Supplementary Information

Crystal structure, magnetic and magnetocaloric properties of the new orthorhombic Y_3Co_2-type $Gd_3Co_{1+x}Ni_{1-x}$ solid solution

Aritz Herrero*[a], Alessia Provino[b,c,d], Ivan R. Aseguinolaza[a], Serena De Negri[b], Davide Peddis[b,e], Pietro Manfrinetti[b,c] and Alberto Oleaga[a]

[a] *Departamento de Física Aplicada, Escuela de Ingeniería de Bilbao, Universidad del País Vasco UPV/EHU, Plaza Torres Quevedo 1, 48013 Bilbao, Spain*

[b] *Department of Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy*

[c] *CNR, Institute SPIN, Corso Perrone 24, 16152 Genova, Italy*

[d] *Department of Material Sciences and Engineering, Alfred University, Alfred, New York 14802, United States*

[e] *CNR, Istitute of Structure of Matter, nM2-lab, Monterotondo Scalo (RM), 00015 Italy*

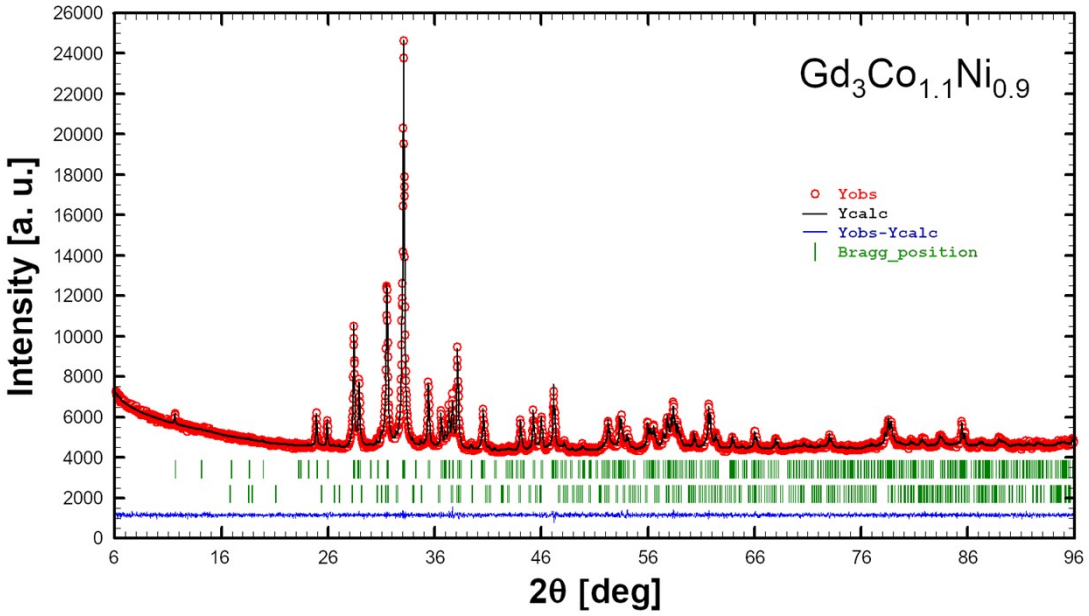

Figure S1. Observed X-ray powder pattern (red circle), and Rietveld refinement profile (black line) for the sample prepared on nominal composition $Gd_3Co_{1.10}Ni_{0.90}$. The lower profile (blue line) gives the difference between observed and calculated data; the Bragg angle positions are indicated by vertical bars (green). The sample contains 96 vol.% of the new $Gd_3Co_{1.10}Ni_{0.90}$ compounds (Y_3Co_2-type, *oP*20, *Pnnm*) (top Bragg angle bars) and 4 vol.% of $Gd_3Co_{1-x}Ni_x$ (x = 0.31) (composition from EDS) (low Bragg angle bars).

