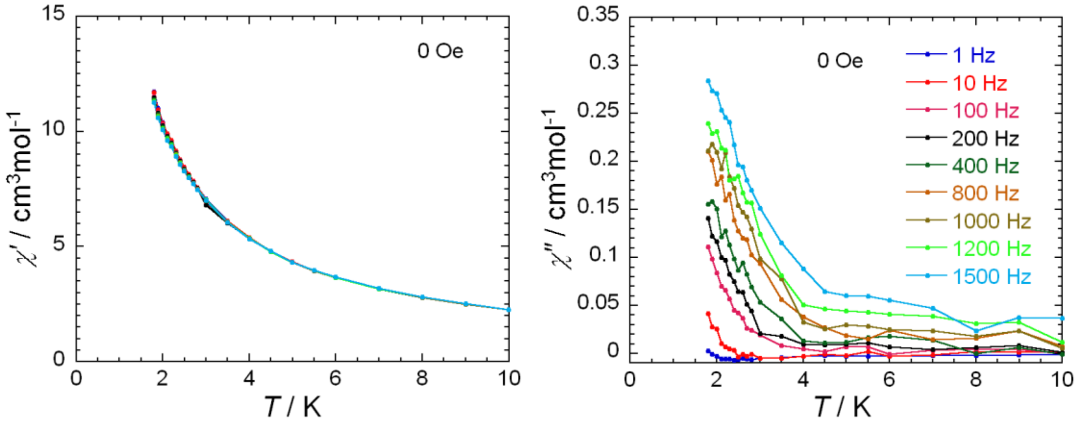


Figure S4. Plots of in-phase (left) and out-of-phase (right) ac susceptibility signals vs. temperature for **8** Fe_2Dy_2 at the indicated oscillation frequencies.

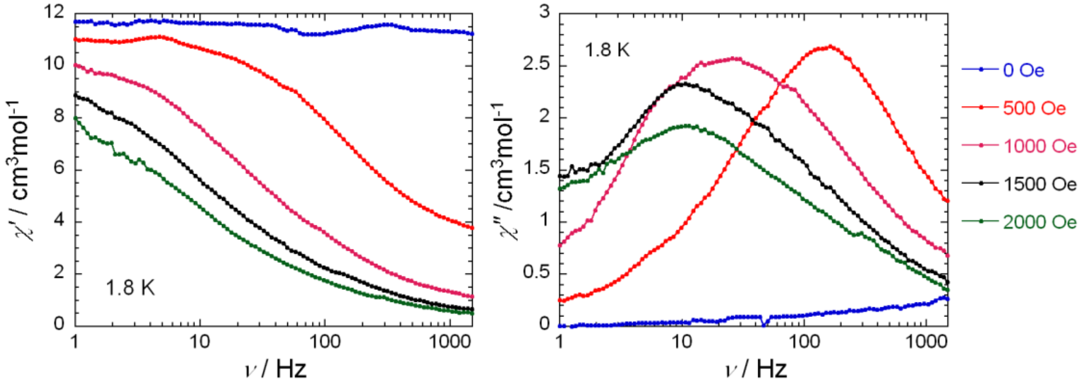


Figure S5. Plots of in-phase (left) and out-of-phase (right) ac susceptibility signals vs. frequency for Fe_2Dy_2 at 1.8 K under the indicated external dc fields.

