

# Supplementary material

## Chiral, heterometallic lanthanide-transition metal complexes by design

Anders Øwre <sup>1</sup>, Morten Vinum <sup>1</sup>, Michal Kern <sup>2</sup>, Joris van Slageren <sup>2</sup>, Jesper Bendix <sup>1\*</sup> and Mauro Perfetti<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100, Copenhagen, DK

<sup>2</sup> Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany.

\* Correspondence: [bendix@kiku.dk](mailto:bendix@kiku.dk), [mauro.perfetti@chem.ku.dk](mailto:mauro.perfetti@chem.ku.dk)

*Single crystal X-ray data*

*Checkcif of the  $\Delta,\Lambda$ -enantiomorph of **PrFe***

*Alternate packing views*

*Intermolecular interactions*

*Magnetization data at variable temperatures*

*Ac susceptibility of **GdGa***

*Powder X-ray diffractograms*

Single crystal X-ray data

Table S1. Crystallographic data for the La-complexes.

[La(hfac)<sub>3</sub>M(acac)<sub>3</sub>]:

	( $\Lambda$ + $\Delta$ , $\Lambda$ )-LaCr	( $\Lambda$ , $\Delta$ )-LaFe
Formula	C <sub>30</sub> H <sub>24</sub> CrF <sub>18</sub> LaO <sub>12</sub>	C <sub>30</sub> H <sub>24</sub> F <sub>18</sub> FeLaO <sub>12</sub>
<i>M<sub>r</sub></i>	1109.40	1113.25
<i>T</i> / K	122	122
Crystal System	Orthorhombic	Orthorhombic
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> / Å	12.6928(15)	12.3655(14)
<i>b</i> / Å	15.7124(19)	16.209(2)
<i>c</i> / Å	20.603(2)	20.711(3)
<i>V</i> / Å <sup>3</sup>	4108.95	4151.16
<i>Z</i>	4	4
$\rho_{\text{calc}}$ / g·cm <sup>-3</sup>	1.793	1.781
$\mu$ / mm <sup>-1</sup>	1.427	1.500
<i>F</i> <sub>000</sub>	2172.0	2180.0
Crystal Size / mm <sup>3</sup>	0.174 · 0.089 · 0.074	0.753 · 0.351 · 0.286
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073Å)	Mo K $\alpha$ ( $\lambda$ = 0.71073Å)
2 $\theta$ range / °	4.574 – 56.564	4.586 – 57.400
Reflec. Collected	72584	103901
Indep. Reflections	10186	10728
<i>R</i> <sub>int</sub> , <i>R</i> <sub><math>\sigma</math></sub>	0.0472, 0.0321	0.0608, 0.0298
Parameters/Restraints	646	584
<i>S</i> (on <i>F</i> <sup>2</sup> )	1.050	1.077
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> ( <i>I</i> ≥ 4 $\sigma$ { <i>I</i> })	0.0676, 0.1767	0.0543, 0.1431
<i>R</i> <sub>1</sub> (All Data)	0.0825	0.0669
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ / e·Å <sup>-3</sup>	1.818 / -1.801	1.983 / -1.812
Flack parameter	0.003(5)	0.00(3)
CCDC deposit #	CCDC 1849716	CCDC 1849717

( $\Lambda$ + $\Delta$ ,...) signifies disorder in the coordination sphere of the lanthanide

Table S2. Crystallographic data for the Gd-complexes.

[Gd(hfac)<sub>3</sub>M(acac)<sub>3</sub>]:

	( $\Lambda$ + $\Delta$ , $\Lambda$ )-GdCr	( $\Lambda$ , $\Delta$ )-GdFe	( $\Lambda$ + $\Delta$ , $\Lambda$ )-GdGa
Formula	C <sub>30</sub> H <sub>24</sub> CrF <sub>18</sub> GdO <sub>12</sub>	C <sub>30</sub> H <sub>24</sub> F <sub>18</sub> FeGdO <sub>12</sub>	C <sub>30</sub> H <sub>24</sub> F <sub>18</sub> GaGdO <sub>12</sub>
$M_r$	1127.74	1131.59	1145.46
$T / K$	122	122	122
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
$a / \text{\AA}$	12.5084(11)	12.2312(9)	12.386
$b / \text{\AA}$	15.8220(13)	16.0108(12)	15.853
$c / \text{\AA}$	20.5746(18)	20.7089(16)	20.547
$V / \text{\AA}^3$	4071.88	4055.45	4034.51
$Z$	4	4	4
$\rho_{\text{calc}} / \text{g}\cdot\text{cm}^{-3}$	1.840	1.853	1.886
$\mu / \text{mm}^{-1}$	2.019	2.117	2.437
$F_{000}$	2200.0	2208.0	2228.0
Crystal Size / mm <sup>3</sup>	0.179 · 0.152 · 0.098	0.086 · 0.079 · 0.055	0.142 · 0.113 · 0.097
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073 $\text{\AA}$ )	Mo K $\alpha$ ( $\lambda$ = 0.71073 $\text{\AA}$ )	Mo K $\alpha$ ( $\lambda$ = 0.71073 $\text{\AA}$ )
2 $\theta$ range / °	4.600 – 51.470	4.630 – 50.050	4.620 – 55.962
Reflec. Collected	76409	52814	87006
Indep. Reflections	7736	7119	9692
$R_{\text{int}}, R_{\sigma}$	0.0339, 0.0209	0.0347, 0.0239	0.0682, 0.0353
Parameters/Restraints	674	579	675
$S$ (on $F^2$ )	1.057	1.254	1.042
$R_1, wR_2$ ( $I \geq 4\sigma\{I\}$ )	0.0476, 0.1159	0.0344, 0.0838	0.0376, 0.0967
$R_1$ (All Data)	0.0510	0.0388	0.0451
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} / \text{e}\cdot\text{\AA}^{-3}$	1.940 / -1.460	1.749 / -0.820	2.431 / -1.084
Flack parameter	0.03(2)	-0.016(16)	0.000(17)
CCDC deposit #	CCDC 1849690	CCDC 1849714	CCDC 1849715

( $\Lambda$ + $\Delta$ ,...) signifies disorder in the coordination sphere of the lanthanide

Table S3. Crystallographic data for the Pr-complexes.

