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Electronic Supplementary Information

Synthesis and molecular structure of pentadienyl complexes of the rare-earth metals

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1. Crystallographic details

Special refinement details:

3-Sc: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group.

3-Y: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure. The structure was refined as an inversion twin with components 0.485, 0.515(8).

3-Gd: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure. Ten reflections at high angle, all with Fo << Fc, seem to have been affected by an unidentified systematic error and were omitted from the refinement.

3-Tb: CH and CH2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens.

3-Dy: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure. The structure was refined as an inversion twin with components 0.431, 0.569(3).

3-Ho: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure.

3-Er: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 and C44 sites are common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen

atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure.

3-Tm: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure.

3-Lu: The t-butyl group at C23 is disordered over two positions. The THF at O2 is also disordered over two positions; the O2 site is common to both. Appropriate restraints were employed to improve refinement stability, but the dimensions of the minor components are not entirely satisfactory. Dimensions of disordered groups should always be interpreted with caution. CH and CH_2 hydrogen atoms of the pentadienyl ligands were refined freely, but with C-H distance restraints (SADI) for chemically equivalent hydrogens. The compound crystallizes by accident in a chiral (Sohncke) space group; it is not enantiomerically pure.

Table S1. Crystallographic data.

Compound reference	**1-La**	**1-Ce**	**1-Pr**	**1-Nd**	**2-Eu**	**2-Sm**	**2-Yb**	**3-Sc**	**3-Y**	**3-Gd**
Chemical formula	$C_{39}H_{69}La$	$C_{39}H_{69}Ce$	$C_{39}H_{69}Pr$	$C_{39}H_{69}Nd$	$C_{30}H_{54}EuO$	$C_{34}H_{62}O_2Sm$	$C_{30}H_{54}OYb$	$C_{47}H_{82}O_2Sc_2$	$C_{47}H_{82}O_2Y_2$	$C_{47}H_{82}O_2Gd_2$
Formula Mass	676.85	678.06	678.85	682.18	582.69	653.19	603.77	769.05	856.95	993.63
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
a/Å	10.4567(5)	10.4528(2)	10.4209(8)	10.4084(4)	9.8002(4)	9.4134(3)	9.8991(2)	10.09676(6)	10.10986(14)	10.1181(5)
b/Å	10.5827(5)	10.5711(3)	10.5363(6)	10.5181(4)	14.2312(6)	19.5281(6)	21.6891(3)	20.06909(10)	20.1309(2)	20.1122(9)
c/Å	20.0128(9)	20.0614(7)	20.0361(15)	20.0441(5)	23.3058(8)	10.0081(4)	14.3974(3)	22.20033(15)	22.7725(2)	22.9975(10)
α/°	78.364(4)	78.275(3)	78.174(6)	78.116(3)	88.589(3)	90	90	90	90	90
β/°	87.397(4)	87.254(3)	87.186(6)	87.094(3)	79.930(3)	114.220(4)	105.345(2)	90	90	90
γ/°	61.049(5)	61.080(4)	61.117(7)	61.100(4)	71.121(4)	90	90	90	90	90
Unit cell volume/Å^3	1894.51(15)	1896.53(9)	1882.2(2)	1876.83(11)	3026.4(2)	1677.81(10)	2980.95(10)	4498.51(5)	4634.67(10)	4679.9(4)
Temperature/K	100(2)	130(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
No. of formula units per unit cell, *Z*	2	2	2	2	4	2	4	4	4	4
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Cu Kα
Absorption coefficient, *μ*/mm^{-1}	1.150	1.222	1.317	1.406	2.090	1.775	3.155	2.835	3.581	18.367
No. of reflections measured	112554	87657	34181	137971	166896	89769	182001	122020	97035	53902
No. of independent reflections	10931	10946	10589	10866	17449	9685	8714	9406	9708	9724
R_{int}	0.0919	0.0645	0.0527	0.0702	0.0798	0.0740	0.0622	0.0618	0.0690	0.1049
Final R_1 values ($I > 2\sigma(I)$)	0.0388	0.0315	0.0361	0.0291	0.0341	0.0288,	0.0269	0.0282	0.0250,	0.0398
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0692	0.0611	0.0652	0.0547	0.0532	0.0546	0.0555	0.0730	0.0601	0.0796
Final R_1 values (all data)	0.0523	0.0400	0.0451	0.0369	0.0542	0.0376	0.0337	0.0292	0.0281,	0.0473
Final $wR(F^2)$ values (all data)	0.0734	0.0642	0.0685	0.0570	0.0582	0.0581	0.0577	0.0739	0.0619	0.0831
Goodness of fit on F^2	1.082	1.059	1.062	1.090	1.054	1.048	1.125	1.031	1.027	1.023
Flack parameter	-	-	-	-	-	-0.025(8)	-	-0.006(3)	0.485(8)	-0.012(4)
$\Delta\rho$ / e Å^{-3}	0.941/-0.548	0.750/-0.447	0.823/-0.794	0.774/-0.563	0.668/-0.570	1.596/-0.860	1.789/-0.889	0.343/-0.359	0.273/-0.592	0.554/-0.711

