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The magnetic structures of Nd_5Si_4 and Nd_5Ge_4

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Abstract

We have determined the magnetic structures of Nd_5Si_4 and Nd_5Ge_4 by means of high-resolution neutron powder diffraction. The crystal space groups of these compounds are tetragonal $P4_12_12$ and orthorhombic $Pnma$, respectively. Their magnetic ordering temperatures are 66(2) and 51(2) K, respectively, and both magnetic structures can be described as canted structures, with net antiferromagnetism in one plane with ferromagnetism perpendicular to that plane. The magnetic space groups are $P4_12_1'2'$ and $Pnm'a'$ and their ferromagnetic ordering directions are [001] and [100], respectively.

1. Introduction

The R_5Si_4 and R_5Ge_4 compounds (R = rare earth) were first studied by Smith *et al* [1, 2] 35 years ago and much work on the crystallography of these compounds has been done with sometimes conflicting structures being reported for some compounds, suggesting that these compounds may, in fact, be polymorphic. However, much less is known about their physical properties, including their magnetic behaviour. Concentrating on the 5:4 compounds, Holzberg *et al* [3] reported the magnetic properties of the R_5Ge_4 series of compounds and Schobinger-Papamantellos reported the magnetic properties of Tb_5Ge_4 [4], Ho_5Ge_4 [5] and Nd_5Ge_4 [6].

The R_5Si_4 and R_5Ge_4 compounds are the subjects of renewed interest in the magnetism community due to the observation of a giant magnetocaloric effect in the $Gd_5(Si, Ge)_4$ compounds by Gschneidner and Pecharsky [7, 8]. Recently, Ritter *et al* [9] reported the magnetic structures of the $Tb_5(Si,Ge)_4$ compounds and showed that there is a strong coupling between the crystallography and magnetism in these compounds. Such a coupling is believed to play an important role in determining the extent of the magnetocaloric effect in such compounds [10]. In particular, Ritter *et al* [9] observed magnetic reorientations below the

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magnetic ordering temperatures right across the $Tb_5(Si_xGe_{1-x})_4$ system, including the end-members Tb_5Si_4 and Tb_5Ge_4. In the intermediate composition range from $x \sim 0.35$ to 0.65 they also observed a change in crystal structure from monoclinic in the paramagnetic regime to orthorhombic below. Such a change in crystal structure accompanying the magnetic ordering was also observed by Gschneidner and Pecharsky [7, 8] in the $Gd_5(Si_xGe_{1-x})_4$ system in the range $x \sim 0.24$–0.50. A magnetic reorientation was observed in the Gd_5Ge_4 end-member but not in Gd_5Si_4.

Recently, Boulet *et al* [11] reported a study of the magnetic and electrical properties of various Nd–Si binary phases, including Nd_5Si_4. They measured a magnetic ordering temperature of 67 K in Nd_5Si_4 and concluded that the magnetic ordering direction of Nd_5Si_4 is the crystallographic *c*-axis but they did not derive the details of the magnetic structure. Gschneidner *et al* [12] reported that the ordering temperatures of Nd_5Si_4 and Nd_5Ge_4 are 71 and 55 K, respectively.

In this paper we present the first determination of the magnetic structure of Nd_5Si_4 by means of high-resolution neutron diffraction. We have also determined the magnetic structure of Nd_5Ge_4, which we will present here, but we will concentrate on Nd_5Si_4 since the magnetic structure of Nd_5Ge_4 has already been reported by Schobinger-Papamantellos and Niggli [6].

2. Experimental methods

The Nd_5Si_4 and Nd_5Ge_4 samples were prepared in a tri-arc furnace with a base pressure less than 6×10^{-7} mbar. Stoichiometric amounts of the pure elements were melted several times under Ti-gettered argon to ensure homogeneity. Powder x-ray diffraction patterns were obtained using Cu Kα radiation on an automated Nicolet–Stoe diffractometer. Ac susceptibility was measured on a Quantum Design PPMS at a frequency of 377 Hz and an ac magnetic field amplitude of 398 A m^{-1}. No dc bias fields were applied during the susceptibility experiments.

Neutron powder diffraction experiments were carried out on ~4 g samples on the DUALSPEC C2 high-resolution powder diffractometer located at the NRU reactor, Chalk River Laboratories, Ontario, operated by Atomic Energy Canada Ltd. The neutron wavelength was 2.3685(1) Å. A review of the neutron scattering facilities at Chalk River, including a description of C2, can be found in [13]. Patterns were obtained for each compound over the temperature range 11–295 K and all diffraction patterns were analysed by the Rietveld method using the FullProf [14] program.