[Pr(hfac) <sub>3</sub> M(acac) <sub>3</sub> ]:			
	( $\Lambda$ + $\Delta$ , $\Lambda$ )-PrCr	( $\Delta$ , $\Lambda$ )-PrFe	( $\Lambda$ + $\Delta$ , $\Lambda$ )-PrGa
Formula	C <sub>30</sub> H <sub>24</sub> CrF <sub>18</sub> O <sub>12</sub> Pr	C <sub>30</sub> H <sub>24</sub> F <sub>18</sub> FeO <sub>12</sub> Pr	C <sub>30</sub> H <sub>24</sub> F <sub>18</sub> GaO <sub>12</sub> Pr
<i>M<sub>r</sub></i>	1111.40	1115.25	1129.12
<i>T</i> / K	122	122	122
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> / Å	12.6186(6)	12.2969(12)	12.495(4)
<i>b</i> / Å	15.7588(8)	16.1579(15)	15.905(5)
<i>c</i> / Å	20.5581(9)	20.7051(18)	20.533(6)
<i>V</i> / Å <sup>3</sup>	4088.06	4113.94	4080.58
<i>Z</i>	4	4	4
$\rho_{\text{calc}}$ / g·cm <sup>-3</sup>	1.806	1.801	1.838
$\mu$ / mm <sup>-1</sup>	1.581	1.659	1.978
<i>F</i> <sub>000</sub>	2180.0	2188.0	2208.0
Crystal Size / mm <sup>3</sup>	0.124 · 0.088 · 0.076	0.105 · 0.086 · 0.073	0.293 · 0.277 · 0.261
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073Å)	Mo K $\alpha$ ( $\lambda$ = 0.71073Å)	Mo K $\alpha$ ( $\lambda$ = 0.71073Å)
2 $\theta$ range / °	4.586 – 50.698	3.934 – 58.256	4.596 – 61.238
Reflec. Collected	52322	108158	134965
Indep. Reflections	7465	11046	12538
<i>R</i> <sub>int</sub> , <i>R</i> <sub><math>\sigma</math></sub>	0.0399, 0.0261	0.0480, 0.0249	0.0369, 0.0213
Parameters/Restraints	646	567	715
<i>S</i> (on <i>F</i> <sup>2</sup> )	1.073	1.094	1.060
<i>R</i> <sub>1</sub> , w <i>R</i> <sub>2</sub> ( <i>I</i> ≥ 4 $\sigma$ { <i>I</i> })	0.0555, 0.1433	0.0389, 0.1026	0.0431, 0.1074
<i>R</i> <sub>1</sub> (All Data)	0.0613	0.0431	0.0516
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ / e·Å <sup>-3</sup>	2.001 / -1.883	1.667 / -1.387	1.961 / -1.646
Flack parameter	-0.006(5)	0.009(17)	-0.008(3)
CCDC deposit #	CCDC 1849718	CCDC 1849719	CCDC 1849713

( $\Lambda$ + $\Delta$ ,...) signifies disorder in the coordination sphere of the lanthanide

## Checkcif of the $\Lambda,\Delta$ -enantiomorph of **PrFe**:

### checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.      CIF dictionary      Interpreting this report

### Datablock: mo\_d8v3475\_2\_0mtotal\_a

---

Bond precision:	C-C = 0.0124 Å	Wavelength=0.71073
Cell:	a=12.274(3)	b=16.101(3)      c=20.668(4)
	alpha=90	beta=90      gamma=90
Temperature:	293 K	
	Calculated	Reported
Volume	4084.5(15)	4084.4(14)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C30 H24 F18 Fe O12 Pr	0.5(C30 H24 F18 Fe O12 Pr)
Sum formula	C30 H24 F18 Fe O12 Pr	C15 H12 F9 Fe0.50 O6 Pr0.50
Mr	1115.25	557.63
Dx, g cm-3	1.814	1.814
Z	4	8
Mu (mm-1)	1.671	1.671
F000	2188.0	2188.0
F000'	2190.42	
h,k,lmax	15,19,25	15,19,25
Nref	7801[ 4344]	7782
Tmin,Tmax	0.420,0.529	0.250,0.746
Tmin'	0.318	
Correction method= # Reported T Limits: Tmin=0.250 Tmax=0.746		
AbsCorr = MULTI-SCAN		
Data completeness=	1.79/1.00	Theta(max)= 25.741
R(reflections)=	0.0369( 7235)	wR2(reflections)= 0.0956( 7782)
S =	1.059	Npar= 566

---

The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level.**  
Click on the hyperlinks for more details of the test.

---

<b>Alert level C</b>		
PLAT090_ALERT_3_C	Poor Data / Parameter Ratio (Zmax > 18) .....	7.67 Note
PLAT094_ALERT_2_C	Ratio of Maximum / Minimum Residual Density ....	2.17 Report
PLAT213_ALERT_2_C	Atom F019 has ADP max/min Ratio .....	3.8 prolat
PLAT213_ALERT_2_C	Atom F12 has ADP max/min Ratio .....	3.4 prolat
PLAT213_ALERT_2_C	Atom F14 has ADP max/min Ratio .....	3.7 prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.2 Ratio
PLAT230_ALERT_2_C	Hirshfeld Test Diff for F15 --C01P .	5.2 s.u.
PLAT234_ALERT_4_C	Large Hirshfeld Difference F13 --C01P	0.16 Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference F17 --C01M	0.19 Ang.
PLAT342_ALERT_3_C	Low Bond Precision on C-C Bonds .....	0.01237 Ang.

---

<b>Alert level G</b>		
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	2 Report
PLAT012_ALERT_1_G	No _shelx_res_checksum Found in CIF .....	Please Check
PLAT042_ALERT_1_G	Calc. and Reported MoietyFormula Strings Differ	Please Check
PLAT045_ALERT_1_G	Calculated and Reported Z Differ by a Factor ...	0.50 Check
PLAT063_ALERT_4_G	Crystal Size Likely too Large for Beam Size ....	0.66 mm
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	10.51 Why ?
PLAT186_ALERT_4_G	The CIF-Embedded .res File Contains ISOR Records	2 Report
PLAT199_ALERT_1_G	Reported _cell_measurement_temperature .....	293 Check
PLAT200_ALERT_1_G	Reported _diffn_ambient_temperature .....	293 Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C00N Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C01A Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C01C Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C01M Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C01P Check
PLAT242_ALERT_2_G	Low 'MainMol' Ueq as Compared to Neighbors of	C014 Check
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels .....	66 Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Pr01 (III) .	3.56 Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Fe02 (III) .	3.17 Info
PLAT850_ALERT_4_G	Check Flack Parameter Exact Value 0.00 and s.u.	0.02 Check
PLAT860_ALERT_3_G	Number of Least-Squares Restraints .....	12 Note

---

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain  
0 **ALERT level B** = A potentially serious problem, consider carefully  
10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight  
20 **ALERT level G** = General information/check it is not something unexpected

