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C Magen[1], C Ritter[2], L Morellon[1,3], P A Algarabel[1] and M R Ibarra[1]

[1] Departamento de Física de la Materia Condensada and Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza and Consejo Superior de Investigaciones Científicas, Pedro Cerbuna 12, 50009 Zaragoza, Spain
[2] Institut Laue-Langevin, Boîte Postale 156, 38042 Grenoble Cédex 9, France

E-mail: morellon@unizar.es

Abstract
The compounds $Nd_5Si_{1.45}Ge_{2.55}$ and $Pr_5Si_{1.5}Ge_{2.5}$ have been investigated by means of magnetization measurements and neutron powder diffraction techniques. These alloys present a room-temperature monoclinic $Gd_5Si_2Ge_2$-type crystallographic structure and, on cooling, both systems order ferromagnetically, at $T_C = 56$ and 32 K, respectively, from a high-temperature paramagnetic to a low-temperature complex canted ferromagnetic state. The monoclinic crystallographic structure remains unchanged upon cooling down to 4 K, demonstrating the existence of a monoclinic ferromagnetic phase, and the possibility of a full decoupling of magnetic and crystallographic degrees of freedom in the 5:4 lanthanide intermetallic compounds.

1. Introduction

The interplay between magnetism and structure has been found to play a paramount role in the physical properties of the $R_5(Si_xGe_{1-x})_4$ pseudobinary alloys, which have become the subject of an extraordinary research activity in the field of the lanthanide intermetallic compounds. As paradigmatic members of the family, the compounds $Gd_5(Si_xGe_{1-x})_4$ combine an unusual number of properties, which include the giant magnetocaloric effect [1], strong magnetoelastic effects [2, 3], giant magnetoresistance [4, 5] and exotic transport phenomena [6–8]. This unexpected phenomenology is based on the possibility of reversibly inducing a first-order coupled magnetic and structural transformation between two layered

[3] Author to whom any correspondence should be addressed. http://wzar.unizar.es/acad/fac/cie/cond-mat/M/morellon.html

crystallographic structures by changing the temperature, applied magnetic field and/or hydrostatic pressure [2, 3, 9–11]. The crystallographic structure is determined by the number of partially covalent Si/Ge–Si/Ge bonds connecting the different layers, and the structural changes are governed by the forming and/or cleavage of all or half of them [12].

Determination of the magnetic structure of $Gd_5(Si_xGe_{1-x})_4$ is one of the most relevant experiments that remains in order to ultimately comprehend the microscopic physical mechanisms controlling this intriguing behaviour. Nevertheless, the huge neutron absorption cross-section of the majority Gd isotope has made this a challenge. Therefore, other 5:4 lanthanide compounds have been the subject of intensive study with the aim of clarifying the magnetoelastic coupling present in these compounds. After the $R_5(Si_xGe_{1-x})_4$ alloys were discovered in 1966 by Smith *et al* [13], the low-temperature magnetic structure was reported first by Schobinger-Papamantellos in R_5Ge_4 (R = Tb, Ho, Nd) [14–16]; all of them crystallize in the Sm_5Ge_4-type *Pnma* orthorhombic phase with different complex canted antiferromagnetic structures. Recently, the temperature–composition crystallographic and magnetic phase diagram of the $Tb_5(Si_xGe_{1-x})_4$ system was determined [17]. Alloys with intermediate compositions $0.4 \leqslant x \leqslant 0.6$ present a $Gd_5Si_2Ge_2$-type monoclinic structure (M, space group $P112_1/a$) at room temperature, and undergo on cooling down a first-order crystallographic–magnetic transformation to a Gd_5Si_4-type orthorhombic (O(I), space group *Pnma*) canted ferromagnetic structure (FM) similarly to the $Gd_5(Si_xGe_{1-x})_4$ compounds in the $0 < x \leqslant 0.5$ composition range. One half of the Si/Ge–Si/Ge pairs, which do not exist in the high-temperature M phase, are reformed through the transformation to the low-temperature O(I) structure. More detailed experiments allowed us to discover the existence of a novel monoclinic and ferromagnetic phase (M–FM) in zero field that sets in on cooling the sample before the M $\rightarrow$ O(I) structural transformation takes place [18], which was previously unknown in the $R_5(Si_xGe_{1-x})_4$ family of compounds. This demonstrates that, in $Tb_5(Si_xGe_{1-x})_4$, the structural and magnetic transitions are not fully coupled, the interaction between crystallographic and magnetic degrees of freedom being more complex than previously thought.