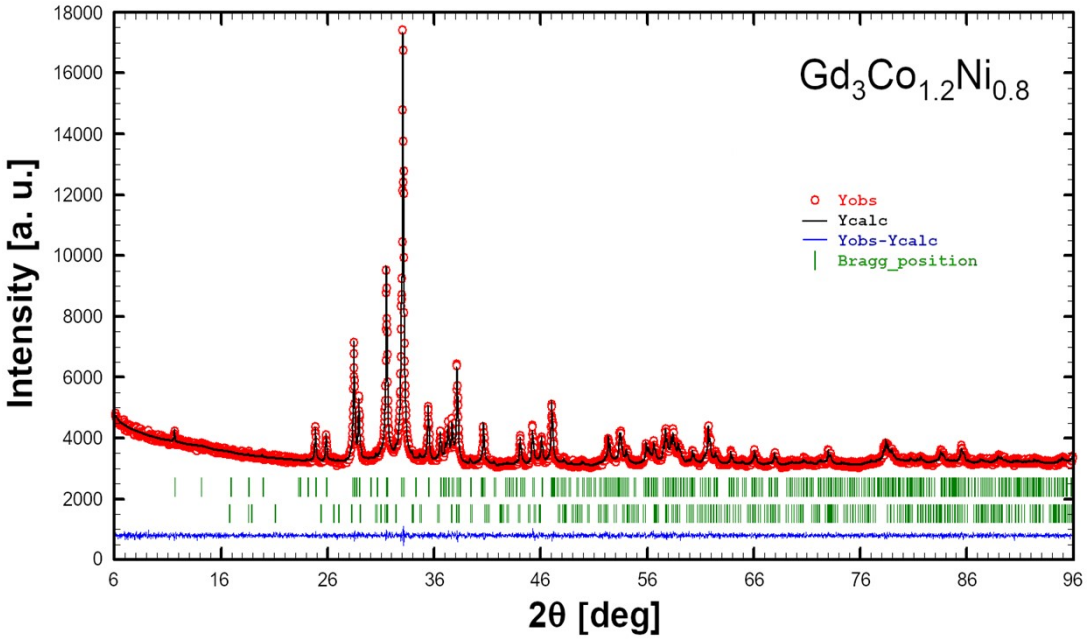

Figure S2. Observed X-ray powder pattern (red circle), and Rietveld refinement profile (black line) for the sample prepared on nominal composition $Gd_3Co_{1.20}Ni_{0.80}$. The lower profile (blue line) gives the difference between observed and calculated data; the Bragg angle positions are indicated by vertical bars (green). The sample contains 97 vol.% of the new $Gd_3Co_{1.20}Ni_{0.80}$ compounds (Y_3Co_2-type, *oP*20, *Pnnm*) (top Bragg angle bars) and 3 vol.% of $Gd_3Co_{1-x}Ni_x$ (x = 0.27) (composition from EDS) (low Bragg angle bars).

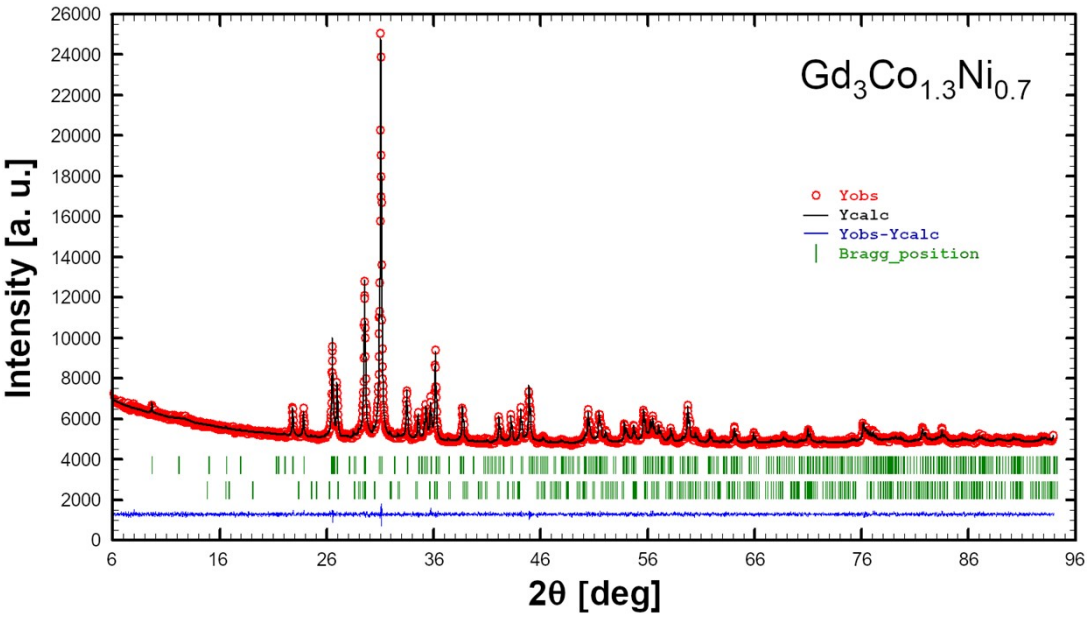

Figure S3. Observed X-ray powder pattern (red circle), and Rietveld refinement profile (black line) for the sample prepared on nominal composition $Gd_3Co_{1.30}Ni_{0.70}$. The lower profile (blue line) gives the difference between observed and calculated data; the Bragg angle positions are indicated by vertical bars (green). The sample contains 97.5 vol.% of the new $Gd_3Co_{1.30}Ni_{0.70}$ compounds (Y_3Co_2-type, *oP*20, *Pnnm*) (top Bragg angle bars) and 2.5 vol.% of $Gd_3Co_{1-x}Ni_x$ (x = 0.22) (composition from EDS) (low Bragg angle bars).