- 5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
14 ALERT type 2 Indicator that the structure model may be wrong or deficient  
3 ALERT type 3 Indicator that the structure quality may be low  
6 ALERT type 4 Improvement, methodology, query or suggestion  
2 ALERT type 5 Informative message, check
-

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special\_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

#### Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

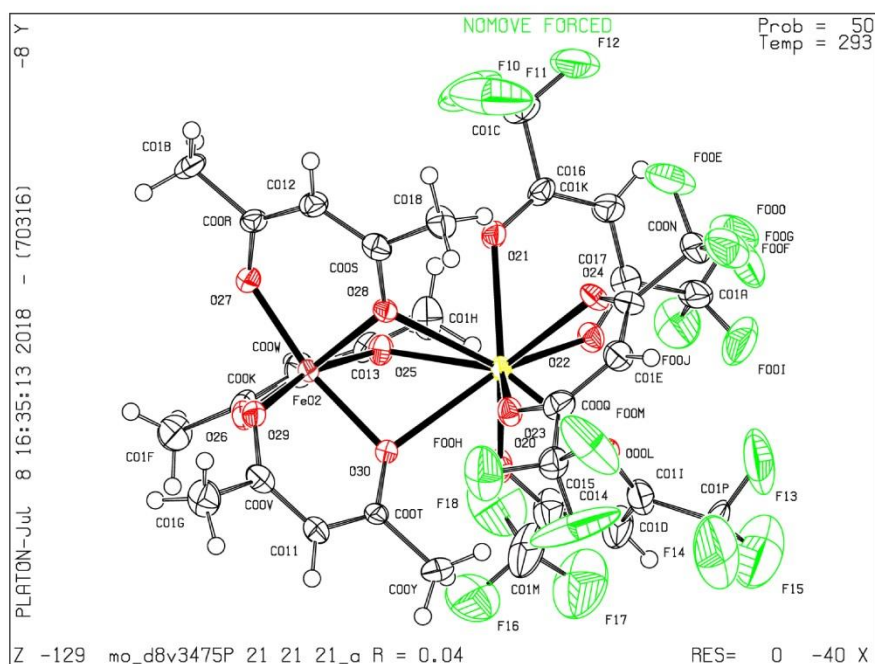
#### Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

---

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock mo\_d8v3475\_2\_0mtotat\_a - ellipsoid plot



### Alternate packing views

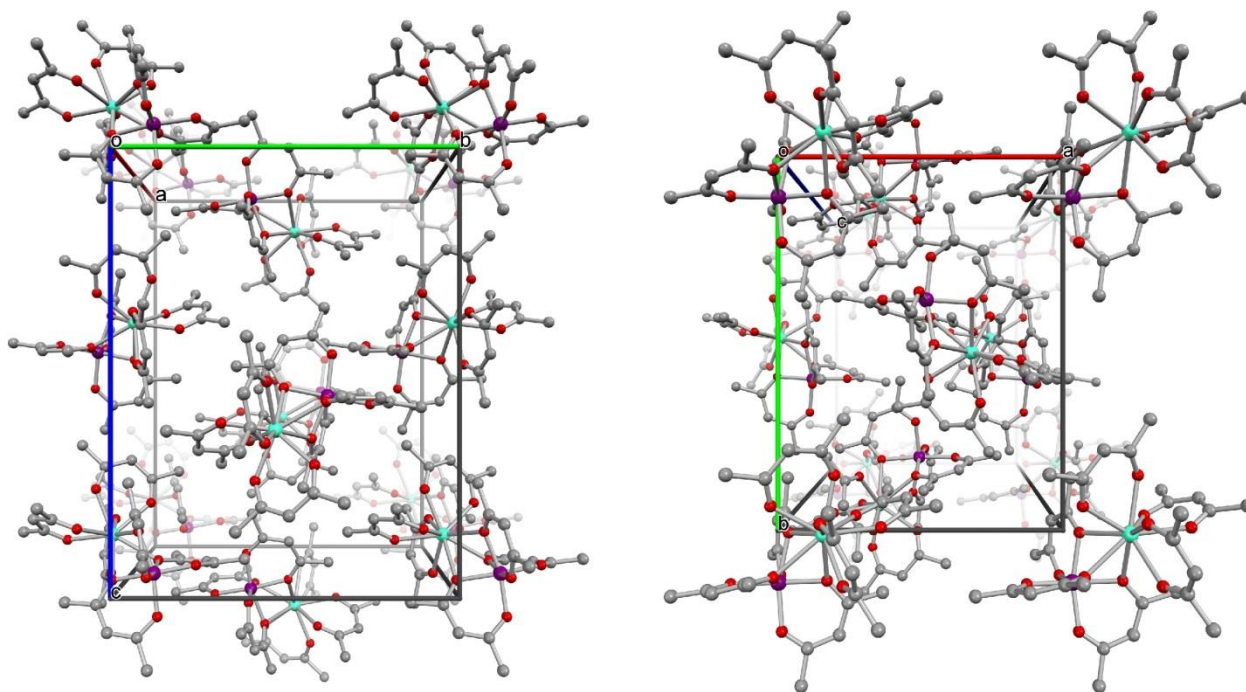


Figure S1. Alternate views of the packing in **GdFe** along the crystallographic *a*-axis (left) and along the crystallographic *c*-axis (right). Hydrogen and fluorine atoms have been omitted for clarity. Color coding: Fe: purple, F: light green, O: red, C: gray, Gd: turquoise.



*Intermolecular interactions*

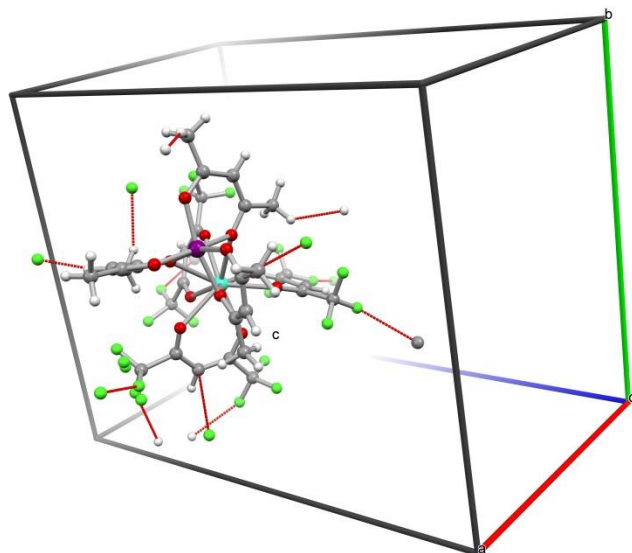


Figure S2. Shortest intermolecular interactions in the packing of **GdFe**. Only one asymmetric unit is shown for clarity.