Although further efforts have been devoted to the study of microscopic magnetic properties of other 5:4 lanthanide compounds such as Nd_5Si_4, Nd_5Ge_4 and Pr_5Ge_4 [19, 20], the possible existence of this M–FM phase in other alloys of this family has not been explored yet. In this work, we have performed a powder neutron diffraction study of the low-temperature magnetic and crystallographic structure in the room-temperature monoclinic alloys $Nd_5Si_{1.45}Ge_{2.55}$ and $Pr_5Si_{1.5}Ge_{2.5}$. We show that the M crystallographic structure remains on cooling down to 4 K in both compounds, clearly demonstrating the possibility of a full decoupling of the magnetic and crystallographic transformations in monoclinic 5:4 alloys. The magnetic structure of both compounds at low temperatures is also determined.

2. Experimental details

$Nd_5Si_{1.45}Ge_{2.55}$ and $Pr_5Si_{1.5}Ge_{2.5}$ alloys were prepared in an arc melting furnace under a high-purity Ar atmosphere from a mixture of the stoichiometric quantities of the constituent elements, 99.9 wt% pure Nd and Pr and 99.9999 wt% pure Si and Ge, all of them purchased from Alfa Aesar. The resulting buttons were remelted several times to ensure homogeneity. Weight losses during melting were negligible and, therefore, the initial nominal compositions were assumed to be unchanged. The quality of each sample was checked by means of powder x-ray diffraction, both samples being essentially single-phase with a room-temperature M crystallographic structure, in agreement with the crystallographic phase diagrams reported by Yang *et al* [21, 22]. Magnetic characterization was performed in
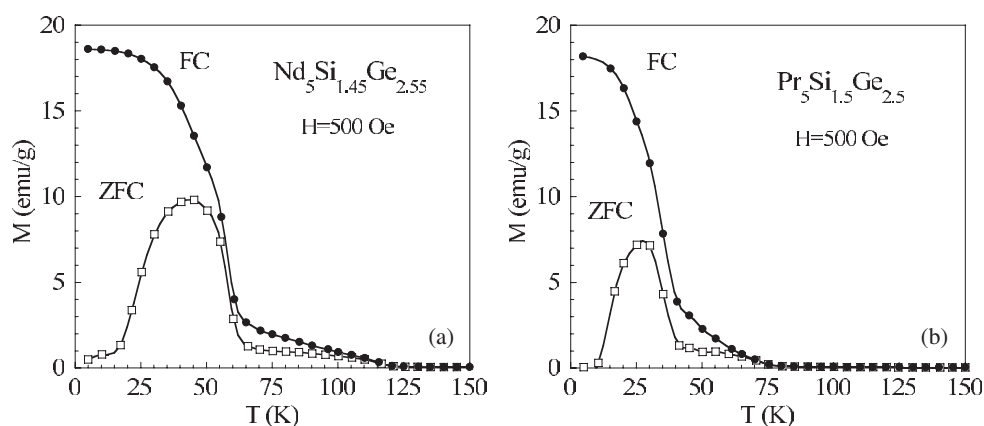
Figure 1. The zero-field cooling and field cooling temperature dependence of the magnetization in (a) $Nd_5Si_{1.45}Ge_{2.55}$ and (b) $Pr_5Si_{1.5}Ge_{2.5}$ in a magnetic field of 500 Oe.

a commercial (Quantum Design) superconducting quantum interference device (SQUID). Neutron diffraction experiments were carried out on the high-resolution powder diffractometer D2B ($\lambda = 1.596$ Å) and the high-intensity powder diffractometer D1B ($\lambda = 2.52$ Å) at the Institute Laue-Langevin (ILL), Grenoble. Neutron diffraction patterns were collected at selected temperatures and angles between $2\theta = 5°$ and $165°$ in D2B. Thermal scans were measured in D1B in the temperature range 4–150 K. Crystallographic and magnetic structures were determined by analysing the neutron diffraction patterns collected in D2B with the Rietveld-method refinement package software FULLPROF [23]. The SARAH representation analysis program of Wills [24] was used in order to obtain the possible magnetic space groups permitted by symmetry restrictions.

