Electronic Supplementary Information (ESI)

Gd_3Ni_2 and $Gd_3Co_xNi_{2-x}$: magnetism and unexpected Co/Ni crystallographic ordering

Alessia Provino,*[abc] Volodymyr Smetana,[ad] Durga Paudyal,[a] Karl A. Gschneidner Jr,[ad] Anja-Verena Mudring,[ad] Vitalij K. Pecharsky,[ad] Pietro Manfrinetti,[abc] Marina Putti[ce]

[a] *The Ames Laboratory, U.S. Department of Energy, Division of Material Science and Engineering, Iowa State University, Ames, IA 50011-3020, U.S.A.*

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

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

[d] *Department of Material Science and Engineering, Iowa State University, Ames, IA 50011-2300, U.S.A.*

[e] *Department of Physics, University of Genova, Via Dodecaneso 33, 16146 Genova, Italy*

Electronic Supplementary Information (ESI) available: Tables of anisotropic thermal displacement parameters, interatomic distances and coordination numbers for Gd_3Ni_2 and Gd_3CoNi. Table of isothermal magnetic entropy change and refrigerant capacity values for Gd_3Ni_2, Gd_3CoNi and $Gd_3Co_xNi_{2-x}$ compounds. Figures of a SEM microphotograph of a Gd_3Ni_2 DTA sample, a typical DSC curve for a Gd_3CoNi specimen and histograms of the distribution of neighboring atoms in Gd_3Ni_2 and Gd_3CoNi. Figures of magnetization and inverse magnetic susceptibility and isothermal magnetization for the substituted $Gd_3Co_xNi_{2-x}$. Figures of isothermal magnetization measured at selected temperatures, Arrott plots and isothermal magnetic entropy change *vs.* temperature for $Gd_3Co_{0.75}Ni_{1.25}$, and $Gd_3Co_{0.85}Ni_{1.15}$.

Table S1 Anisotropic thermal displacement parameters of Gd_3Ni_2 and Gd_3CoNi. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$; for all atoms $U_{12} = U_{23} = 0$.

Atom	U_{11} [Å^2]	U_{22} [Å^2]	U_{33} [Å^2]	U_{13} [Å^2]
Gd_3Ni_2				
Gd1	0.0143(7)	0.0149(5)	0.0152(6)	0.0054(4)
Gd2	0.0160(6)	0.0152(5)	0.0162(5)	0.0063(4)
Gd3	0.0153(7)	0.0149(5)	0.0165(5)	0.0062(4)
Ni1	0.0173(18)	0.0225(14)	0.0181(14)	0.0048(12)
Ni2	0.0175(18)	0.0166(14)	0.0274(16)	0.0071(12)
Gd_3CoNi				
Gd1	0.0075(6)	0.0140(6)	0.0100(6)	0.0026(4)
Gd2	0.0092(6)	0.0160(7)	0.0104(6)	0.0033(4)
Gd3	0.0088(6)	0.0140(6)	0.0120(6)	0.0040(4)
Ni	0.0090(14)	0.0143(18)	0.0231(19)	0.0028(12)
Co	0.0150(14)	0.0184(17)	0.0179(17)	0.0048(12)

Table S2 Interatomic distances for $d_{obs}/\Sigma r_M \leq 1.25$ and coordination numbers (CN) in Gd_3Ni_2 compound.

Central atom	Ligands	d [Å]	$d_{obs}/\Sigma r_M$
Gd1- (CN = 17)	2 Gd1	3.727(1)	1.034
(Gd10Ni7)	1 Gd1	3.560(3)	0.988
	2 Gd1	3.671(2)	1.019
	1 Gd2	4.098(2)	1.137
	1 Gd3	4.353(2)	1.208
	2 Gd2	3.565(1)	0.989
	1 Gd3	3.548(2)	0.984
	2 Ni1	2.947(3)	0.967
	2 Ni1	2.851(3)	0.935
	2 Ni2	2.946(3)	0.966
	1 Ni2	3.105(3)	1.019
Gd2- (CN = 14)	1 Gd1	4.098(2)	1.137
(Gd11Ni3)	2 Gd1	3.565(1)	0.989
	2 Gd2	3.727(1)	1.034
	1 Gd2	3.606(3)	1.001
	1 Gd3	3.621(2)	1.005
	2 Gd3	3.659(2)	1.015
	2 Gd3	3.663(1)	1.016
	1 Ni1	2.853(3)	0.936
	2 Ni2	2.809(3)	0.922