### Magnetization data at variable temperatures

The magnetization curves recorded at different temperatures were simulated using the Hamiltonian described in the main text.

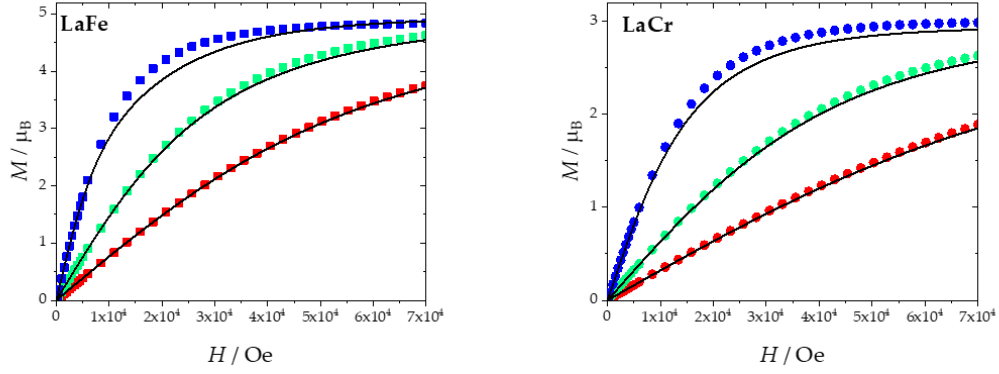


Figure S3. Magnetization curves of **LaTM** recorded at  $T = 1.8, 5$  and  $10$  K. Symbols are the experimental points and lines are the simulations.

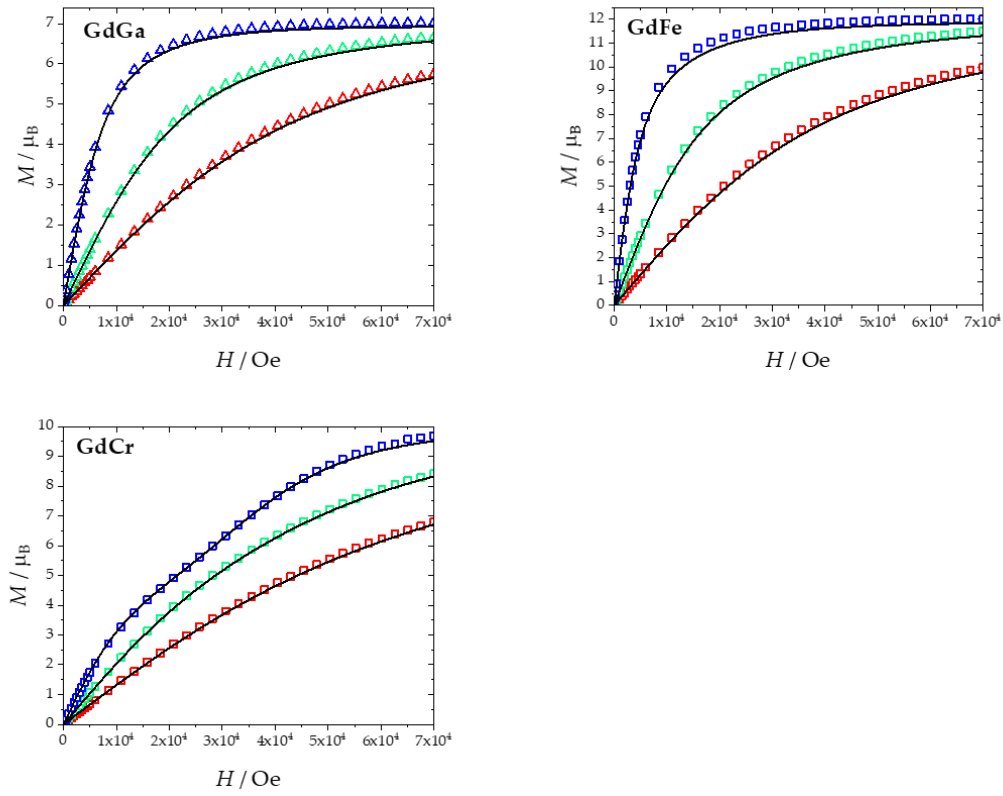


Figure S4. Magnetization curves of **GdTM** recorded at  $T = 1.8, 5$  and  $10$  K. Symbols are the experimental points and lines are the simulations.

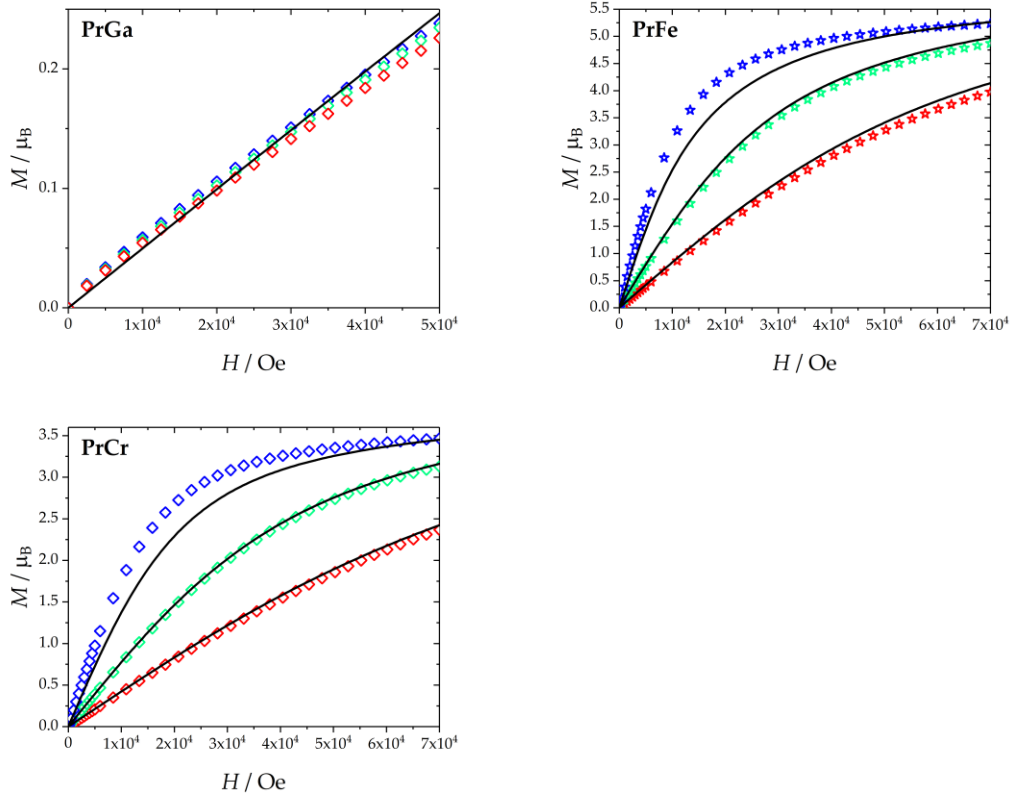


Figure S5. Magnetization curves of **PrTM** recorded at  $T = 1.8, 5$  and  $10$  K. Symbols are the experimental points and lines are the simulations.