3. Results and discussion

Results from zero-field cooling and field cooling magnetization experiments performed on $Nd_5Si_{1.45}Ge_{2.55}$ at a magnetic field of 500 Oe are plotted in figure 1(a). A clear ferromagnetic transition is found at $T_C = 56$ K. A small anomaly is also detected at $T \sim 115$ K, which should correspond to a minor amount of an impurity phase with a higher T_C undetectable by means of x-ray analysis. The presence of this secondary phase was already confirmed in a monoclinic $Nd_5Si_2Ge_2$ alloy [26] and suggested to be a ferromagnetic Gd_5Si_4-type O(I) secondary phase [25, 26]. Magnetization measurements showed no observable thermal hysteresis near T_C within the experimental resolution, indicating the second-order character of the transition. Magnetic anisotropy due to the rare-earth ions is reflected in the significantly low value of the magnetization at low temperatures in the zero-field cooling measurement. The inverse magnetic susceptibility shows a typical Curie–Weiss behaviour in the paramagnetic regime. The paramagnetic Curie temperature derived from fitting the high-temperature (150–250 K) data is $\Theta_P = -2.9(6)$ K and the effective paramagnetic moment per Nd atom is $\mu_{eff} = 2.53(2)$ μ_B, which is rather low in comparison with the theoretical value of 3.63 μ_B expected for the paramagnetic Nd^{3+} free ion. Figure 1(b) shows a qualitatively similar behaviour of the compound $Pr_5Si_{1.5}Ge_{2.5}$. Magnetic ordering sets in at a lower temperature of $T_C = 32$ K, in agreement with the well-known dependence of the Curie temperature with the rare-earth total angular moment J given by the de Gennes factor $(g_J - 1)^2 J(J + 1)$. As for the $Nd_5Si_{1.45}Ge_{2.55}$ compound, no hysteresis is found and a small anomaly is seen at $T \sim 75$ K.

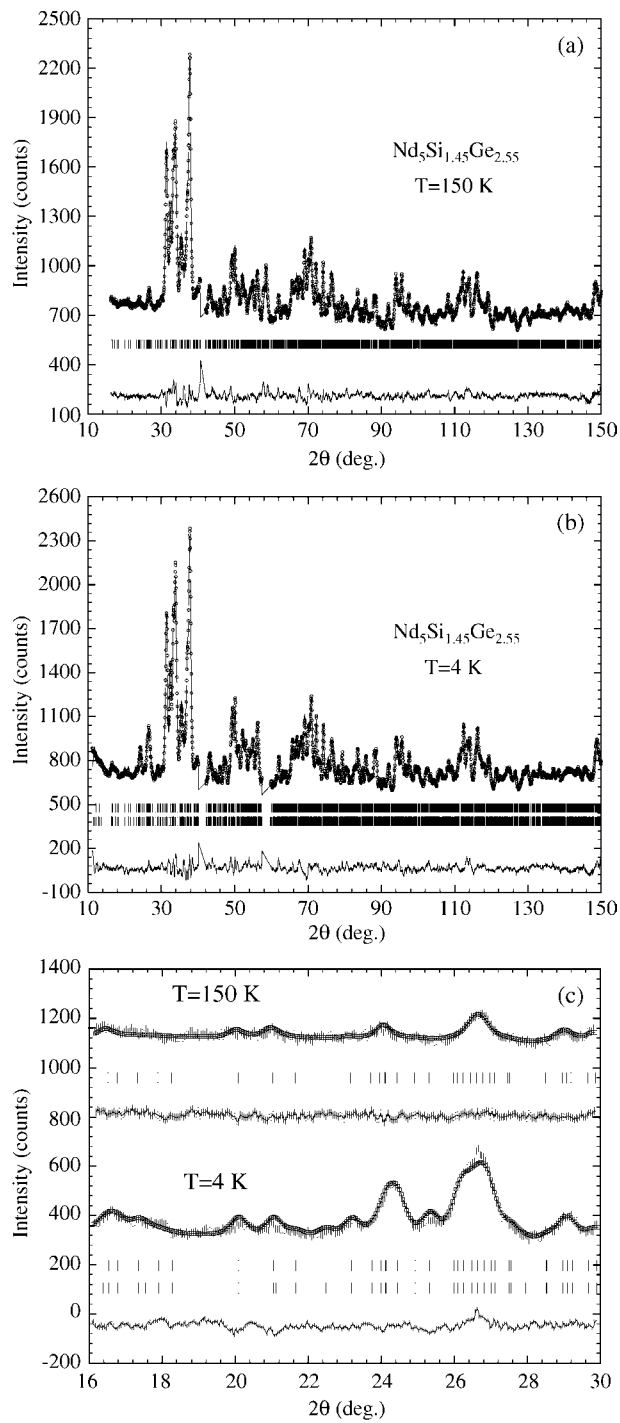**Figure 2.** Neutron powder diffraction patterns of $Nd_5Si_{1.45}Ge_{2.55}$ at 150 K (a) and 4 K (b). The experiment (dots), the refinement (line) and the difference (line at the bottom) are represented. (c) Comparison of the spectra at 150 and 4 K in the lower-angle region with the strongest magnetic reflections. Crystallographic and magnetic reflections are marked with vertical bars.