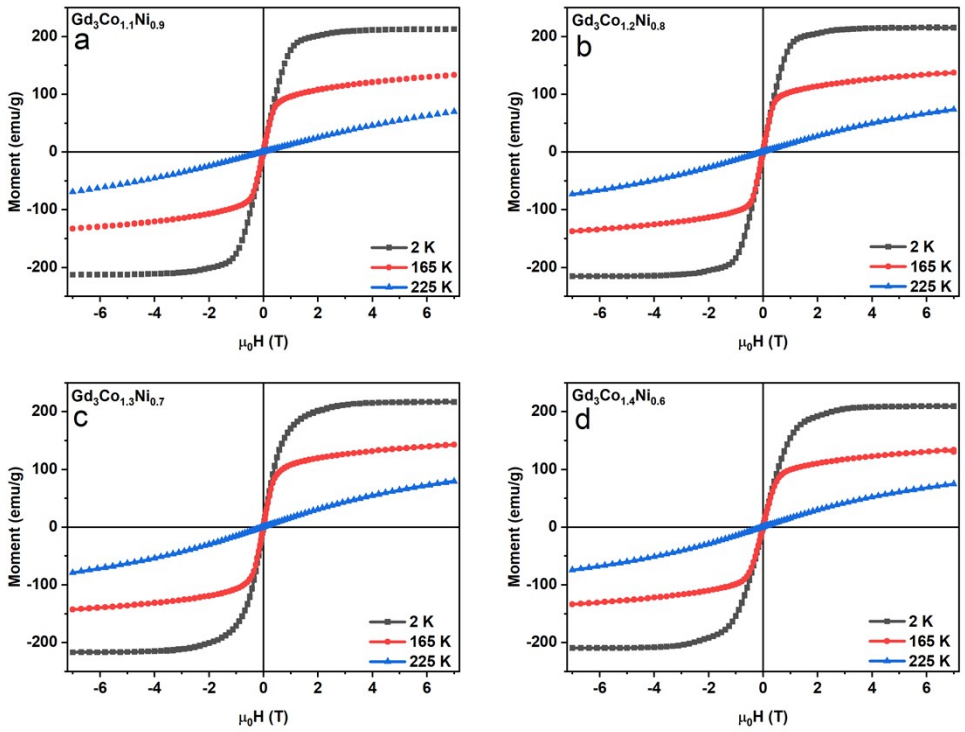

Figure S4. Isothermal magnetization loops at 2, 165 and 225 K for $Gd_3Co_{1.1}Ni_{0.9}$ (a), $Gd_3Co_{1.2}Ni_{0.8}$ (b), $Gd_3Co_{1.3}Ni_{0.7}$ (c) and $Gd_3Co_{1.4}Ni_{0.6}$ (d).

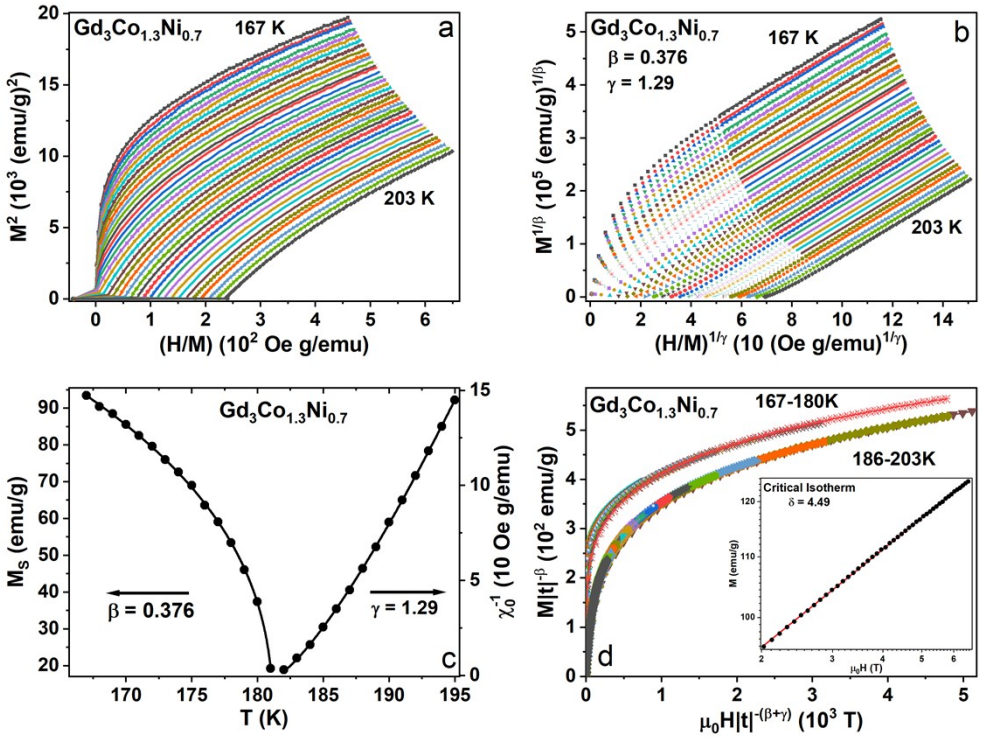

Figure S5. Critical behavior analysis for $Gd_3Co_{1.1}Ni_{0.9}$. Arrott Plot representation (a), Modified Arrott Plot representation with the correct critical exponents (b), fitting of M_S and χ^{-1}_0 to Eqs. (1) and (2) correspondingly (c), magnetic equation of state (d) and the inset on the latter panel shows the fitting of the critical isotherm to Eq. (3).