#### Ac susceptibility of **GdGa**

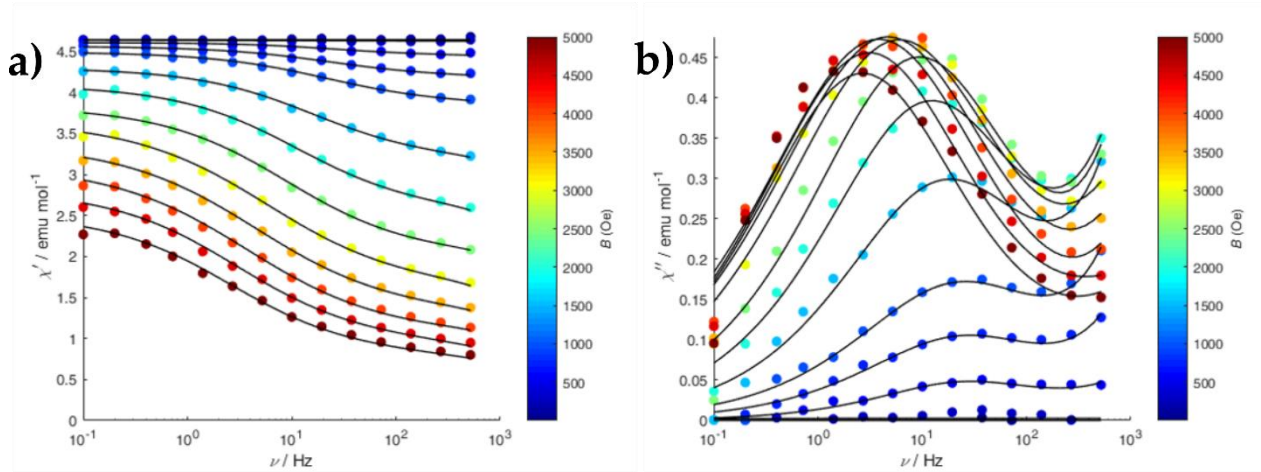


Figure S6 (a) Real and (b) Imaginary part of the ac magnetic susceptibility of **GdGa** recorded at  $T = 1.8$  K. Symbols are the experimental points and black lines are the fit based on the Cole-Cole formulas [1].

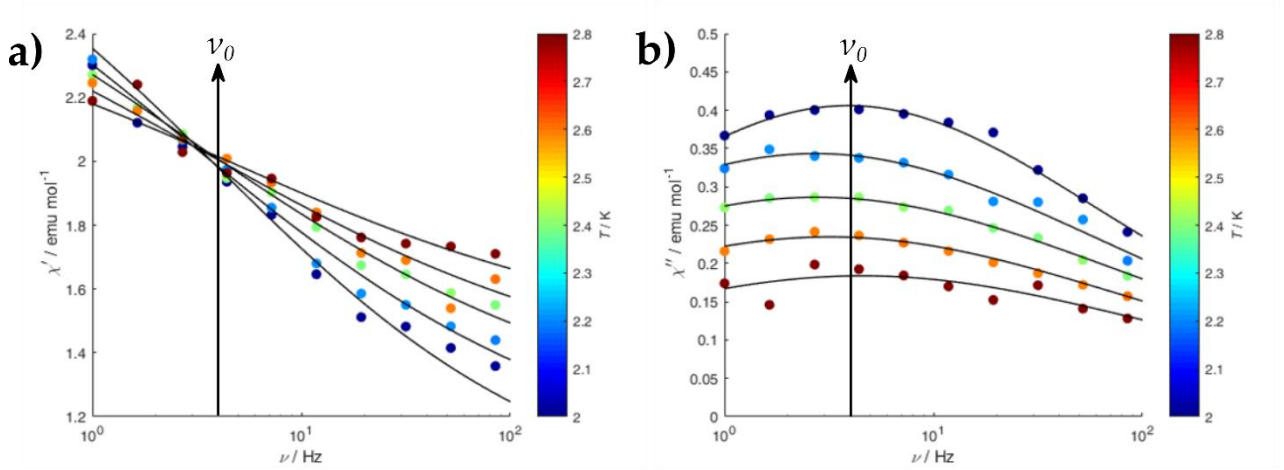


Figure S7 (a) Real and (b) Imaginary part of the ac magnetic susceptibility of **GdGa** recorded at  $B = 4000$  Oe. Symbols are the experimental points and black lines are the fit using Cole-Cole formulas [1]. The black arrow refers to the temperature-independent relaxation frequency obtained from the fitting of the field scan

The field dependence of the extracted relaxation rate ( $\tau^{-1}$ ) for the slow process was fitted considering a single tunnelling process using the equation:

$$\tau^{-1} = \frac{B_1}{1+B_2 H^2} \quad (1)$$

where  $B_1$  and  $B_2$  are empirical parameters.

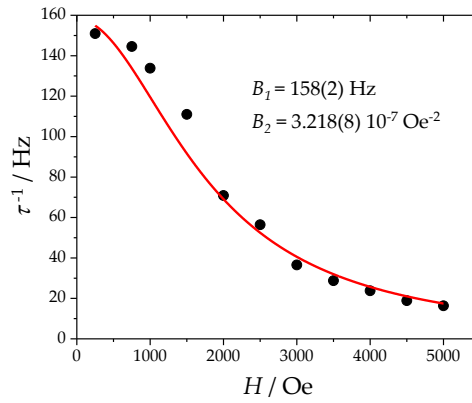


Figure S8. Field dependence of the relaxation time extracted from the fit of the real and imaginary ac susceptibility at  $T = 1.8$  K (Figure S6). Symbols are the experimental points and the red line is the fit using eq. (1).