Table 1. Summary of the refined parameters of $Nd_5Si_{1.45}Ge_{2.55}$: crystallographic space group, lattice parameters, cell volume, atomic coordinates and reliability factors.

		150 K			4 K
Space group		$P112_1/a$			$P112_1/a$
a (Å)		7.7762(7)			7.7674(7)
b (Å)		15.102(1)			15.0967(9)
c (Å)		7.9421(4)			7.9324(3)
γ (deg)		93.853(5)			93.859(5)
V (Å^3)		932.7(1)			930.2(1)
Nd1 (4e)	x	0.327(1)	Nd1 (4e)	x	0.333(1)
	y	0.2439(4)		y	0.2430(4)
	z	0.0047(7)		z	0.0057(7)
Nd2A (4e)	x	−0.0066(8)	Nd2A (4e)	x	−0.0043(8)
	y	0.1002(4)		y	0.1002(3)
	z	0.1852(7)		z	0.1820(7)
Nd2B (4e)	x	0.0294(8)	Nd2B (4e)	x	0.0291(8)
	y	0.3971(4)		y	0.3974(4)
	z	0.1787(8)		z	0.1791(8)
Nd3A (4e)	x	0.3618(9)	Nd3A (4e)	x	0.358(1)
	y	0.8819(4)		y	0.8853(4)
	z	0.1642(7)		z	0.1665(7)
Nd3B (4e)	x	0.329(1)	Nd3B (4e)	x	0.326(1)
	y	0.6218(4)		y	0.6223(4)
	z	0.1786(8)		z	0.1818(8)
M1 (4e)	x	0.952(1)	M1 (4e)	x	0.950(1)
	y	0.2492(5)		y	0.2526(5)
	z	0.8991(9)		z	0.9013(8)
M2 (4e)	x	0.212(1)	M2 (4e)	x	0.215(1)
	y	0.2522(5)		y	0.2513(4)
	z	0.3690(9)		z	0.3681(8)
M3A (4e)	x	0.205(1)	M3A (4e)	x	0.208(1)
	y	0.9579(5)		y	0.9573(5)
	z	0.4679(9)		z	0.4735(9)
M3B (4e)	x	0.140(1)	M3B (4e)	x	0.143(1)
	y	0.5444(5)		y	0.5444(4)
	z	0.470(1)		z	0.474(1)
R_p/R_w (%)		1.9/2.5			2.3/2.9
R_{Bragg} (%)		5.3			4.9
R_{mag} (%)					7.3
χ^2		3.0			6.8