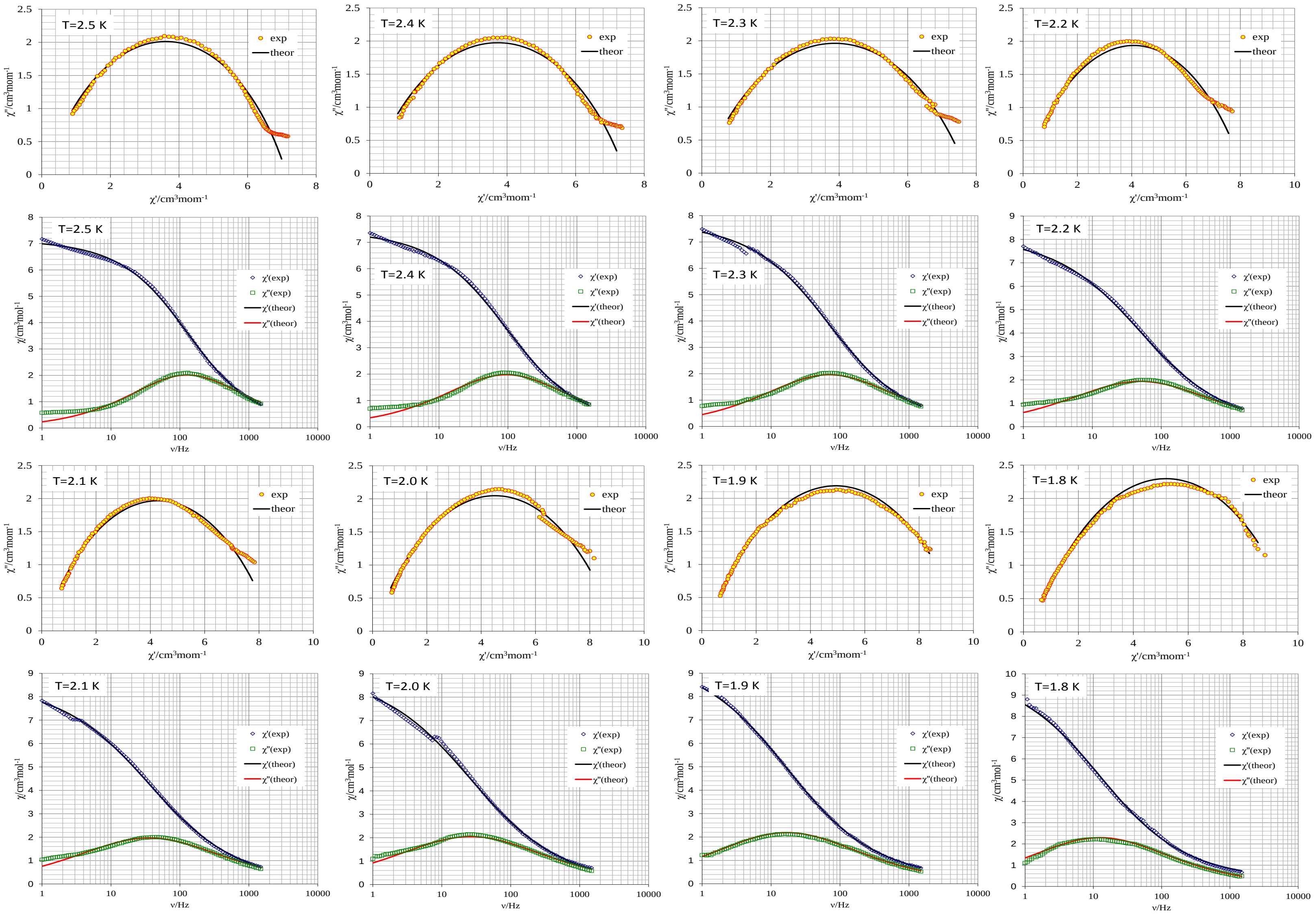


Figure S6 Cole-Cole plot data

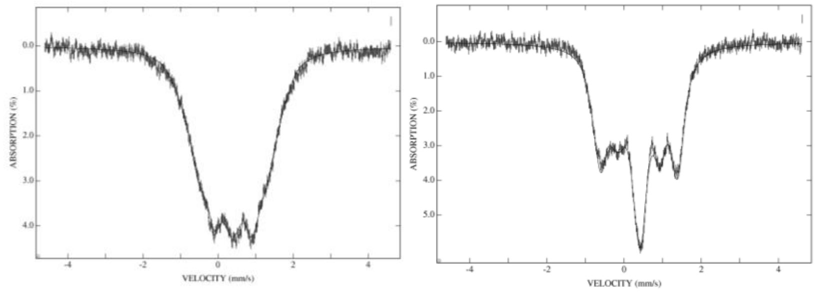


Figure S 7. The ^{57}Fe Mössbauer spectra for Fe_2Dy_2 (top, left) and Fe_2Tb_2 (top, right) at 3K, applied field of 5 T and Fe_2Gd_2 (bottom, left) and Fe_2Ho_2 (bottom, right) at 3K, applied field of 4 T. The solid lines are the spectral simulations for $\Delta E_Q = 0.94$ mm/s, $\delta = 0.49$ mm/s, $H_{eff} = 5.0$ T and $\eta = 1.0$ for Fe_2Dy_2, $\Delta E_Q = 0.92$ mm/s, $\delta = 0.50$ mm/s, $H_{eff} = 5.0$ T and $\eta = 0.9$ for Fe_2Tb_2, $\Delta E_Q = 0.91$ mm/s, $\delta = 0.50$ mm/s, $H_{eff} = 3.3$ T and $\eta = 0.7$ for Fe_2Gd_2, and $\Delta E_Q = 0.96$ mm/s, $\delta = 0.48$ mm/s, $H_{eff} = 4.0$ T and $\eta = 1.0$ for Fe_2Ho_2, assuming an isolated ground state with S = 0.

Table S8. Mössbauer data for Fe_2Ln_2 compounds.

Compound	T, K	δ[a], mm/s	ΔE_Q or ε, mm/s	Γ, mm/s	B_{eff}, T
Fe_2Y_2	50	0.499(1)	0.999(1)	0.418(1)	-
	3	0.497(1)	0.982(2)	0.382(4)	-