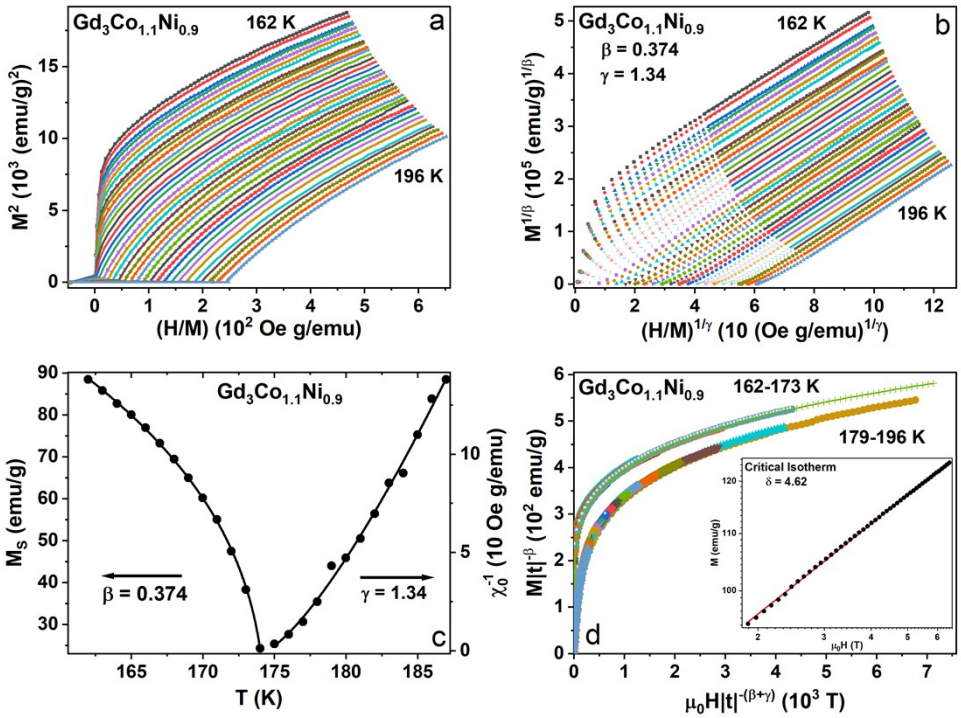

Figure S6. Critical behavior analysis for $Gd_3Co_{1.3}Ni_{0.7}$. Arrott Plot representation (a), Modified Arrott Plot representation with the correct critical exponents (b), fitting of M_S and χ^{-1}_0 to Eqs. (1) and (2) correspondingly (c), magnetic equation of state (d) and the inset on the latter panel shows the fitting of the critical isotherm to Eq. (3).