A similar effect was already observed for $Pr_5Si_2Ge_2$ by Yang *et al* and attributed to a minor amount of tetragonal $P4_12_12$ structure, which, in fact, could be stabilized with an adequate heat treatment [27]. The paramagnetic Curie temperature and effective magnetic moment are $\Theta_P = -21.2(3)$ K and $\mu_{eff} = 2.38(2)$ μ_B (fitted between 150 and 250 K), also remarkably lower than the theoretical value of 3.58 μ_B for the Pr^{3+} ion. The coincidence of a negative paramagnetic Curie temperature and a small effective paramagnetic moment for both alloys might also be related to the existence of antiferromagnetic correlations in the paramagnetic state, as already proposed for the Ge-rich $Gd_5(Si_xGe_{1-x})_4$ compounds [28].
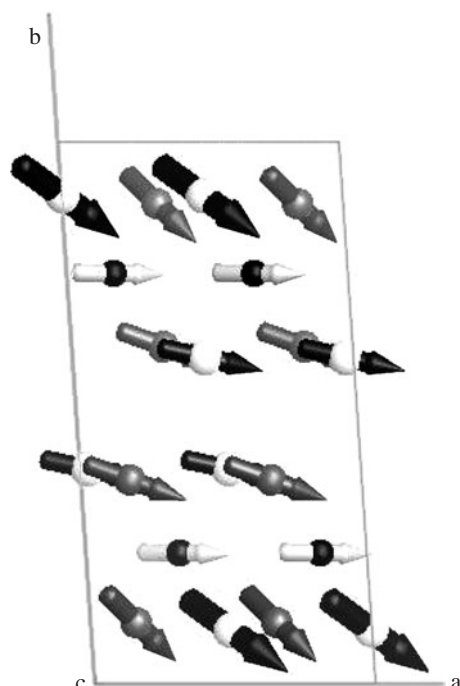
Figure 3. A schematic representation of the spin arrangement projected along the c-axis in Nd$_5$Si$_{1.45}$Ge$_{2.55}$ at 5 K.

Neutron powder diffraction spectra collected from D2B at 150 and 4 K in Nd$_5$Si$_{1.45}$Ge$_{2.55}$ are represented in figures 2(a), (b). The crystallographic parameters refined for both sets of data such as lattice parameters, atomic coordinates, reliability factors and magnetic moments are listed in tables 1 and 2. It is confirmed that at 150 K our system presents a monoclinic $P112_1/a$ Gd$_5$Si$_2$Ge$_2$-type M crystallographic phase, this structure being retained at 4 K. The temperature dependent data from D1B show the appearance of small additional peaks and the growth of some nuclear reflections at $T_C \cong 54$ K which are associated with the onset of a new monoclinic magnetic phase. A comparison of the D2B spectra at 150 K (PM) and 4 K (FM) in the lower-angle region with the strongest magnetic reflections has also been plotted in figure 2(c). Representation analysis [24] allows, for the propagation vector $\tau = (0\ 0\ 0)$, four different magnetic space groups in the $P112_1/a$ crystallographic space group which are the Shubnikov groups $P112_1/a$, $P112_1'/a$, $P112_1/a'$ and $P112_1'/a'$. The combination of magnetic modes that describes the different magnetic space groups for the 4e site is detailed in table 3. By far the best refinement of the magnetic contribution to the neutron diffractogram is obtained using the magnetic modes $F_xF_yG_z$ of the magnetic space group $P112_1'/a$. The resulting magnetic moment arrangement of Nd$_5$Si$_{1.45}$Ge$_{2.55}$ at 4 K is depicted in figure 3. Although the magnetization is mainly oriented along the a-axis, a canting in the b and c directions is obtained from the refinements, with large canting angles (θ) with respect to the a direction of $\sim$50° in Nd2A and $\sim$55° in Nd3A positions, and smaller θs in the Nd1, Nd2B and Nd3B sites ($\sim$23°, 15° and 22°, respectively). This fact and the weak antiferromagnetic coupling along the c-axis introduced by the G$_z$ mode imply an extremely complex magnetic structure. This spin arrangement compares reasonably with that found by Cadogan *et al* in Nd$_5$Ge$_4$ [19], where a
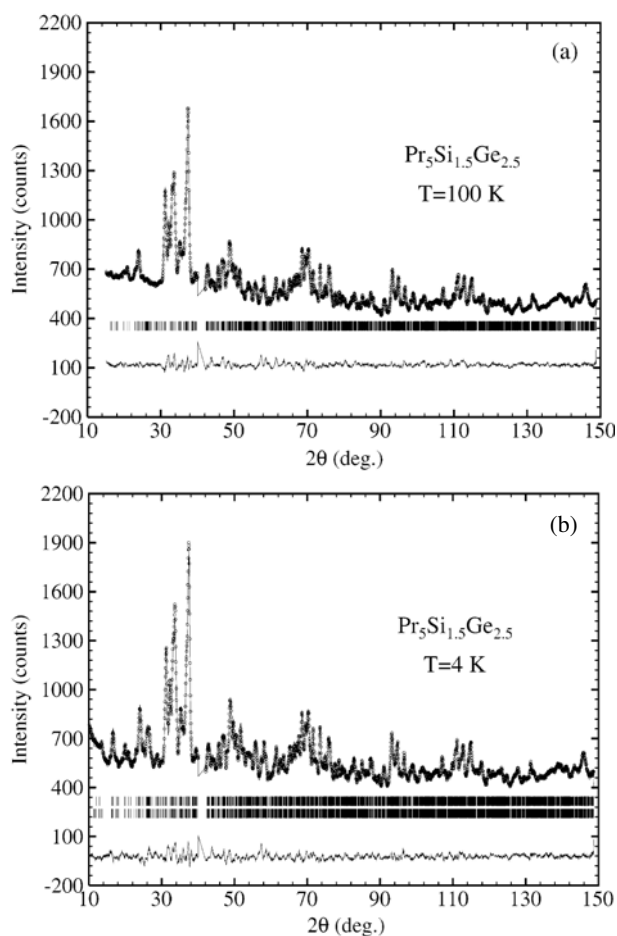
Figure 4. Neutron powder diffraction patterns of $Pr_5Si_{1.5}Ge_{2.5}$ at 100 K (a) and 4 K (b). The experiment (dots), the refinement (line) and the difference (line at the bottom) are represented. Crystallographic and magnetic reflections are marked with vertical bars.