3. Results and discussion

3.1. Nd_5Si_4

The Nd_5Si_4 sample was two-phase, with ~5 wt% of hexagonal Nd_5Si_3 (space group $P6_3/mcm$) as an impurity which was included in all pattern refinements reported here.

In figure 1 we show the ac susceptibility traces of Nd_5Si_4 and Nd_5Ge_4. The magnetic ordering temperatures deduced from standard Curie–Weiss fits to the high-temperature regions of these data yield magnetic ordering temperatures of 66(2) and 51(2) K for Nd_5Si_4 and Nd_5Ge_4, respectively. Both magnetic ordering peaks in the susceptibility traces are sharp, albeit slightly asymmetric, and we see no evidence of further magnetic reorientation events in the magnetically ordered regimes, in contrast to the Tb- and Gd-based systems discussed earlier.

In figure 2 we show the neutron diffraction patterns of Nd_5Si_4 obtained at 295 and 12 K. In table 1 we give the atomic position parameters of Nd_5Si_4 derived from the refinement of the neutron diffraction pattern obtained at 295 K, which comprises only nuclear scattering.

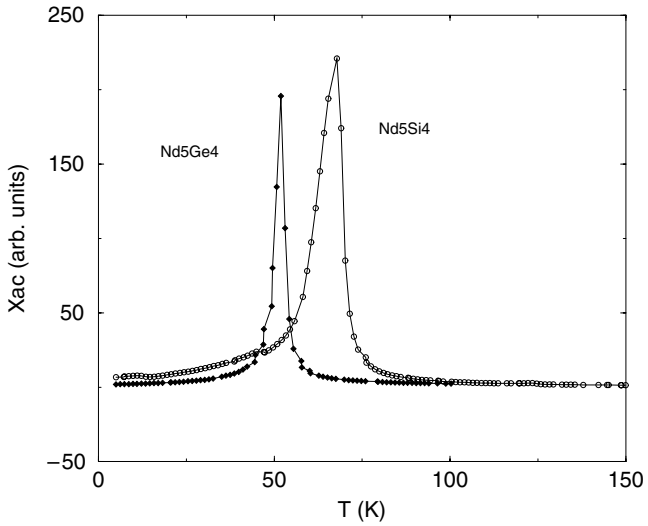

Figure 1. Ac susceptibility traces of Nd_5Si_4 (open circles) and Nd_5Ge_4 (filled diamonds).

Table 1. Refined atomic positions in Nd_5Si_4 at 295 K (obtained with an overall isotropic thermal parameter (B_{iso}) of 0.84 Å^2).

Atom	Site	x	y	z
Nd	4a	0.1901(21)	0.1901(21)	0
Nd	8b	0.0142(14)	0.1326(17)	0.6192(12)
Nd	8b	0.9861(17)	0.3667(17)	0.2025(6)
Si	8b	0.0529(30)	0.2810(28)	0.8070(12)
Si	8b	0.2826(31)	0.3270(34)	0.6926(12)

The crystal structure of Nd_5Si_4 is tetragonal with the space group $P4_12_12$ (No 92). The structure type is that of Zr_5Si_4 and there are three Nd sites and two Si sites. The lattice parameters (at 295 K) determined by neutron diffraction are $a = 7.8760(8)$ Å and $c = 14.8010(18)$ Å. The standard refinement 'R-factors (%)' are: R(Bragg) $= 6.2$ and R(weighted profile) $= 8.4$.

Comparison of the neutron patterns taken at 295 K (above the ordering temperature) and 12 K (below the ordering temperature) shows magnetic contributions to nuclear scattering peaks in addition to the appearance of additional peaks not allowed by the crystal space group. This is most clearly illustrated by the appearance of a strong magnetic (001) peak at $2\theta = 9°$. Thus, we may conclude that the magnetic structure of Nd_5Si_4 is neither a simple ferromagnet nor an antiferromagnet, but is most probably a combination of the two, i.e. a canted ferromagnet (*vide infra*).