Central atom	Ligands	d [Å]	$d_{obs}/\Sigma r_M$
Gd3- (CN = 16)	1 Gd1	3.548(2)	0.984
(Gd11Ni5)	1 Gd2	3.621(2)	1.005
	2 Gd2	3.659(2)	1.015
	2 Gd2	3.663(1)	1.016
	2 Gd3	3.727(1)	1.034
	1 Gd1	4.353(2)	1.208
	2 Gd3	3.716(2)	1.031
	2 Ni1	2.931(3)	0.962
	2 Ni2	2.860(3)	0.938
	1 Ni2	3.751(3)	1.231
Ni1- (CN = 9)	2 Gd1	2.947(3)	0.967
(Gd7Ni2)	2 Gd1	2.851(3)	0.935
	1 Gd2	2.853(3)	0.936
	2 Gd3	2.931(3)	0.962
	1 Ni1	2.655(6)	1.065
	1 Ni2	2.663(4)	1.069
Ni2- (CN = 9)	1 Gd1	3.105(3)	1.019
(Gd8Ni1)	2 Gd1	2.946(3)	0.966
	2 Gd2	2.809(3)	0.922
	1 Gd3	3.751(3)	1.231
	2 Gd3	2.860(3)	0.938
	1 Ni1	2.663(4)	1.069

Table S3 Interatomic distances for $d_{obs}/\Sigma r_M \leq 1.25$ and coordination numbers (CN) in Gd_3CoNi compound.

Central atom	Ligands	d [Å]	$d_{obs}/\Sigma r_M$
Gd1- (CN = 17)	2 Gd1	3.812(1)	1.058
(Gd10Co3Ni4)	1 Gd1	3.574(2)	0.992
	2 Gd1	3.664(2)	1.017
	1 Gd2	3.854(2)	1.069
	1 Gd3	4.174(2)	1.158
	2 Gd2	3.524(2)	0.978
	1 Gd3	3.552(2)	0.986
	2 Ni	2.926(3)	0.960
	2 Ni	2.896(3)	0.950
	2 Co	2.944(3)	0.964
	1 Co	3.259(4)	1.067
Gd2- (CN = 14)	1 Gd1	3.854(2)	1.069
(Gd11Co2Ni)	2 Gd1	3.524(2)	0.978
	2 Gd2	3.812(1)	1.058
	1 Gd2	3.608(2)	1.001
	1 Gd3	3.649(2)	1.012
	2 Gd3	3.654(1)	1.014
	2 Gd3	3.617(2)	1.004
	1 Ni	2.920(4)	0.958
	2 Co	2.771(2)	0.907

Central atom	Ligands	d [Å]	$d_{obs}/\Sigma r_M$
Gd3- (CN = 16)	1 Gd1	3.552(2)	0.986
(Gd11Co3Ni2)	1 Gd2	3.649(2)	1.012
	2 Gd2	3.654(1)	1.014
	2 Gd2	3.617(2)	1.004
	2 Gd3	3.812(1)	1.058
	1 Gd1	4.174(2)	1.158
	2 Gd3	3.699(2)	1.026
	2 Ni	2.901(3)	0.952
	2 Co	2.874(3)	0.941
	1 Co	3.534(4)	1.157
Ni- (CN = 9)	2 Gd1	2.926(3)	0.960
(Gd7CoNi)	2 Gd1	2.896(3)	0.950
	1 Gd2	2.920(4)	0.958
	2 Gd3	2.901(3)	0.952
	1 Ni	2.569(7)	1.031
	1 Co	2.565(5)	1.027
Co- (CN = 9)	1 Gd1	3.259(4)	1.067
(Gd8Ni1)	2 Gd1	2.944(3)	0.964
	2 Gd2	2.771(2)	0.907
	1 Gd3	3.534(4)	1.157
	2 Gd3	2.874(3)	0.941
	1 Ni	2.565(5)	1.027

Table S4 Isothermal magnetic entropy change ($-\Delta S_M$) and refrigerant capacity (RC) of Gd_3Ni_2, $Gd_3Co_xNi_{2-x}$ (x = 0.75, 0.85), and Gd_3CoNi.

Compound	Co [at.%]	$-\Delta S_M$ [J/Kg K]					RC_{FWHM} [J/Kg]			
		10 kOe	20 kOe	30 kOe	40 kOe	50 kOe	10 kOe	20 kOe	30 kOe	50 kOe
Gd_3Ni_2	0	2.1	3.9	5.4	6.8	8.0	50	153	276	542
$Gd_3Co_{0.75}Ni_{1.25}$	15	2.3	4.2	5.8	7.2	8.5	56	160	281	537
$Gd_3Co_{0.85}Ni_{1.15}$	17	2.3	4.2	5.7	7.1	8.3	63	164	(273)	(506)
Gd_3CoNi	20	2.3	4.2	5.7	7.1	8.3	73	180	298	546

Data in brackets are not comparable with the other values (calculated using ΔT values obtained by extrapolating the two tails of the −ΔS *vs.* T curve).