ferromagnetic ordering along the a-axis was determined, and antiferromagnetic coupling was observed in the b and c directions. It is worth noting that the Nd atoms located near the partially covalent Si/Ge–Si/Ge bonds present a stronger ferromagnetic coupling than those sites found near the broken bonds, in accordance with the result obtained for the M–FM intermediate phase found in $Tb_5Si_2Ge_2$ [18], where it was suggested that the presence of bonds enhances the FM superexchange interaction between the nearby Tb ions via Si/Ge–Si/Ge covalent-like bonds.

Neutron diffraction patterns collected at 100 and 4 K from D2B from $Pr_5Si_{1.5}Ge_{2.5}$ are displayed in figure 4, and the crystallographic and magnetic refinement parameters obtained from them are listed in tables 4 and 5. As in the previous case, the crystallographic structure remains the same in the whole temperature range down to 4 K. Figure 5 shows a thermodiffractogram from 5 to 85 K collected on cooling in D1B. The high-temperature monoclinic reflections do not disappear at the Curie temperature $T_C \cong 35$ K, but increase partially due to the new magnetic contribution to the nuclear Bragg peaks. The growth of the magnetic reflections is smooth and progressive as expected from a second-order ferromagnetic
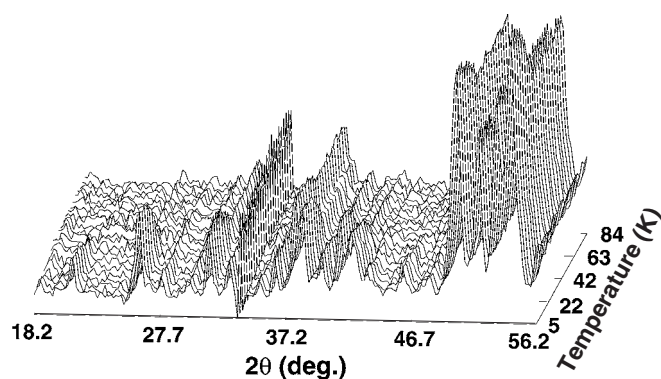
Figure 5. The temperature dependence of the neutron powder diffraction pattern of $Pr_5Si_{1.5}Ge_{2.5}$ taken from D1B.

Table 2. Magnetic moment components in $Nd_5Si_{1.45}Ge_{2.55}$ at 4 K.