To determine the magnetic structure of Nd_5Si_4 we carried out a group theory analysis of the possible magnetic space groups and magnetic ordering modes derived from the $P4_12_12$ space group. There are seven magnetic space groups associated with the $P4_12_12$ crystal space group [15], namely $P4_12_12$, $P4_1'2_12'$, $P4_12_1'2'$, $P4_1'2_1'2$, $P_c4_12_12$, $P_C4_12_12$ and $P_I4_12_12$. We omit the 'grey' group $P4_12_121'$ since it does not correspond to an ordered magnetic structure. We can rule out the last three of these seven groups due to the fact that we do not observe any additional magnetic peaks involving half-integer Miller indices. The behaviour of the magnetic moments within the remaining four magnetic space groups can then be deduced by

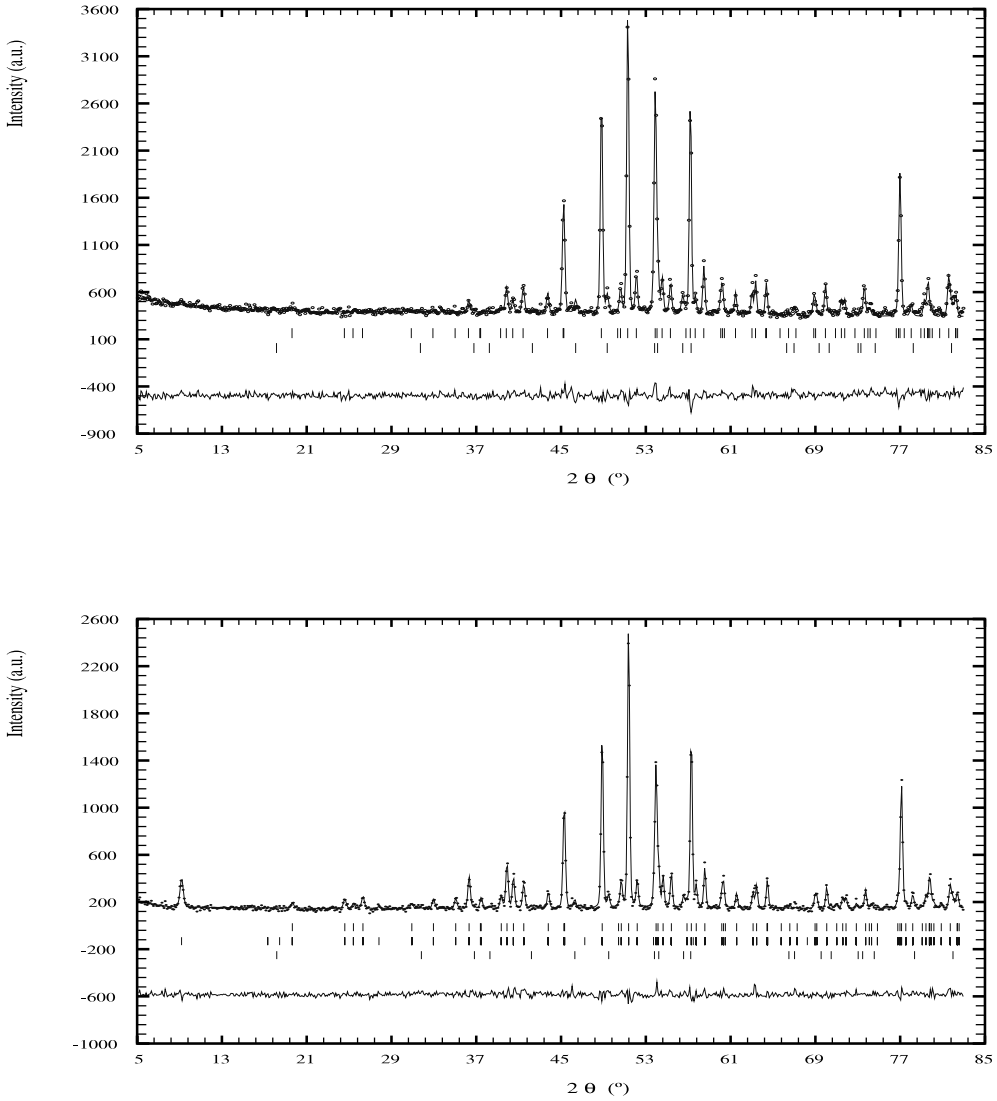

Figure 2. Neutron powder diffraction patterns of Nd_5Si_4 at 295 K (top) and 12 K (bottom). The Bragg markers (top to bottom) are Nd_5Si_4 and Nd_5Si_3 in the 295 K pattern, and Nd_5Si_4 (nuclear), Nd_5Si_4 (magnetic) and Nd_5Si_3 in the 12 K pattern.

Table 2. Character table of the 422 group (using the notation of Joshua [16]).