Fe_2Gd_2	77	0.492(2)	0.919(2)	0.467(4)	-
	3	0.501(1)	0.911(2)	0.412(3)	-
Fe_2Dy_2	25	0.502(1)	0.947(6)	0.583(7)	-
	3	0.497(2) [b] 0.497(2) [b]	0.938(4) 0.014(1)	0.607(7) 0.58(2)	- 11.94
Fe_2Tb_2	3	0.500(1)	0.922(2)	0.362(3)	-
Fe_2Ho_2	3	0.482(1)	0.96(2)	0.384(3)	-

[a] Relative to α-Fe at room temperature. The statistical errors are given in parentheses.
[b] Constrained to the same value for both spectra.

Calculation details

Table S9. The table containing the $H[S,M_{S,}\ S,M_S]| \equiv H[S,M_{S,}\ S,M_S]|\{J_z^A, J_z^B\}$ diagonal elements of the block Hamiltonian matrices, independently running as function of the four possible combinations of $J_z^A = \pm 15/2$ and $J_z^B = \pm 15/2$.[a]

$H[(0,0);(0,0)] = 0$	$H[(4,-4);(4,-4)] = -20J_{dd} - 2j_zJ_z^A - 2j_zJ_z^B$ $H[(4,-3);(4,-3)] = -20J_{dd} - \frac{3j_zJ_z^A}{2} - \frac{3j_zJ_z^B}{2}$ $H[(4,-2);(4,-2)] = -20J_{dd} - j_zJ_z^A - j_zJ_z^B$ $H[(4,-1);(4,-1)] = -20J_{dd} - \frac{j_zJ_z^A}{2} - \frac{j_zJ_z^B}{2}$