Table S2. Crystallographic data.

Compound reference	**3-Tb**	**3-Dy**	**3-Ho**	**3-Er**	**3-Tm**	**3-Lu**
Chemical formula	$C_{47}H_{82}O_2Tb_2$	$C_{47}H_{82}Dy_2O_2$	$C_{47}H_{82}Ho_2O_2$	$C_{47}H_{82}Er_2O_2$	$C_{47}H_{82}O_2Tm_2$	$C_{47}H_{82}Lu_2O_2$
Formula Mass	996.97	1004.13	1008.99	1013.65	1016.99	1029.07
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
a/Å	10.1015(3)	10.08630(14)	10.0948(6)	10.0818(2)	10.0795(2)	10.0804(3)
b/Å	20.1033(6)	20.1130(2)	20.1399(8)	20.1270(4)	20.1224(3)	20.1583(6)
c/Å	22.8992(7)	22.8082(3)	22.7545(9)	22.6200(4)	22.5603(4)	22.4603(7)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
Unit cell volume/Å^3	4650.3(2)	4627.00(10)	4626.2(4)	4589.97(15)	4575.77(14)	4564.0(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
No. of formula units per unit cell, *Z*	4	4	4	4	4	4
Radiation type	Mo Kα	Cu Kα	Cu Kα	Mo Kα	Mo Kα	Cu Kα
Absorption coefficient, *μ*/mm^{-1}	3.050	17.315	6.423	3.665	3.886	8.316
No. of reflections measured	240759	96707	95054	122576	271096	84586
No. of independent reflections	11535	9678	9657	13338	13355	9514
R_{int}	0.1225	0.0797	0.1239	0.0635	0.0701	0.0967
Final R_1 values ($I > 2\sigma(I)$)	0.0330	0.0254	0.0417	0.0253	0.0262	0.0329
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0703	0.0596	0.0901	0.0450	0.0539	0.0752
Final R_1 values (all data)	0.0428	0.0283	0.0523	0.0319	0.0324	0.0393
Final $wR(F^2)$ values (all data)	0.0747	0.0611	0.0950	0.0470	0.0564	0.0787
Goodness of fit on F^2	1.049	1.028	1.048	1.093	1.106	1.026
Flack parameter	-0.034(11)	0.431(3)	-0.035(9)	-0.026(6)	-0.019(8)	-0.037(12)
$\Delta\rho$ / e Å^{-3}	1.228/-0.997	0.501/-1.047	0.418/-0.945	0.708/-0.568	1.839/-0.585	0.560/-1.012

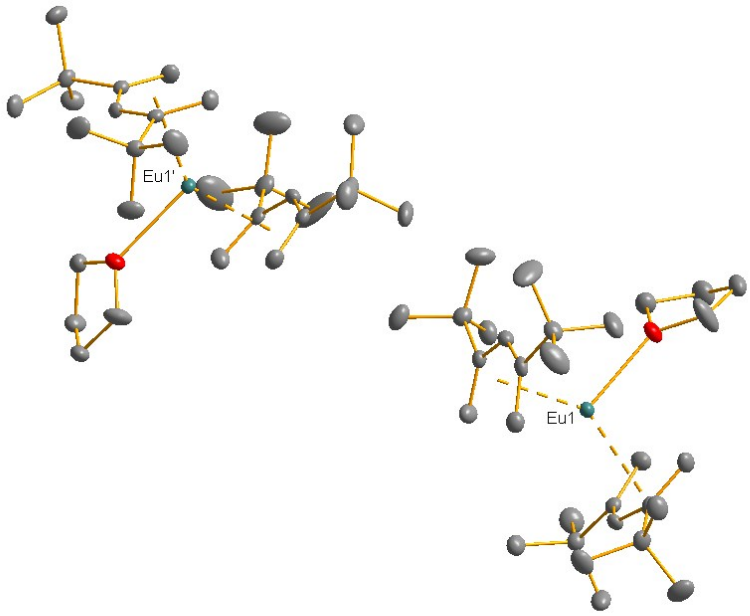

Figure S1. Molecular structure of **1-Eu** with two independent molecules in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level.