Representation	E	$C_{4z}^{\pm}$	C_{2z}	C_{2xy}	C_{2ab}	Magnetic space group
Γ_1	+1	+1	+1	+1	+1	$P4_12_12$
Γ_2	+1	+1	+1	−1	−1	$P4_12_1'2'$
Γ_3	+1	−1	+1	+1	−1	$P4_1'2_12'$
Γ_4	+1	−1	+1	−1	+1	$P4_1'2_1'2$

considering the character table of the 422 group which underpins these magnetic space groups, shown in table 2.

Table 3. Atomic positions and generating operations of the Nd 4a sites in Nd_5Si_4.

Atom number	X	Y	Z	Generating operation	Moment
1	x	x	0	Identity	(μ_x, μ_y, μ_z)
2	$-x$	$-x$	$\frac{1}{2}$	$2(0\,0\,\frac{1}{2})[0\,0\,z]$	$(-\mu_x, -\mu_y, \mu_z)$
3	$-x+\frac{1}{2}$	$x+\frac{1}{2}$	$\frac{1}{4}$	$4^+(0\,0\,\frac{1}{4})[0\,\frac{1}{2}\,z]$	$(-\mu_y, \mu_x, \mu_z)$
4	$x+\frac{1}{2}$	$-x+\frac{1}{2}$	$\frac{3}{4}$	$4^-(0\,0\,\frac{3}{4})[\frac{1}{2}\,0\,z]$	$(\mu_y, -\mu_x, \mu_z)$

The point group of the Nd 8b sites is *1* which leads to a completely arbitrary magnetic moment direction with no restrictions dictated by symmetry. The Nd 4a site has the point group $\cdot\cdot 2$ indicating a twofold rotation axis along the planar diagonal directions $\langle 110\rangle$, corresponding to C_{2ab} in the character table. The admissible magnetic point groups of the Nd 4a site are:

- $\cdot\cdot 2$ with the Nd magnetic moment parallel to the twofold axis (from the Γ_1 and Γ_4 representations); and
- $\cdot\cdot 2'$ with the Nd magnetic moment perpendicular to the twofold axis (from the Γ_2 and Γ_3 representations).

The four Nd 4a sites are related to each other by the generating operations given in table 3, using the standard notation employed in the *International X-ray Crystallography Tables* to describe crystallographic operations [17]. Now, if we denote the magnetic moment components of atom 1 by μ_x, μ_y and μ_z, we deduce the moments of the remaining three 4a atoms as shown in table 3, ignoring any time-reversal operations at this stage.

The final magnetic structures can then be derived from the character table for each possible magnetic space group by incorporating the characters of the generating operations, which takes into account the effects of time reversal.

We note here that:

- Γ_1 and Γ_4 yield a $\cdot\cdot 2$ magnetic point group for the 4a sites so the magnetic moment must be parallel to the twofold axis; i.e. the moment must lie in the tetragonal *a–b* plane and hence $\mu_z = 0$;
- Γ_2 and Γ_3 yield a $\cdot\cdot 2'$ magnetic point group for the 4a sites so the magnetic moment must be perpendicular to the twofold axis; i.e. the moment may have components in the plane and also along the tetragonal *c*-axis;
- the magnitudes μ_x and μ_y must be equal to ensure that the planar component lies along a $\langle 110\rangle$ diagonal direction.

These magnetic modes are shown schematically in figure 3, projected onto the tetragonal *a–b* basal plane.

As stated earlier, the magnetic moment orientations at the Nd 8b sites are not subject to any symmetry-related restrictions. In table 4 we show the atomic positions of the eight Nd 8b sites and their generating operations.

Thus, we have four possible magnetic structures for Nd_5Si_4 which we write in table 5 using the standard notation for the magnetic modes, namely $F = \{++++\}$, $G = \{+-+-\}$, $C = \{++--\}$ and $A = \{+---\}$. We use the superscript notation (+ or −) to represent the moment orientations of the eight Nd 8b atoms as two symmetry-related groups of four. For example, G_x^+ represents $\{+-+-+-+-\}$ and G_x^- represents $\{+-+---+-\}$.