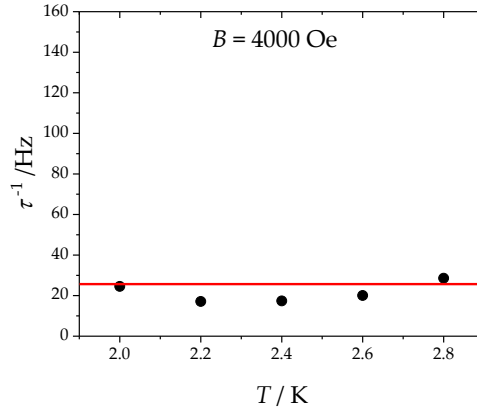


Figure S9. Temperature dependence of the relaxation rate extracted from the fit of the real and imaginary ac susceptibility at  $H = 4000$  Oe (Figure S7). Symbols are the experimental points and the red line is the value extracted using eq (1) at  $H = 4000$  Oe ( $\tau^{-1} = 25.6$  Hz). The  $y$  scale was chosen to be equal to the one of Figure S8, in order to emphasize the small variation of the relaxation time.

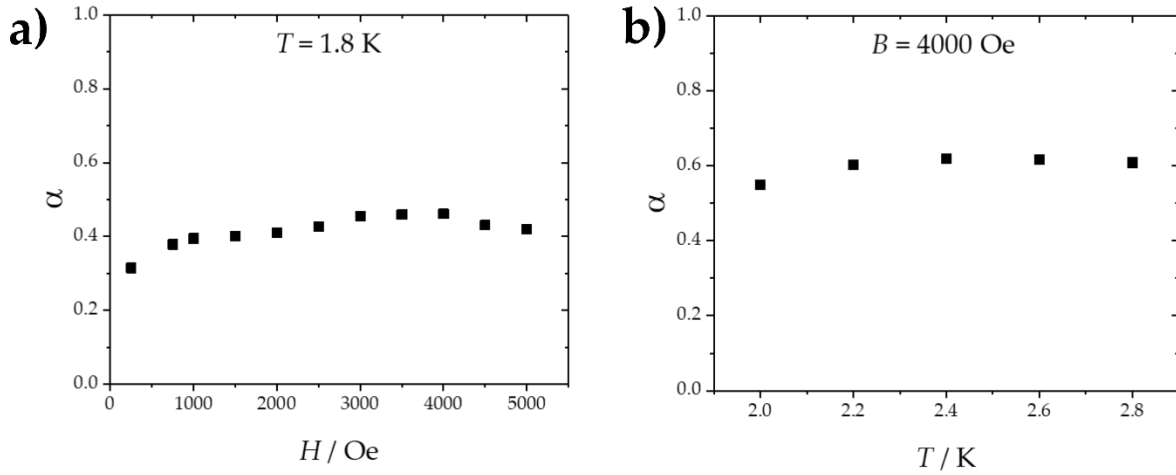


Figure S10. Width of the relaxation times distribution as a function of field at  $T = 1.8$  K (a) and as a function of temperature at  $H = 4000$  Oe (b).

Substituting the best fit parameters in eq. (1), it is possible to calculate the expected temperature independent relaxation frequency at the optimum field of  $H = 4000$  Oe:  $\nu_0 = (2\pi\tau_0)^{-1} = 4.1$  Hz. This frequency is close to the position of the inflexion point of the real part of the magnetic susceptibility or, equivalently, to the peak in the imaginary susceptibility at all the measured temperatures (black arrow in Figure S7). Indeed, the relaxation rate has an almost constant value (Figure S9).

### Powder X-ray diffractograms

The samples were ground in an agate mortar, and measured in a poly(methyl methacrylate) sample holder. This particular sample holder gives rise to a slight curvature in the low-angle background. The simulated powder patterns were calculated from the relevant .cif files using the Mercury 3.7 software.<sup>2</sup>

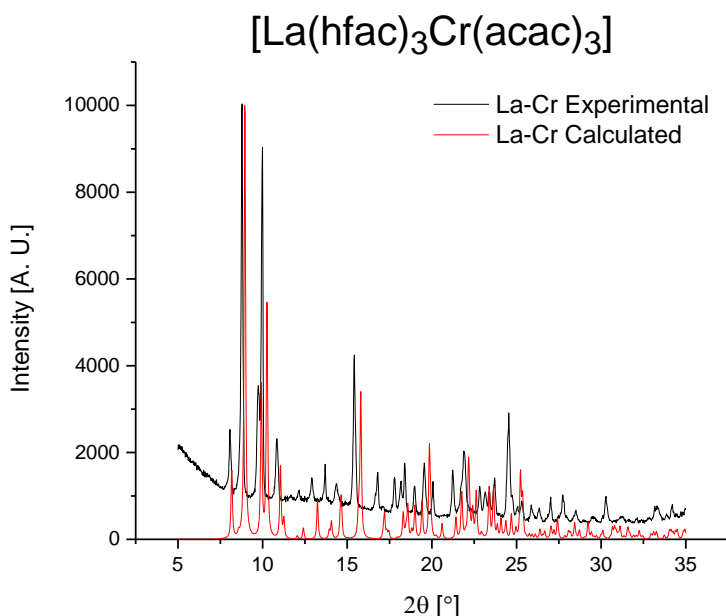


Figure S11. Powder X-ray diffractogram of **LaCr**.

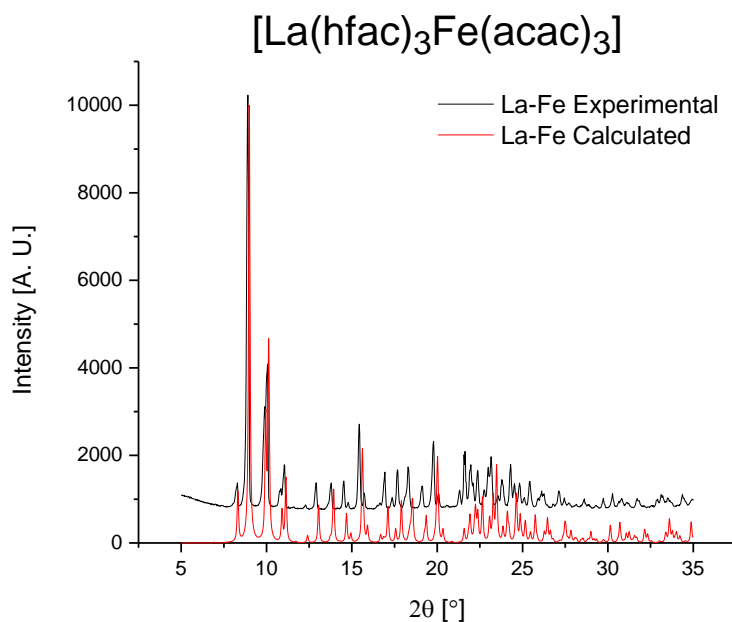


Figure S12. Powder X-ray diffractogram of **LaFe**.