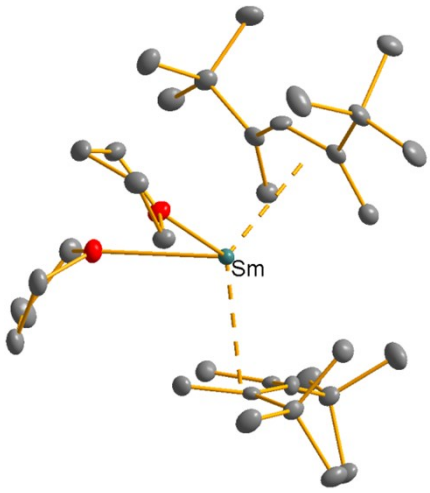

Figure S2. Molecular structure of **1-Sm**. Thermal ellipsoids are drawn at the 50% probability level.

2. Solid-state Magnetic Susceptibility Studies

Table S3. Parameters determined based on a fit of the $1/\chi$ vs. T data by use of the Curie-Weiss law for **1-M**, **2-M** and **3-M** (with M, as outlined in the first row of the table).

Complex	C (K cm^3 mol^{-1})	θ (K)	[c]	$\mu_{eff,C}$ (μ_B)	$\mu_{eff,300K}$ (μ_B)	$\mu_{eff,calc}$ (μ_B)
1-Ce	0.821(1)	-46.1(2)	T > 50 K	2.56(1)	2.39	2.54 [a]
1-Pr	1.698(8)	-16.6(8)	T > 50 K	3.69(1)	3.62	3.58 [a]
1-Nd	1.83(1)	-40(1)	T > 50 K	3.83(1)	3.64	3.62 [a]
2-Sm	2.571(8)	-218(1)	T > 150 K	4.54(1)	3.43	0 [a]
2-Eu	7.111(1)	0.01(2)	T > 2.6 K	7.54(1)	7.56	7.94 [a]
3-Gd	15.74(2)	2.3(3)	T > 100 K	11.22(1)	11.28	11.23 [b]
3-Tb	22.4(1)	-2.9(1)	T > 100 K	13.39(3)	13.36	13.75 [b]
3-Dy	27.8(1)	-2.3(2)	T > 100 K	14.91(3)	14.89	15.06 [b]
3-Ho	27.6(1)	-9.1(1)	T > 100 K	14.86(3)	14.65	15.00 [b]
3-Er	23.4(1)	-11.2(1)	T > 100 K	13.68(3)	13.47	13.55 [b]
3-Tm	15.26(1)	-18.7(2)	T > 100 K	11.05(1)	10.74	10.69 [b]

[a] calculated with $g_J\sqrt{J(J+1)}$. [b] calculated with $\sqrt{2}\,g_J\sqrt{J(J+1)}$; [c] temperatures used for the fit.