The best fit to the 12 K neutron diffraction pattern of Nd_5Si_4 was obtained with the Γ_2 representation, corresponding to the magnetic space group $P4_12_12'$. The refinement *R*-factors (%) for the best fit are: $R(\text{Bragg}) = 5.1$, $R(F) = 4.0$ and $R(\text{mag}) = 7.7$. For comparison,

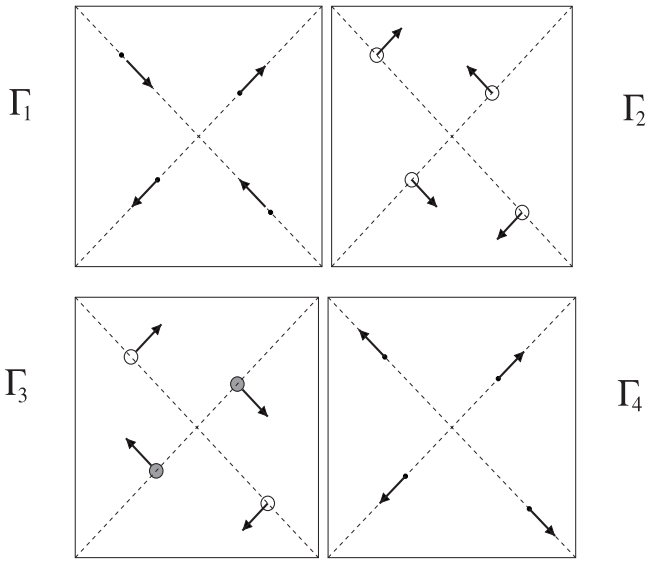

Figure 3. Possible magnetic structures of the Nd 4a site in Nd_5Si_4 projected onto the tetragonal a–b plane. Γ_1 and Γ_4 are planar whereas Γ_2 and Γ_3 have components along the c-axis, as denoted by the filled or unfilled circles which represent components either into the plane or out of the plane.

Table 4. Atomic positions and generating operations of the Nd 8b sites in Nd_5Si_4.

Atom number	X	Y	Z	Generating operation	Moment
1	x	y	z	Identity	(μ_x, μ_y, μ_z)
2	$-x$	$-y$	$z+\frac{1}{2}$	$2(0\,0\,\frac{1}{2})[0\,0\,z]$	$(-\mu_x, -\mu_y, \mu_z)$
3	$-y+\frac{1}{2}$	$x+\frac{1}{2}$	$z+\frac{1}{4}$	$4^+(0\,0\,\frac{1}{4})[0\,\frac{1}{2}\,z]$	$(-\mu_y, \mu_x, \mu_z)$
4	$y+\frac{1}{2}$	$-x+\frac{1}{2}$	$z+\frac{3}{4}$	$4^-(0\,0\,\frac{3}{4})[\frac{1}{2}\,0\,z]$	$(\mu_y, -\mu_x, \mu_z)$
5	$-x+\frac{1}{2}$	$y+\frac{1}{2}$	$-z+\frac{1}{4}$	$2(0\,\frac{1}{2}\,0)[\frac{1}{4}\,y\,\frac{1}{8}]$	$(-\mu_x, \mu_y, -\mu_z)$
6	$x+\frac{1}{2}$	$-y+\frac{1}{2}$	$-z+\frac{3}{4}$	$2(\frac{1}{2}\,0\,0)[x\,\frac{1}{4}\,\frac{3}{8}]$	$(\mu_x, -\mu_y, -\mu_z)$
7	y	x	$-z$	$2[x\,x\,0]$	$(\mu_y, \mu_x, -\mu_z)$
8	$-y$	$-x$	$-z+\frac{1}{2}$	$2[x\,-x\,\frac{1}{4}]$	$(-\mu_y, -\mu_x, -\mu_z)$

Table 5. Nd 4a and 8b site magnetic modes in Nd_5Si_4.

Representation	4a mode	8b mode	Magnetic space group
Γ_1	A_xG_y	$A_x^-G_y^+F_z^-$	$P4_12_12$
Γ_2	$A_xG_yF_z$	$A_x^+G_y^-F_z^+$	$P4_12_1'2'$
Γ_3	$G_xA_yC_z$	$G_x^-A_y^+C_z^-$	$P4_1'2_12'$
Γ_4	G_xA_y	$G_x^+A_y^-C_z^+$	$P4_1'2_1'2$

the corresponding R-factors for the second-best fit are 10.8, 8.2 and 27.1, respectively, for the Γ_4 representation. The refined Nd magnetic moment components are given in table 6.

The net magnetization of Nd_5Si_4 is zero along the directions a (or b) whereas there is a significant magnetization along the tetragonal c-axis, corresponding to an average Nd magnetic moment of 2.58(7) μ_B. The Nd moments shown in table 6 are less than the 'free-ion' moment of Nd^{3+} ion of 3.27 μ_B, most probably due to the fact that the measurement

Table 6. Nd magnetic moment components in Nd_5Si_4 at 12 K.