$$H[(1,-1);(1,-1)] = -2J_{dd} - \frac{j_z J_z^A}{2} - \frac{j_z J_z^B}{2}$$

$$H[(1,0);(1,0)] = -2J_{dd}$$

$$H[(1,1);(1,1)] = -2J_{dd} + \frac{j_z J_z^A}{2} + \frac{j_z J_z^B}{2}$$

$$H[(2,-2);(2,-2)] = -6J_{dd} - j_z J_z^A - j_z J_z^B$$

$$H[(2,-1);(2,-1)] = -6J_{dd} - \frac{j_z J_z^A}{2} - \frac{j_z J_z^B}{2}$$

$$H[(2,0);(2,0)] = -6J_{dd}$$

$$H[(2,1);(2,1)] = -6J_{dd} + \frac{j_z J_z^A}{2} + \frac{j_z J_z^B}{2}$$

$$H[(2,2);(2,2)] = -6J_{dd} + j_z J_z^A + j_z J_z^B$$

$$H[(3,-3);(3,-3)] = -12J_{dd} - \frac{3j_z J_z^A}{2} - \frac{3j_z J_z^B}{2}$$

$$H[(3,-2);(3,-2)] = -12J_{dd} - j_z J_z^A - j_z J_z^B$$

$$H[(3,-1);(3,-1)] = -12J_{dd} - \frac{j_z J_z^A}{2} - \frac{j_z J_z^B}{2}$$

$$H[(3,0);(3,0)] = -12J_{dd}$$

$$H[(3,1);(3,1)] = -12J_{dd} + \frac{j_z J_z^A}{2} + \frac{j_z J_z^B}{2}$$

$$H[(3,2);(3,2)] = -12J_{dd} + j_z J_z^A + j_z J_z^B$$

$$H[(3,3);(3,3)] = -12J_{dd} + \frac{3j_z J_z^A}{2} + \frac{3j_z J_z^B}{2}$$

$$H[(4,0);(4,0)] = -20J_{dd}$$

$$H[(4,1);(4,1)] = -20J_{dd} + \frac{j_z J_z^A}{2} + \frac{j_z J_z^B}{2}$$

$$H[(4,2);(4,2)] = -20J_{dd} + j_z J_z^A + j_z J_z^B$$

$$H[(4,3);(4,3)] = -20J_{dd} + \frac{3j_z J_z^A}{2} + \frac{3j_z J_z^B}{2}$$

$$H[(4,4);(4,4)] = -20J_{dd} + 2j_z J_z^A + 2j_z J_z^B$$

$$H[(5,-5);(5,-5)] = -30J_{dd} - \frac{5j_z J_z^A}{2} - \frac{5j_Z J_z^B}{2}$$

$$H[(5,-4);(5,-4)] = -30J_{dd} - 2j_z J_z^A - 2j_z J_z^B$$

$$H[(5,-3);(5,-3)] = -30J_{dd} - \frac{3j_z J_z^A}{2} - \frac{3j_z J_z^B}{2}$$

$$H[(5,-2);(5,-2)] = -30J_{dd} - j_z J_z^A - j_z J_z^B$$

$$H[(5,-1);(5,-1)] = -30J_{dd} - \frac{j_z J_z^A}{2} - \frac{j_z J_z^B}{2}$$

$$H[(5,0);(5,0)] = -30J_{dd}$$

$$H[(5,1);(5,1)] = -30J_{dd} + \frac{j_z J_z^A}{2} + \frac{j_z J_z^B}{2}$$

$$H[(5,2);(5,2)] = -30J_{dd} + j_z J_z^A + j_z J_z^B$$

$$H[(5,3);(5,3)] = -30J_{dd} + \frac{3j_z J_z^A}{2} + \frac{3j_z J_z^B}{2}$$

$$H[(5,4);(5,4)] = -30J_{dd} + 2j_z J_z^A + 2j_z J_z^B$$

$$H[(5,5);(5,5)] = -30J_{dd} + \frac{5j_z J_z^A}{2} + \frac{5j_z J_z^B}{2}$$

[a] The phenomenological Hamiltonian for Fe_2Dy_2 system is based on Heisenberg interaction between Fe(III) ions (the J_{dd} parameter) and Ising like Fe-Dy effects (the $j_z \equiv j_{df}$ parameter), involving the $J_z = \pm 15/2$ states on lanthanide and $|S,M\rangle|J,J_z^A\rangle|J,J_z^B\rangle$ product wavefunctions.