4e site	μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)	μ (μ_B)
Nd1	2.3(1)	0.1(2)	0.9(1)	2.5(1)
Nd2A	2.4(2)	1.9(2)	1.7(1)	3.7(2)
Nd2B	2.7(2)	0.6(2)	0.2(1)	2.8(1)
Nd3A	1.6(2)	1.8(2)	1.6(1)	3.0(1)
Nd3B	2.6(2)	1.0(2)	0.2(1)	2.8(1)

Table 3. The sign convention for the four permitted magnetic modes for the non-equivalent symmetry positions 4e in the $P112_1/a$ space group.

	Position			Magnetic space group			
				$P112_1/a$	$P112_1/a'$	$P112'_1/a$	$P112'_1/a'$
i		4e		$C_x C_y A_z$	$G_x G_y F_z$	$F_x F_y G_z$	$A_x A_y C_z$
1	x	y	z	$+ + +$	$+ + +$	$+ + +$	$+ + +$
2	$1/2 - x$	$-y$	$1/2 + z$	$+ + -$	$- - +$	$+ + -$	$- - +$
3	$-x$	$-y$	$-z$	$- - -$	$+ + +$	$+ + +$	$- - -$
4	$1/2 + x$	y	$1/2 - z$	$- - +$	$- - +$	$+ + -$	$+ + -$

transition. One can clearly see the appearance of additional reflections at lower angles reflecting the existence of an antiferromagnetic coupling of the spins. Again the $P112'_1/a$ magnetic space group gives the most accurate refinement of the magnetic contribution at low temperature with the $F_x F_y G_z$ magnetic modes for the 4e sites, and a schematic representation of the orientation of the magnetic moments is depicted in figure 6. The magnetic structure is qualitatively similar to the one obtained for $Nd_5Si_{1.45}Ge_{2.55}$. However, rather different canting angles with respect to the a-axis are calculated, $\theta_{Pr1} \sim 18°$, $\theta_{Pr2A} \sim 23°$, $\theta_{Pr2B} \sim 41°$, $\theta_{Pr3A} \sim 15°$ and $\theta_{Pr3B} \sim 7°$. A general trend towards smaller canting angles than in the previous case is observed. No correlation can be deduced for $Pr_5Si_{1.5}Ge_{2.5}$ between the location of the Pr ions with respect to the covalent Si/Ge–Si/Ge bonds and the magnetic moment values. These results clearly contrast with the already reported magnetic structure of orthorhombic *Pnma* Pr_5Ge_4 [20], where two different magnetic transitions have been detected. Furthermore, the first of these multiple magnetic transformations is associated with a differentiated ordering of the Pr1 sites

Table 4. Summary of the refined parameters of $Pr_5Si_{1.5}Ge_{2.5}$: crystallographic space group, lattice parameters, cell volume, atomic coordinates and reliability factors.

		100 K			4 K
Space group		$P112_1/a$			$P112_1/a$
a (Å)		7.839(1)			7.832(2)
b (Å)		15.197(3)			15.202(3)
c (Å)		7.993(1)			7.935(2)
γ (deg)		93.998(5)			93.859(5)
V (Å^3)		952.2(3)			944.8(4)
Pr1 (4e)	x	0.330(1)	Pr1 (4e)	x	0.326(1)
	y	0.2421(5)		y	0.2486(5)
	z	0.0053(7)		z	0.0081(7)
Pr2A (4e)	x	−0.0055(9)	Pr2A (4e)	x	−0.0095(9)
	y	0.1002(4)		y	0.0978(4)
	z	0.1840(8)		z	0.1850(7)
Pr2B (4e)	x	0.036(1)	Pr2B (4e)	x	0.033(1)
	y	0.3975(5)		y	0.3990(5)
	z	0.1832(8)		z	0.1826(9)
Pr3A (4e)	x	0.358(1)	Pr3A (4e)	x	0.360(1)
	y	0.8843(5)		y	0.8831(5)
	z	0.1615(8)		z	0.1636(9)
Pr3B (4e)	x	0.325(1)	Pr3B (4e)	x	0.325(1)
	y	0.6211(5)		y	0.6224(4)
	z	0.1790(9)		z	0.1789(8)
M1 (4e)	x	0.9515(6)	M1 (4e)	x	0.9537(8)
	y	0.2492(5)		y	0.2517(4)
	z	0.8991(9)		z	0.8982(7)
M2 (4e)	x	0.2140(7)	M2 (4e)	x	0.2129(9)
	y	0.2525(3)		y	0.2521(4)
	z	0.3741(5)		z	0.3735(7)
M3A (4e)	x	0.2138(6)	M3A (4e)	x	0.2098(8)
	y	0.9575(3)		y	0.9572(4)
	z	0.4676(5)		z	0.4696(7)
M3B (4e)	x	0.1450(6)	M3B (4e)	x	0.1472(7)
	y	0.5432(3)		y	0.5425(4)
	z	0.4690(6)		z	0.4710(7)
R_p/R_w (%)		1.9/2.5			2.1/2.7
R_{Bragg} (%)		5.3			3.69
R_{mag} (%)					5.0
χ^2		3.0			6.5