Site	μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)	Total moment (μ_B)
4a	0.36(4)	0.36(4)	2.34(6)	2.39(6)
8b	0.33(4)	0.43(4)	2.41(6)	2.47(6)
8b	1.38(4)	0.58(4)	2.35(6)	2.79(6)

Table 7. Refined atomic positions in Nd_5Ge_4 at 295 K (obtained with an overall isotropic thermal parameter (B_{iso}) of 0.52 Å^2).

Atom	Site	x	y	z
Nd	4c	0.2888(23)	$\frac{1}{4}$	0.0020(20)
Nd	8d	0.1197(12)	0.1161(7)	0.3429(13)
Nd	8d	0.9757(13)	0.0991(10)	0.8176(15)
Ge	4c	0.9159(20)	$\frac{1}{4}$	0.1032(18)
Ge	4c	0.1801(17)	$\frac{1}{4}$	0.6373(19)
Ge	8d	0.2197(14)	0.9567(7)	0.5305(14)

was made at $T/T_C = 0.16$. Crystal-field quenching may also be a factor. Our observation of ferromagnetism along the tetragonal c-axis of Nd_5Si_4 is in agreement with the magnetization measurements of Boulet *et al* [11].

3.2. Nd_5Ge_4

Schobinger-Papamantellos and Niggli [6] have previously reported neutron diffraction measurements on Nd_5Ge_4 and they determined the magnetic space group to be $Pnm'a'$. We have also studied Nd_5Ge_4 and here we will present a very brief summary of our structure determination, which is in full agreement with that of Schobinger-Papamantellos and Niggli [6].

The Nd_5Ge_4 sample was two-phase, with ∼10 wt% of hexagonal Nd_5Ge_3 as an impurity. This impurity phase was included in all pattern refinements reported here.

In figure 4 we show the neutron diffraction patterns of Nd_5Ge_4 obtained at 295 and 11 K. Our ac susceptibility work shows that Nd_5Ge_4 orders magnetically at 51(2) K, compared with the values of 52 K determined by Schobinger-Papamantellos and Niggli [6] and 54 K determined by Gschneidner *et al* [12]. In table 7 we give the atomic parameters of Nd_5Ge_4 derived from the refinement of the neutron diffraction pattern obtained at 295 K, which comprises only nuclear scattering. The crystal structure of Nd_5Ge_4 is orthorhombic with the space group $Pnma$ (No 62). There are three Nd sites and three Ge sites and the structure type is that of Sm_5Ge_4. The lattice parameters (at 295 K) determined by neutron diffraction are $a = 7.8684(9)$ Å, $b = 15.1207(16)$ Å and $c = 7.9628(9)$ Å. The refinement 'R-factors (%)' are: R(Bragg) = 5.3, R(weighted profile) = 8.4.

As was the case with Nd_5Si_4, there are magnetic contributions to nuclear scattering peaks in addition to the appearance of additional peaks not allowed by the crystal space group. This is most clearly illustrated by the appearance of a strong magnetic (111) peak at $2\theta = 26°$.

There are eight possible magnetic space groups associated with the $Pnma$ crystal space group [15], as shown in table 8. The point group of the Nd 8d sites is 1 which leads to a completely arbitrary magnetic moment direction. The 4c site has the point group $\cdot m \cdot$, i.e. with a mirror plane whose normal is along the crystal b-axis and the possible admissible magnetic point groups of the 4c site are:

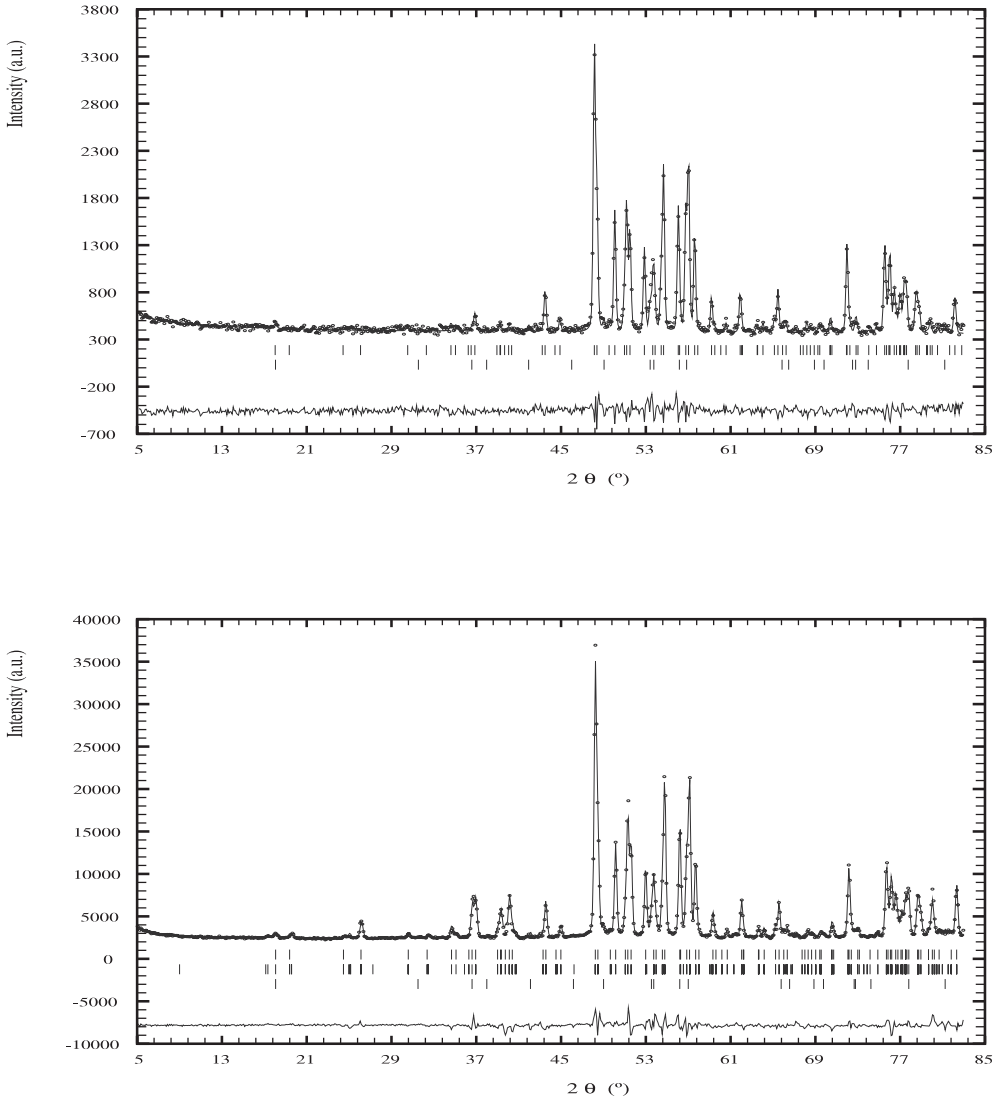

Figure 4. Neutron powder diffraction patterns of Nd_5Ge_4 obtained at 295 K (top) and 11 K (bottom). The Bragg markers (top to bottom) are Nd_5Ge_4 and Nd_5Ge_3 in the 295 K pattern, and Nd_5Ge_4 (nuclear), Nd_5Ge_4 (magnetic) and Nd_5Ge_3 in the 11 K pattern.

- $\cdot m \cdot$ with the Nd magnetic moment perpendicular to the mirror plane (from the Γ_1^+, Γ_2^+, Γ_3^- or Γ_4^- representations). Thus, the moment must lie along [010] and hence μ_x and $\mu_z = 0$;
- $\cdot m' \cdot$ with the Nd magnetic moment lying in the mirror plane (from the Γ_3^+, Γ_4^+, Γ_1^- or Γ_2^- representations), so $\mu_y = 0$.

The possible magnetic modes for the Nd 4c and 8d sites in Nd_5Ge_4 are shown in table 8.

The best fit to the 11 K neutron diffraction pattern of Nd_5Ge_4 is obtained with the Γ_3^+ structure, corresponding to the magnetic space group $Pnm'a'$. The refinement R-factors (%) for the best fit are: $R(\text{Bragg}) = 6.7$, $R(F) = 4.8$ and $R(\text{mag}) = 11.7$. For comparison, the corresponding R-factors for the second-best fit are 10.1, 7.2 and 20.9, respectively, for the Γ_4^+ representation. The refined Nd magnetic moment components are given in table 9.

Table 8. Nd 4c and 8d site magnetic modes in Nd_5Ge_4.