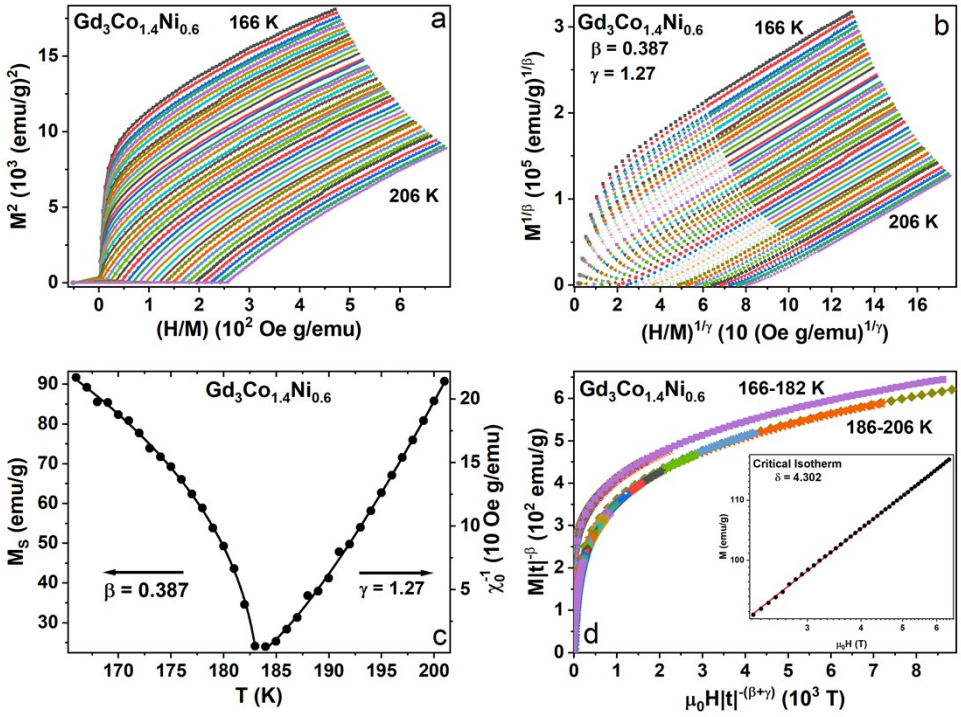

Figure S7. Critical behavior analysis for $Gd_3Co_{1.4}Ni_{0.6}$. Arrott Plot representation (a), Modified Arrott Plot representation with the correct critical exponents (b), fitting of M_S and χ^{-1}_0 to Eqs. (1) and (2) correspondingly (c), magnetic equation of state (d) and the inset on the latter panel shows the fitting of the critical isotherm to Eq. (3).

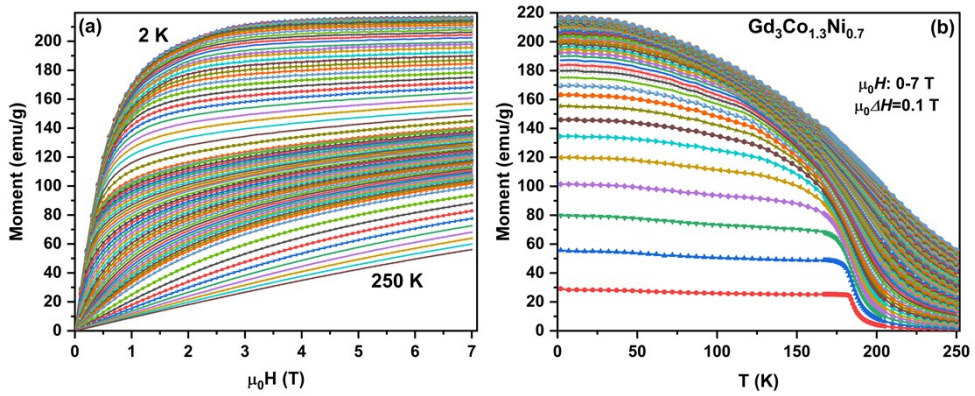

Figure S8. *M(H)* isotherms from 2K to 250 K (a) and *M(T)* isofields (extracted from the isotherms) from 0.1 to 7 T with field steps of 0.1 T (b) for $Gd_3Co_{1.3}Ni_{0.7}$.

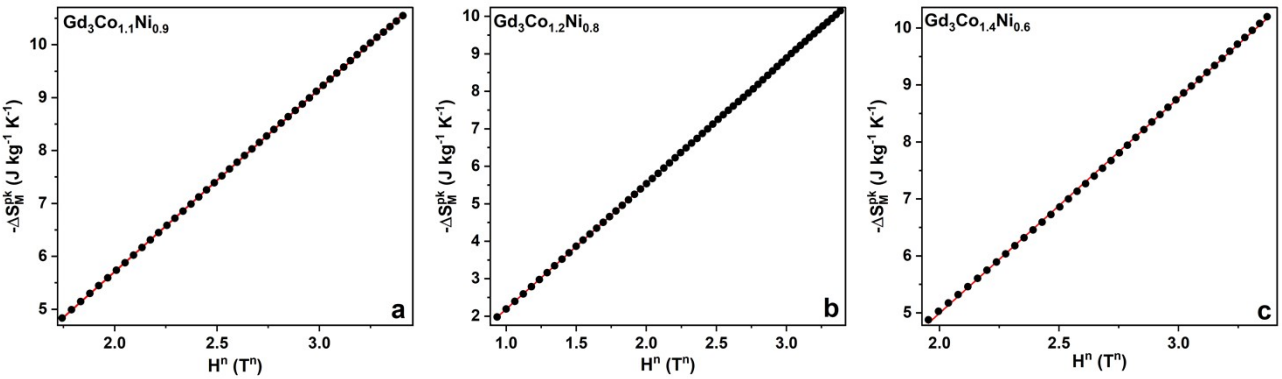

Figure S9. Field dependence of the magnetic entropy change peak for $Gd_3Co_{1.1}Ni_{0.9}$ (a), $Gd_3Co_{1.2}Ni_{0.8}$ (b) and $Gd_3Co_{1.4}Ni_{0.6}$ (c). Red line is a linear fit to be used as a visual guide.