located in the centre of the cubes, which order ferromagnetically at $T_{C1} \sim 42$ K, whereas Pr2 and Pr3 positions located at the surface of the slabs are essentially zero on cooling down until their subsequent magnetic ordering occurs at $T_{C2} \sim 25$ K.

4. Conclusions

The compounds $Nd_5Si_{1.45}Ge_{2.55}$ and $Pr_5Si_{1.5}Ge_{2.5}$ have been investigated by means of magnetization measurements and neutron powder diffraction experiments. These alloys
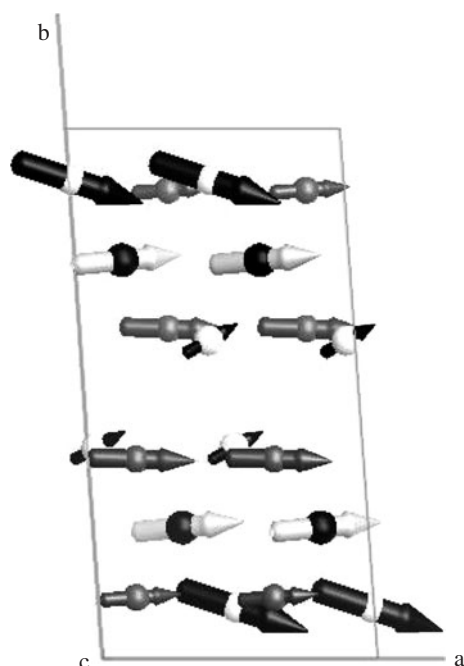
Figure 6. A schematic representation of the spin arrangement projected along the *c*-axis in $Pr_5Si_{1.5}Ge_{2.5}$ at 5 K.

Table 5. Magnetic moment components in $Pr_5Si_{1.5}Ge_{2.5}$ at 4 K.

4e site	μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)	μ (μ_B)
Pr1	2.62(5)	0.2(1)	0.9(1)	2.76(6)
Pr2A	3.02(9)	0.9(1)	0.77(8)	3.29(8)
Pr2B	1.36(7)	0.9(1)	0.88(8)	1.8(1)
Pr3A	1.92(7)	0.4(1)	0.5(1)	1.99(7)
Pr3B	2.54(7)	0.2(1)	0.0(9)	2.56(7)

present a room-temperature monoclinic ($P112_1/a$) $Gd_5Si_2Ge_2$-type crystallographic structure. On cooling, both systems order ferromagnetically, at Curie temperatures of $T_C = 56$ and 32 K, respectively, from a high-temperature paramagnetic state to a low-temperature complex canted ferromagnetic structure. The monoclinic crystallographic structure remains unchanged upon cooling down to 4 K demonstrating the possibility of a full decoupling of magnetic and crystallographic degrees of freedom in the 5:4 lanthanide intermetallic compounds with the M structure. $Nd_5Si_{1.45}Ge_{2.55}$ at 4 K is a canted ferromagnet presenting a monoclinic $P112_1'/a$ magnetic space group with a $F_xF_yG_z$ magnetic mode for the 4e sites. The magnetization is mainly oriented along the *a*-axis, although large canting angles are also observed. Nd sites located near the bonds experience a stronger FM coupling than those sites situated distant from them, suggesting that the existence of the bonds tends to favour a ferromagnetic ordering. $Pr_5Si_{1.5}Ge_{2.5}$ orders ferromagnetically with the same magnetic space group, and the magnetization is also oriented along the *a* direction. Although the canting is smaller than in the Nd compound, no similar pattern associated with the location of the bonds can be inferred. Further experiments on other compositions are under way to confirm this point.

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