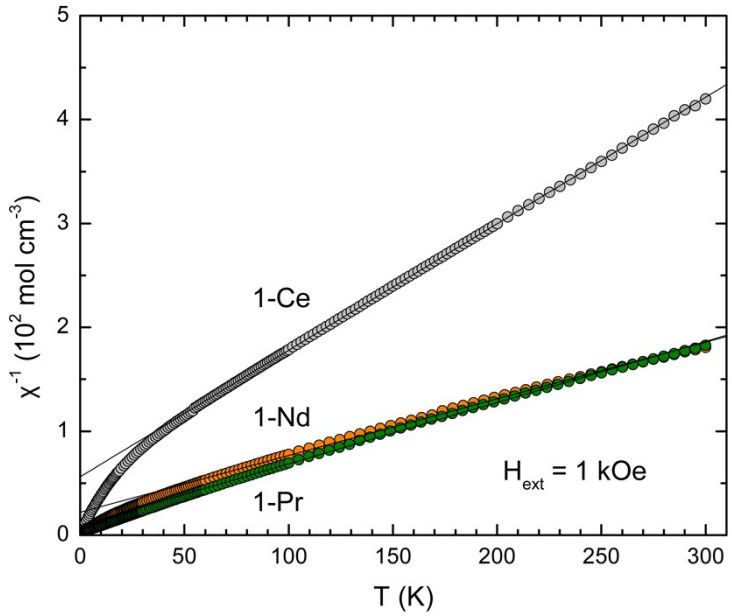

Figure S3. Inverse magnetic susceptibility (χ^{-1}) vs. T plots for **1-Ce** (grey), **1-Nd** (orange) and **1-Pr** (green) recorded at temperatures between T = 2.6 and 300 K with an applied magnetic field of H_{ext} = 1 kOe. Symbols: experimental data; lines: adaptation of the Curie-Weiss law with parameters that are summarized in Table S3.

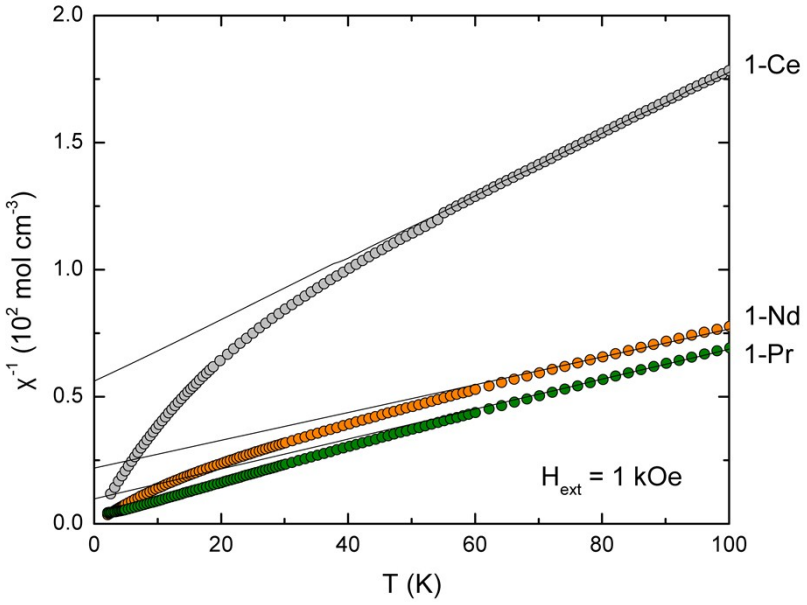

Figure S4. The same as in Figure S3, but with modified *x*- and *y*-axis (to better illustrate the low-temperature data).

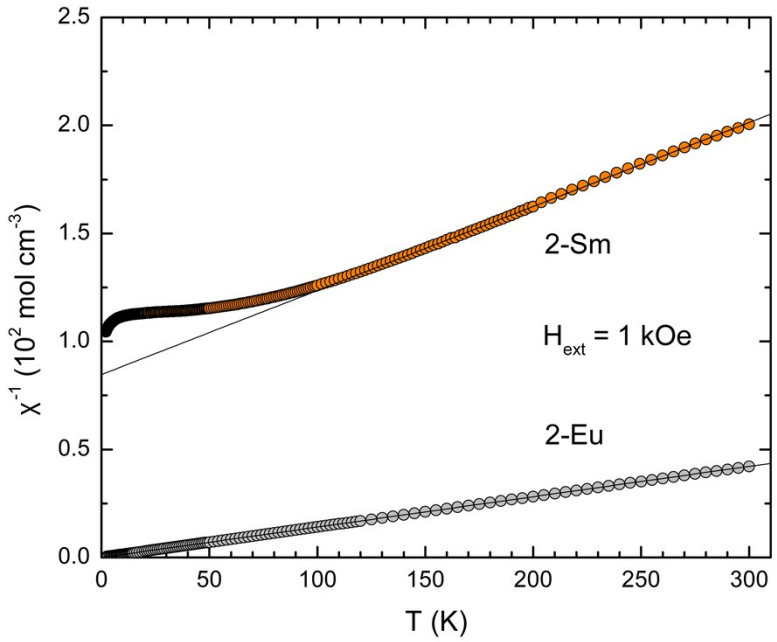

Figure S5. Inverse magnetic susceptibility (χ^{-1}) vs. T plots for **2-Sm** and **2-Eu** recorded at temperatures between T = 2.6 and 300 K with an applied magnetic field of H_{ext} = 1 kOe. Symbols: experimental data; lines: adaptation of the Curie-Weiss law with parameters that are summarized in Table S3.