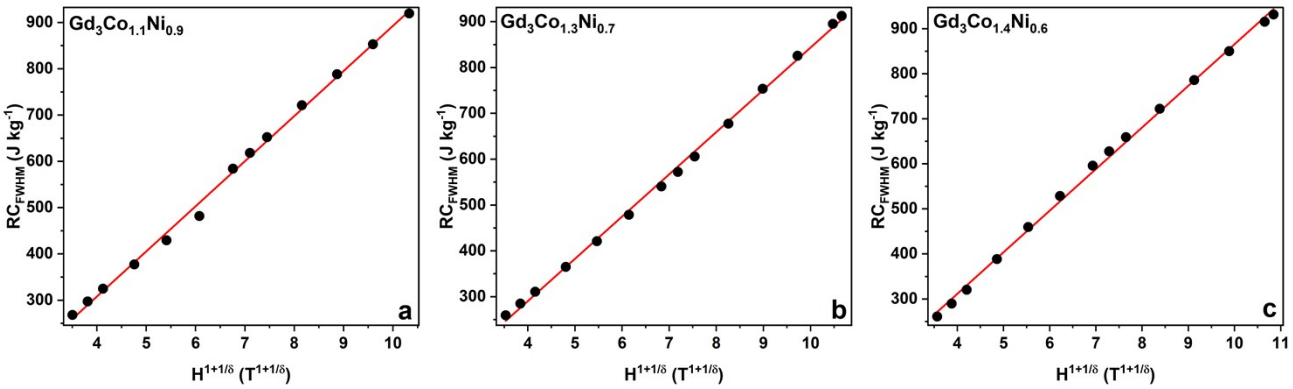

Figure S10. Field dependence of RC_{FWHM} for $Gd_3Co_{1.1}Ni_{0.9}$ (a), $Gd_3Co_{1.3}Ni_{0.7}$ (b) and $Gd_3Co_{1.4}Ni_{0.6}$ (c). Red line is a linear fit to be used as a visual guide.

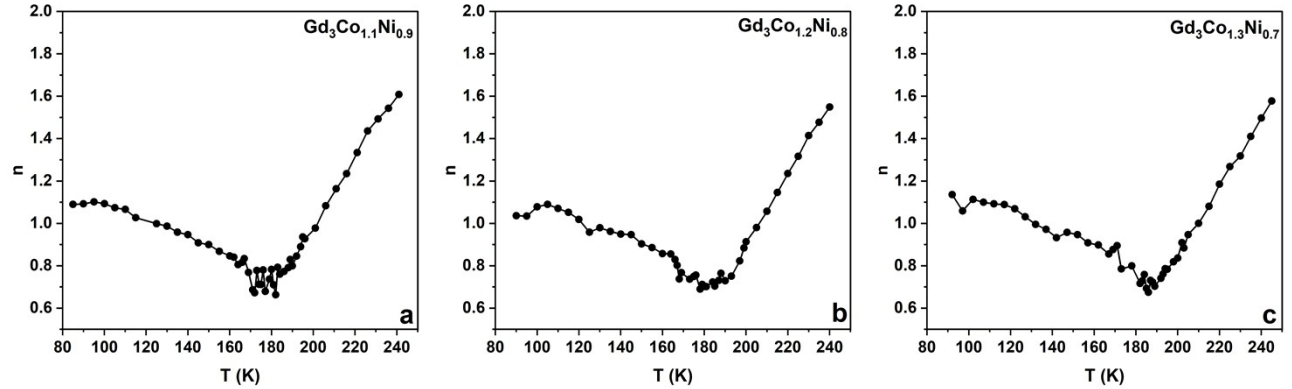

Figure S11. Temperature dependence of the *n* exponent for $Gd_3Co_{1.1}Ni_{0.9}$ (a), $Gd_3Co_{1.2}Ni_{0.8}$ (b) and $Gd_3Co_{1.3}Ni_{0.7}$ (c) at 7 T.

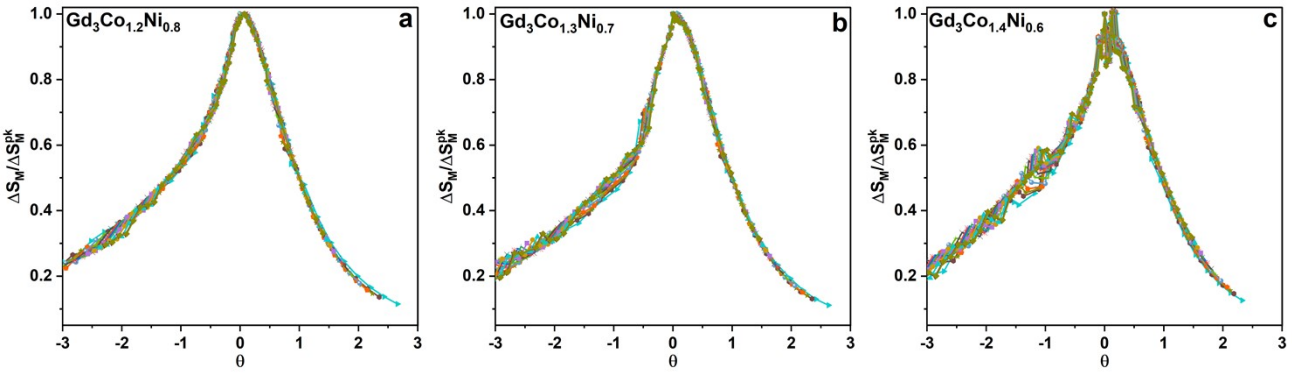

Figure S12. Universal curve for $Gd_3Co_{1.2}Ni_{0.8}$ (a), $Gd_3Co_{1.3}Ni_{0.7}$ (b) and $Gd_3Co_{1.4}Ni_{0.6}$ (c).