EPR spectra

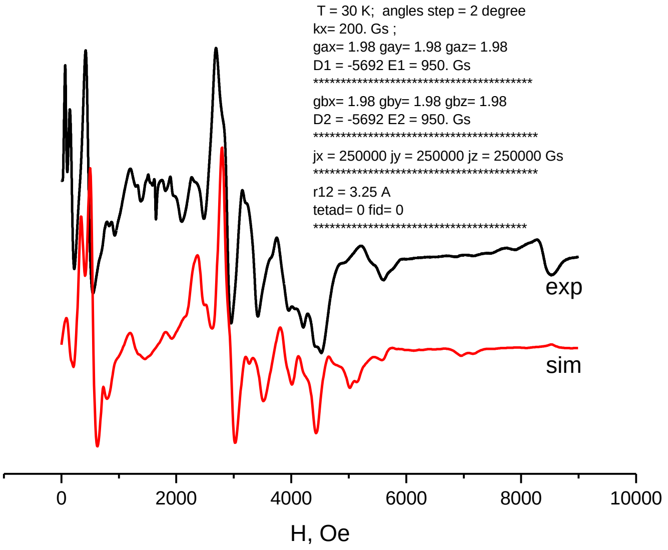


Figure S10a. Experimental (black) spectrum of compound Fe_2Y_2 in X-band at T=30K and simulated spectrum (red) of Fe(III)-Fe(III) dimer with $S_1=S_2=5/2$, J = -6.5 cm^{-1}, D_{Fe} = -0.266 cm^{-1}, E_{Fe}= 0.044 cm^{-1}, g=1.98. Dipole-dipole contribution was taken into account using the model of point dipoles for R=3.25 A.

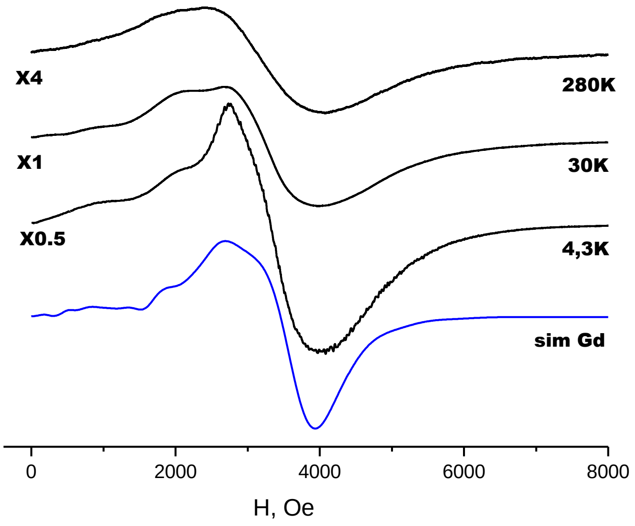


Figure S10b. EPR spectra of Fe_2Gd_2 cluster (**6**) in the X-band at various temperatures. Spectra are shown with different relative gain values given on the left. The simulated spectrum (blue trace) for a single Gd^{III} ion with S=7/2, D=0.037 cm^{-1}, E=0.0033 cm^{-1} gives a satisfactory fit to the low temperature spectrum of compound **6**.

Table S11. The table containing the $H[S,M_{S,}\ S',M_{S}']\equiv H[S,M_{S,}\ S',M_{S}']\{J_z^{A}, J_z^{B}\}$ non-diagonal elements of the block Hamiltonian matrices, independently running as function of the four possible combinations of $J_z^{A}= \pm 15/2$ and $J_z^{B}= \pm 15/2$. [a]