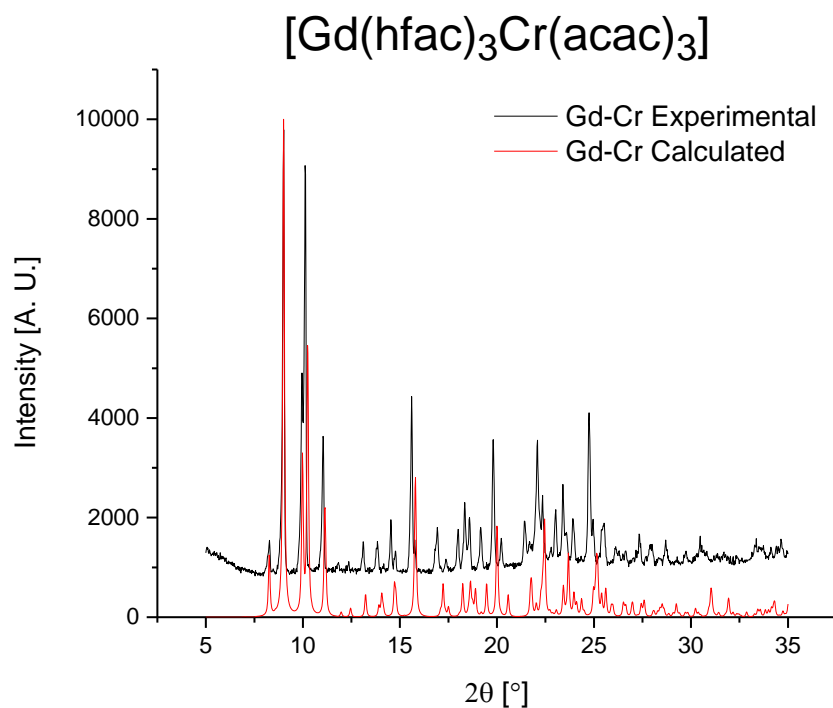


Figure S13. Powder X-ray diffractogram of **GdCr**.

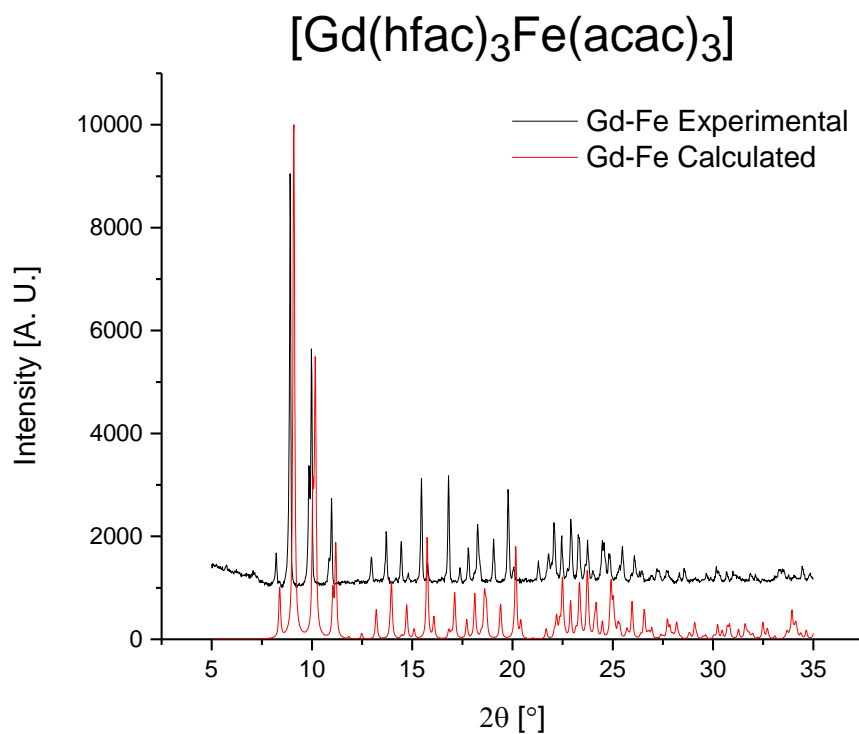


Figure S14. Powder X-ray diffractogram of **GdFe**.

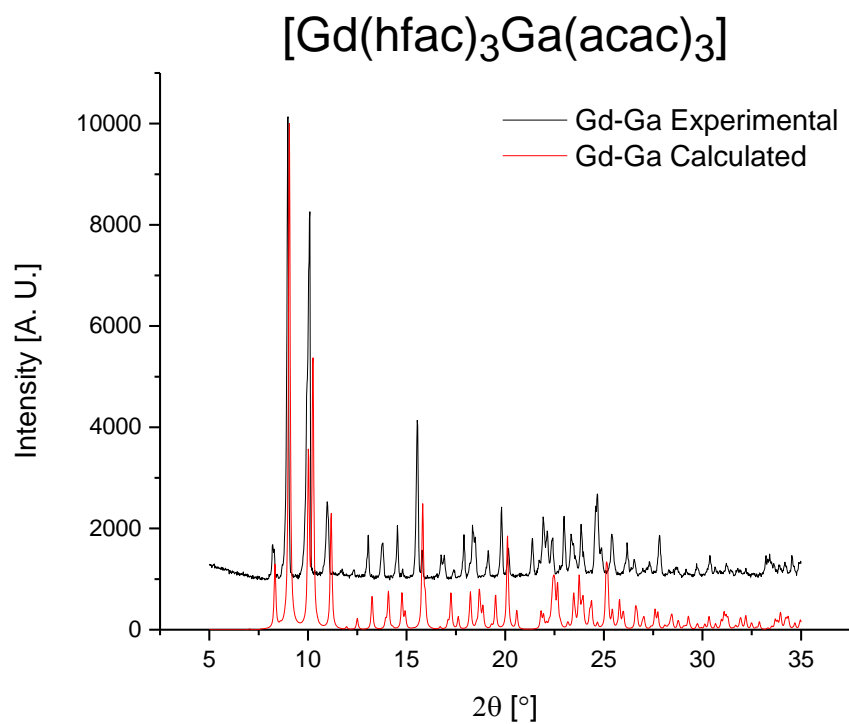


Figure S15. Powder X-ray diffractogram of **GdGa**.