Table S1. Crystal data and structure refinement details for the $Gd_3Co_{1.1}Ni_{0.9}$ compound at T = 293(2) K.

Compound	**$Gd_3Co_{1.1}Ni_{0.9}$**
CSD code	2401455
Final stoichiometry	$Gd_3Co_{1.1}Ni_{0.9}$
Formula weight [g/mol]	589.401
Structural prototype	Y_3Co_2
Pearson symbol	*oP*20
Crystal system	Orthorhombic
Space group	*Pnmm* (No. 58)
a [Å]	9.5467(3)
b [Å]	12.5543(3)
c [Å]	3.8477(1)
Unit cell volume [Å^3]	461.16(2)
Unit formula per cell, *Z*	4
Calculated density, ρ [g/cm^3]	8.489
Absorption coefficient, μ [mm^{-1}]	49.809
F(000)	988
Crystal description	Irregular shape
Crystal size [mm]	0.03 × 0.04 × 0.05
Theta range [°]	2.68 ≤ ϑ ≤ 36.32
Index ranges *h*, *k*, *l*	–15 ≤ *h* ≤ 15
	–20 ≤ *k* ≤ 17
	–6 ≤ *l* ≤ 5
Reflections collected	12431
Independent reflection	1247
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameter	1247/0/32
Goodness of fit on F^2	1.053
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0222, *wR*2 = 0.0398
R indices (all data)	*R*1 = 0.0356, *wR*2 = 0.0429
R_{int}/R_{sym}	0.0444/0.0254
Largest diff. peak and hole [e$^-$/Å^3]	+1.326, –1.556

Table S2. Standardized atomic coordinates for the $Gd_3Co_{1.10}Ni_{0.90}$ (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58) compound obtained from the Rietveld refinement on the powder pattern prepared on the nominal composition $Gd_3Co_{1.10}Ni_{0.90}$ (Gd60Co22Ni18); R_{wp} = 11.5 %, χ^2 = 1.23. (*) the Co/Ni occupancy, as suggested by single crystal analysis was not refined.

Atom	Wyckoff site	Atomic coordinates			B_{iso} [Å^2]	Occupancy
		x	*y*	*z*		
Gd1	4*g*	0.19011(5)	0.63089(6)	0	1.11(2)	1
Gd2	4*g*	0.62781(8)	0.10789(5)	0	1.26(2)	1
Gd3	4*g*	0.43760(5)	0.36296(7)	0	1.58(2)	1
Co	4*g*	0.13543(19)	0.24192(10)	0	1.82(4)	1
Co/Ni	4*g*	0.12400(19)	0.03417(10)	0	1.57(4)	0.10/0.90*

Phase 1: **$Gd_3Co_{1.10}Ni_{0.90}$** (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58)
Frac. % = 96.0(7) vol.%
a = 9.54630(7) Å, *b* = 12.55423(9) Å, c = 3.85076(3)Å, V_{obs} = 461.500(6) Å^3
R_B = 2.04 %, R_F = 2.96 %
Phase 2: **$Gd_3Co_{0.69}Ni_{0.31}$** (Fe_3C-type, *oP*16, *Pnma*, No. 62) (composition from EDS; not refined)
Fract. % = 4.0(3) vol.%
a = 7.0180(1) Å, *b* = 9.5752(2) Å, *c* = 6.3262(1) Å, V_{obs} = 425.10(1) Å^3
R_B = 7.78 %, R_F = 6.47 %; B_{over} = 0.6(1) Å^2

Table S3. Standardized atomic coordinates for the $Gd_3Co_{1.20}Ni_{0.80}$ (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58) compound obtained from the Rietveld refinement on the powder pattern prepared on the nominal composition $Gd_3Co_{1.20}Ni_{0.80}$ (Gd60Co24Ni16); R_{wp} = 14.1 %, χ^2 = 1.20. (*) the Co/Ni occupancy, as suggested by single-crystal analysis, was not refined.