	$H[(4,-3);(3,-3)]=\frac{1}{3}\sqrt{5}\,j_z J_z^A-\frac{1}{3}\sqrt{5}\,j_z J_z^B$
$H[(1,0);(0,0)]=\frac{1}{2}\sqrt{\frac{35}{3}}\,j_z J_z^A-\frac{1}{2}\sqrt{\frac{35}{3}}\,j_z J_z^B$	$H[(4,-2);(3,-2)]=2\sqrt{\frac{5}{21}}\,j_z J_z^A-2\sqrt{\frac{5}{21}}\,j_z J_z^B$
	$H[(4,-1);(3,-1)]=5\sqrt{\frac{1}{21}}\,j_z J_z^A-5\sqrt{\frac{1}{21}}\,j_z J_z^B$
$H[(2,-1);(1,-1)]=2\sqrt{\frac{2}{5}}\,j_z J_z^A-2\sqrt{\frac{2}{5}}\,j_z J_z^B$	$H[(4,1);(3,1)]=5\sqrt{\frac{1}{21}}\,j_z J_z^A-5\sqrt{\frac{1}{21}}\,j_z J_z^B$
$H[(2,0);(1,0)]=4\sqrt{\frac{2}{15}}\,j_z J_z^A-4\sqrt{\frac{2}{15}}\,j_z J_z^B$	$H[(4,3);(3,3)]=\frac{1}{3}\sqrt{5}\,j_z J_z^A-\frac{1}{3}\sqrt{5}\,j_z J_z^B$
$H[(2,-1);(1,-1)]=2\sqrt{\frac{2}{5}}\,j_z J_z^A-2\sqrt{\frac{2}{5}}\,j_z J_z^B$	
	$H[(5,-4);(4,-4)]=\frac{1}{2}\,j_z J_z^A-\frac{1}{2}\,j_z J_z^B$
$H[(3,-2);(2,-2)]=\frac{3}{2}\sqrt{\frac{3}{7}}\,j_z J_z^A-\frac{3}{2}\sqrt{\frac{3}{7}}\,j_z J_z^B$	$H[(5,-3);(4,-3)]=\frac{2}{3}\,j_z J_z^A-\frac{2}{3}\,j_z J_z^B$
$H[(3,-1);(2,-1)]=3\sqrt{\frac{6}{35}}\,j_z J_z^A-3\sqrt{\frac{6}{35}}\,j_z J_z^B$	$H[(5,-2);(4,-2)]=\frac{1}{2}\sqrt{\frac{7}{3}}\,j_z J_z^A-\frac{1}{2}\sqrt{\frac{7}{3}}\,j_z J_z^B$
$H[(3,0);(2,0)]=\frac{9}{2}\sqrt{\frac{3}{35}}\,j_z J_z^A-\frac{9}{2}\sqrt{\frac{3}{35}}\,j_z J_z^B$	$H[(5,-1);(4,-1)]=\sqrt{\frac{2}{3}}\,j_z J_z^A-\sqrt{\frac{2}{3}}\,j_z J_z^B$
$H[(3,1);(2,1)]=3\sqrt{\frac{6}{35}}\,j_z J_z^A-3\sqrt{\frac{6}{35}}\,j_z J_z^B$	$H[(5,0);(4,0)]=\frac{5}{6}\,j_z J_z^A-\frac{5}{6}\,j_z J_z^B$
$H[(3,2);(2,2)]=\frac{3}{2}\sqrt{\frac{3}{7}}\,j_z J_z^A-\frac{3}{2}\sqrt{\frac{3}{7}}\,j_z J_z^B$	$H[(5,1);(4,1)]=\sqrt{\frac{2}{3}}\,j_z J_z^A-\sqrt{\frac{2}{3}}\,j_z J_z^B$
	$H[(5,2);(4,2)]=\frac{1}{2}\sqrt{\frac{7}{3}}\,j_z J_z^A-\frac{1}{2}\sqrt{\frac{7}{3}}\,j_z J_z^B$
	$H[(5,3);(4,3)]=\frac{2}{3}\,j_z J_z^A-\frac{2}{3}\,j_z J_z^B$
	$H[(5,4);(4,4)]=\frac{1}{2}\,j_z J_z^A-\frac{1}{2}\,j_z J_z^B$

[a] The phenomenological Hamiltonian for Fe_2Dy_2 system is based on Heisenberg interaction between Fe(III) ions (the J_{dd} parameter) and Ising like Fe-Dy effects (the $j_z\equiv j_{df}$ parameter), involving the $J_z=\pm 15/2$ states on lanthanide and $|S,M\rangle|J,J_z^{A}\rangle|J,J_z^{B}\rangle$ product wavefunctions.