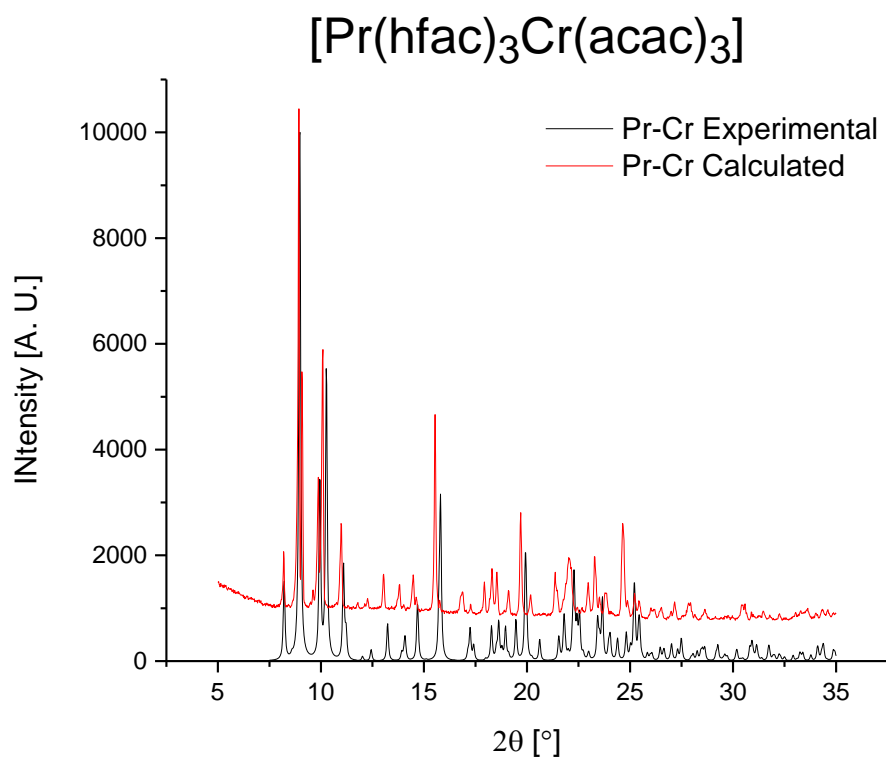


Figure S16. Powder X-ray diffractogram of **PrCr**.



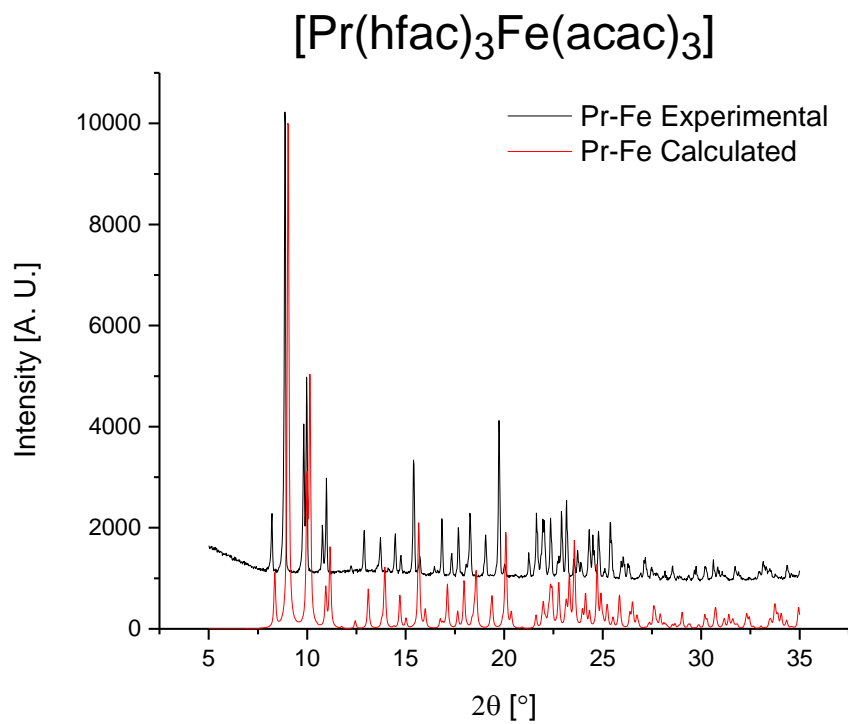


Figure S17. Powder X-ray diffractogram of **PrFe**.

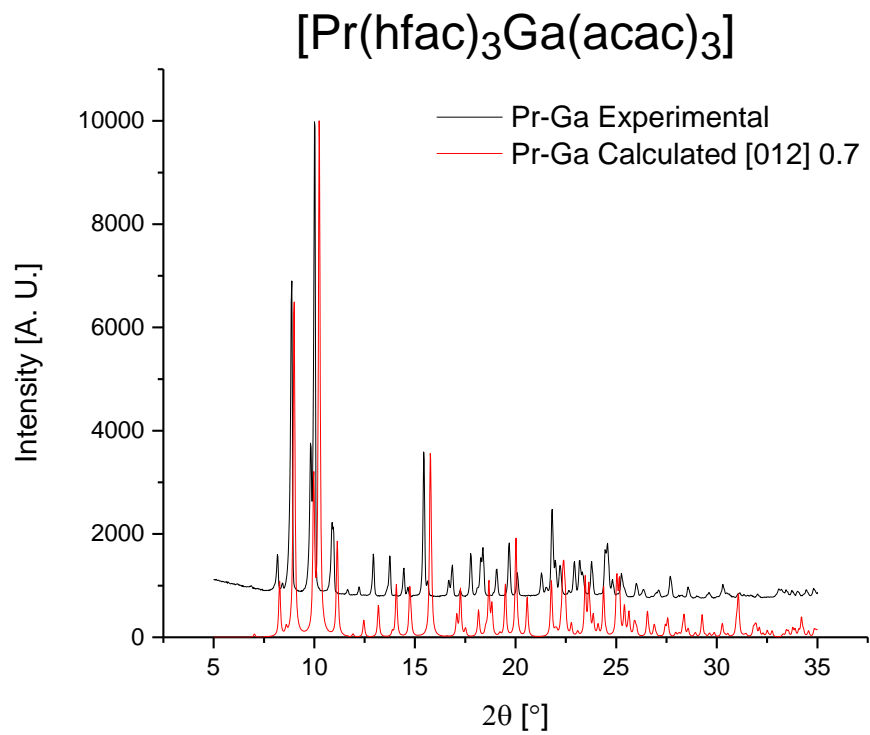


Figure S18. Powder X-ray diffractogram of **PrGa**.

#### References:

1. Cole, K.S.; Cole, R.H. Dispersion and absorption in dielectrics i. Alternating current characteristics. *The Journal of chemical physics* **1941**, *9*, 341–351.
2. Macrae, C.F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: Visualization and Analysis of Crystal Structures. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.