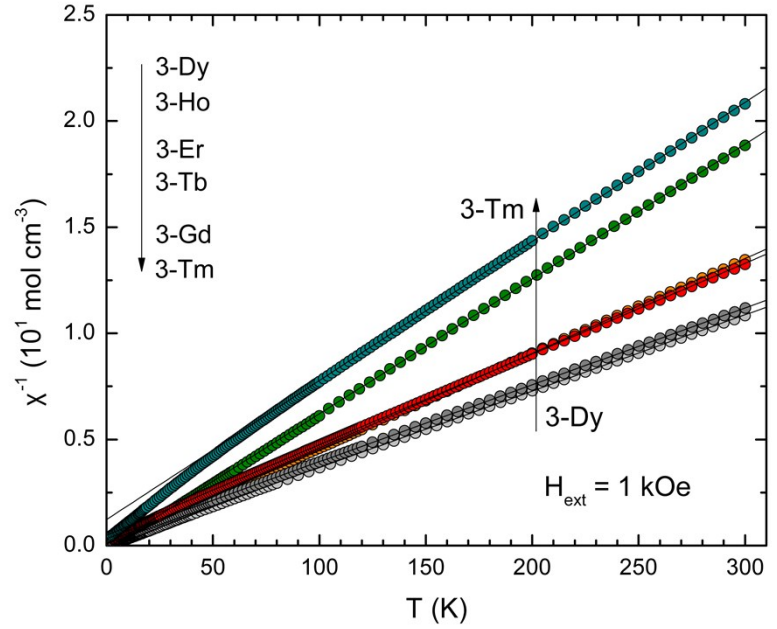

Figure S6. Inverse magnetic susceptibility (χ^{-1}) vs. T plots for **3-M** (M = Gd (green), Tb (orange), Dy (light grey), Ho (grey), Er (red), Tm (turquoise)) recorded at temperatures between T = 2.6 and 300 K with an applied magnetic field of H_{ext} = 1 kOe. Symbols: experimental data; lines: adaptation of the Curie-Weiss law with parameters that are summarized in Table S3.

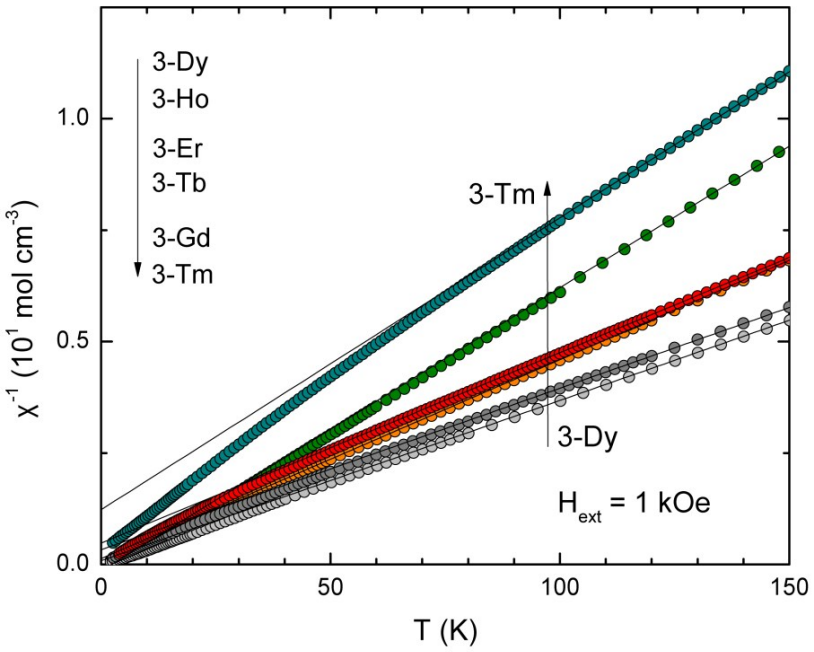

Figure S7. The same as in Figure S6, but with modified *x*- and *y*-axis (to better illustrate the low-temperature data).