Atom	Wyckoff site	Atomic coordinates			B_{iso} [Å^2]	Occupancy
		x	*y*	*z*		
Gd1	4*g*	0.19024(6)	0.62920(7)	0	1.42(2)	1
Gd2	4*g*	0.62743(9)	0.10818(6)	0	1.06(2)	1
Gd3	4*g*	0.43625(6)	0.36303(9)	0	1.92(2)	1
Co	4*g*	0.13792(23)	0.23896(13)	0	2.09(4)	1
Co/Ni	4*g*	0.12060(22)	0.03480(12)	0	1.46(4)	0.20/0.80*

Phase 1: **$Gd_3Co_{1.20}Ni_{0.80}$** (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58)
Frac. % = 97.0(7) vol.%
a = 9.53985(5) Å, *b* = 12.52858(7) Å, c = 3.85995(2)Å, V_{obs} = 461.344(4) Å^3
R_B = 2.23 %, R_F = 3.46 %
Phase 2: **$Gd_3Co_{0.73}Ni_{0.27}$** (Fe_3C-type, *oP*16, *Pnma*, No. 62) (composition from EDS; not refined)
Fract. % = 3.0(1) vol.%
a = 7.0322(3) Å, *b* = 9.5644(4) Å, *c* = 6.3265(3) Å, V_{obs} = 425.51(3) Å^3
R_B = 11.5 %, R_F = 7.37 %

Table S4. Standardized atomic coordinates for the $Gd_3Co_{1.30}Ni_{0.70}$ (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58) compound obtained from the Rietveld refinement on the powder pattern prepared on the nominal composition $Gd_3Co_{1.30}Ni_{0.70}$ (Gd60Co26Ni14); R_{wp} = 12.8 %, χ^2 = 1.21. (*) the composition, as obtained from EDS, was kept constant and Co/Ni occupancy was not refined.

Atom	Wyckoff site	Atomic coordinates			B_{iso} [Å^2]	Occupancy
		x	*y*	*z*		
Gd1	4*g*	0.18951(5)	0.62852(7)	0	1.40(2)	1
Gd2	4*g*	0.62731(8)	0.11052(6)	0	1.50(2)	1
Gd3	4*g*	0.43272(5)	0.36319(8)	0	2.06(2)	1
Co	4*g*	0.13510(22)	0.23330(12)	0	2.31(4)	1
Co/Ni	4*g*	0.12611(20)	0.03182(11)	0	0.22(3)	0.30/0.70*

Phase 1: **$Gd_3Co_{1.30}Ni_{0.70}$** (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58)
Frac. % = 97.5(6) vol.%
a = 9.53395(4) Å, *b* = 12.50503(5) Å, c = 3.86907(2)Å, V_{obs} = 461.280(3) Å^3
R_B = 2.58 %, R_F = 4.30 %
Phase 2: **$Gd_3Co_{0.78}Ni_{0.22}$** (Fe_3C-type, *oP*16, *Pnma*, No. 62) (composition from EDS; not refined)
Fract. % = 2.5(1) vol.%
a = 7.0353(2) Å, *b* = 9.5678(2) Å, *c* = 6.3224(2) Å, V_{obs} = 425.57(2) Å^3
R_B = 14.2 %, R_F = 12.7 %

Table S5. Standardized atomic coordinates for the $Gd_3Co_{1.40}Ni_{0.60}$ (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58) compound obtained from the Rietveld refinement on the powder pattern prepared on the nominal composition $Gd_3Co_{1.40}Ni_{0.60}$ (Gd60Co28Ni12); R_{wp} = 12.0 %, χ^2 = 1.24. (*) the composition, as obtained from EDS, was kept constant and Co/Ni occupancy was not refined.

Atom	Wyckoff site	Atomic coordinates			B_{iso} [Å^2]	Occupancy
		x	*y*	*z*		
Gd1	4*g*	0.18914(6)	0.62921(7)	0	1.32(2)	1
Gd2	4*g*	0.62619(9)	0.10938(5)	0	1.07(2)	1
Gd3	4*g*	0.43753(6)	0.36315(8)	0	1.37(2)	1
Co	4*g*	0.13713(21)	0.23436(12)	0	1.12(4)	1
Co/Ni	4*g*	0.11333(18)	0.03193(12)	0	1.05(4)	0.40/0.60*

Phase 1: **$Gd_3Co_{1.40}Ni_{0.60}$** (Y_3Co_2-type, *oP*20, *Pnnm*, No. 58)
Frac. % = 98.2(6) vol.%
a = 9.52957(7) Å, *b* = 12.49058(8) Å, c = 3.87524(2)Å, V_{obs} = 461.269(5) Å^3
R_B = 1.61 %, R_F = 1.98 %
Phase 2: **$Gd_3Co_{0.77}Ni_{0.23}$** (Fe_3C-type, *oP*16, *Pnma*, No. 62) (composition from EDS; not refined)
Fract. % = 1.8(1) vol.%
a = 7.0324(2) Å, *b* = 9.5649(2) Å, *c* = 6.3188(1) Å, V_{obs} = 425.03(2) Å^3
R_B = 12.7 %, R_F = 7.66 %