Representation	4c mode	8d mode	Magnetic space group
Γ_1^+	G_y	$A_x^+G_y^+C_z^+$	$Pnma$
Γ_2^+	F_y	$C_x^+F_y^+A_z^+$	$Pn'ma'$
Γ_3^+	F_xG_z	$F_x^+C_y^+G_z^+$	$Pnm'a'$
Γ_4^+	G_xF_z	$G_x^+A_y^+F_z^+$	$Pn'm'a$
Γ_1^-	A_xC_z	$A_x^-G_y^-C_z^-$	$Pn'm'a'$
Γ_2^-	C_xA_z	$C_x^-F_y^-A_z^-$	$Pnm'a$
Γ_3^-	C_y	$F_x^-C_y^-G_z^-$	$Pn'ma$
Γ_4^-	A_y	$G_x^-A_y^-F_z^-$	$Pnma'$

Table 9. Nd magnetic moment components in Nd_5Ge_4 at 11 K.

Site	μ_x (μ_B)	μ_y (μ_B)	μ_z (μ_B)	Total moment (μ_B)
4c	1.84(4)	0	0.16(6)	1.85(6)
8d	2.79(4)	1.01(4)	1.12(6)	3.17(6)
8d	2.47(4)	0.14(4)	1.20(6)	2.75(6)

The net magnetization of Nd_5Ge_4 is zero along the b- and c-directions whereas there is a significant magnetization along the orthorhombic a-axis [100]. The average Nd magnetic moment at 11 K in Nd_5Ge_4 is 2.74(7) μ_B.

4. Conclusions

We have determined the magnetic structures of Nd_5Si_4 and Nd_5Ge_4 by means of high-resolution neutron powder diffraction. The magnetic space group of Nd_5Si_4 is $P4_12'_12'$ which corresponds to the Γ_2 representation of the underlying 422 group. Nd_5Si_4 is antiferromagnetic in the tetragonal basal plane and ferromagnetic along the c-axis. At 12 K, the ferromagnetic order gives an average Nd moment along the c-axis of 2.37(7) μ_B and an average total Nd moment of 2.58(7) μ_B.

The magnetic space group of Nd_5Ge_4 is $Pnm'a'$ which corresponds to the Γ_3^+ representation of the underlying mmm group. Nd_5Ge_4 is antiferromagnetic along the orthorhombic b- and c-axes and ferromagnetic along the a-axis. At 11 K, the ferromagnetic order gives an average Nd moment along the a-axis of 2.47(7) μ_B and an average total Nd moment of 2.74(7) μ_B.

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References

[1] Smith G S, Tharp A G and Johnson Q 1966 *Nature* **210** 1148–9
[2] Smith G S, Tharp A G and Johnson Q 1967 *Acta Crystallogr.* **22** 940–3
[3] Holzberg F, Gambino R J and McGuire T R 1967 *J. Phys. Chem. Solids* **28** 2283–9
[4] Schobinger-Papamantellos P 1978 *J. Phys. Chem. Solids* **39** 197–205

[5] Schobinger-Papamantellos P 1979 *J. Physique Coll. Suppl.* **40** C5 156–8
[6] Schobinger-Papamantellos P and Niggli A 1981 *J. Phys. Chem. Solids* **42** 583–6
[7] Gschneidner K A Jr and Pecharsky V K 2000 *Annu. Rev. Mater. Sci.* **30** 387–429
[8] Pecharsky V K and Gschneidner K A Jr 2001 *Adv. Mater.* **13** 683–6
[9] Ritter C, Morellon L, Algarabel P A, Magen C and Ibarra M R 2002 *Phys. Rev.* B **65** 094405
[10] Rao G H 2000 *J. Phys.: Condens. Matter* **12** L93–9
[11] Boulet P, Weitzer F, Hiebl K and Noël H 2001 *J. Alloys Compounds* **315** 75–81
[12] Gschneidner K A Jr, Pecharsky V K, Pecharsky A O, Ivtchenko V V and Levin E M 2000 *J. Alloys Compounds* **303–4** 214–22
[13] Powell B M 1990 *Neutron News* **1** 16–20
[14] Rodríguez-Carvajal J 1993 *Physica* B **192** 55–69
[15] Opechowski W and Guccione R 1965 *Magnetism* vol IIA, ed G T Rado and H Suhl (New York: Academic) ch 3, pp 105–65
[16] Joshua S J 1991 *Symmetry Principles and Magnetic Symmetry in Solid State Physics* (Bristol: Hilger)
[17] Hahn T (ed) 1996 *International Tables for Crystallography* vol A, 4th edn (Dordrecht: Kluwer Academic)