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THE CANTED FERRIMAGNETIC STRUCTURE OF Nd_5Ge_4 BY NEUTRON DIFFRACTION

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Abstract—The chemical and magnetic structures of the intermetallic compound Nd_5Ge_4 were determined from neutron diffraction powder data. In contrast to the isomorphous heavy rare-earth compounds, Nd_5Ge_4 orders with a canted ferrimagnetic arrangement below $T_c = 52$ K. The ordered Nd moments are 2.6, 3.1 and 2.4 μ_B for the three sites respectively. The magnetic space group is $Pnm'a'$ and the plane of easy magnetization (010).

INTRODUCTION

Nd_5Ge_4, like the isomorphous RE_5Ge_4 (RE = rare earth) compounds, is orthorhombic ($a = 7.86$ Å, $b = 15.06$ Å, $c = 7.93$ Å, $Z = 4$) and has the Sm_5Ge_4 structure type[1, 2]. There are two 8(d) and one 4(c) symmetry positions occupied by the RE atoms. Holtzberg[3] has investigated the magnetic properties of only the heavy RE-compounds of this structure type.

The magnetic structures of Tb_5Ge_4 and Ho_5Ge_4 determined by neutron diffraction[4, 5] at 4.2 and 18 K, respectively, explain the observed metamagnetic behaviour. The two structures, although described by different Shubnikov space groups, $Pnm'a'$ and $Pn'm'a'$, have the same plane of easy magnetization (010), parallel to the characteristic layers of the structure. The magnetic moments within each layer are almost parallel. The antiferromagnetic compensation is realized through a sign change of the magnetic moments through the antisymmetry center $\bar{1}'$. From the field-dependent neutron data it was also stated that very weak fields applied in the (010) plane induce a phase transition from an antiferro- to a ferromagnetic space group, while the anisotropy field in the perpendicular direction is much higher (15–25 kOe).

In this context is seems of interest to study the magnetic structure and properties of Nd_5Ge_4. We describe here a model for the magnetic structure of Nd_5Ge_4 based on neutron diffraction data, and we also report the temperature dependence of the strongest magnetic line.

EXPERIMENTAL

For the sample preparation we used the method described in Refs. [4, 5]. The sample was found to be single phase from X-ray powder diffraction obtained with a data Guinier focusing camera using Cu Kα radiation. The neutron diffraction powder data were recorded with the double axis spectrometer at the reactor Saphir, Würenlingen ($\lambda = 2.346$ Å) at the temperatures 293 and 4.2 K. The observed neutron intensities were corrected for absorption and evaluated by the line profile analysis method[6].

†A refinement with recently published form factors[11] did not show a significant variation of the refined parameters.

NUCLEAR STRUCTURE AT 293 K

The refinement of the nuclear intensities was based on the parameters given in [2] for Sm_5Ge_4. The scattering lengths used were $b_{Nd} = 7.5$ and $b_{Ge} = 8.19F$. The resulting reliability factors $R_n = 0.07$ and $R_{wp} = 0.13$ (weighted profile) are satisfactory. The overall temperature factor is 0.76 Å^2. The refined parameters are given in Table 1 and the calculated profile in Fig. 1(b).

THE MAGNETIC STRUCTURE AT 4.2 K

At liquid helium temperature the neutron diagram shows that the magnetic lines may be indexed in terms of the chemical cell, i.e. $k = 0$. Beside the very weak intensities 100 and 001, the magnetic reflections obey the extinction rules of the space group $Pnma$, which indicates that the main magnetic component is ferromagnetic.

Making use of group theoretical predictions[7, 8] for $k = 0$ and assuming no lowering of symmetry, we find three possible magnetic space groups which may have a ferromagnetic mode. From the very weak 202 and 230 magnetic lines, both having contributions from the Nd positions to their structure factors, we conclude that the ferromagnetic mode is along x (Fig. 2) and that $Pnm'a'$–Sh_{62}^{447} is the most probable magnetic space group.

The magnetic modes of the 8(d) and 4(c) positions in the $Pnm'a'$ magnetic space group are: $F_{BX}(++++++++)$, $A_{BY}(+--++--+)$, $G_{BZ}(+-+-+-+-)$ and $F_X(++++)$, $C_Z(++--)$.

The refined structure on the basis of this model explains the 4.2 K neutron data, and the R factors are satisfactory (Table 1). The positional parameters are taken from the 293 K data. Some of the calculated and observed intensities are given in Table 2 for comparison. The Nd form factor† used is from Ref. [10].

Within the limits of the profile method[9] and the choice of the refined parameters (Table 1), Nd_5Ge_4 can be considered as a two-dimensional canted ferrimagnet. However for a direct evidence of the small antiferromagnetic component, single crystal data would be needed.

The three different Nd positions have no moment component perpendicular to the (010) atomic nets (G, S, C), therefore the structure is defined by giving the

Table 1. Refined parameters from neutron intensities of Nd_5Ge_4 at 293 and 4.2 K. The estimated standard deviations are in parenthesis and correspond to the last digit. μ is the ordered moment of Nd and μ_{xyz} its x, y, z components; a, b, c the lattice constants. *Rexp* is the expected agreement value depending on the statistical accuracy of the data. *Rn, Rm, Rwp* the agreement values for nuclear, magnetic and weighted profile intensities[6]

T [K]	Rexp / Rn / Rw_p / Rm	a / b / c [Å]	at Pos.	Nd(1) 8(d)	Nd(2) 8(d)	Nd(3) 4(c)	Ge(1) 8(d)	Ge(2) 4(c)	Ge(3) 4(c)
293	0.05	7.841(3)	x	0.118(2)	0.980(1)	0.302(2)	0.222(1)	0.918(2)	0.190(2)
	0.08	15.071(5)	y	0.115(1)	0.097(1)	0.25	0.955(1)	0.25	0.25
	0.12	7.937(4)	z	0.348(1)	0.806(2)	0.018(2)	0.526(1)	0.102(2)	0.665(2)
4.2	0.05	7.819(3)	$\mu[\mu_B]$	2.64(9)	3.05(8)	2.4(1)	Overall temperature		
	0.06	15.020(4)	μ_x "	2.39(8)	2.75(8)	2.4(1)	factor = 0.76 Å^2		
	0.11	7.917(3)	μ_y "	-0.6 (2)	-0.2 (3)				
	0.09		μ_z "	-0.92(9)	1.29(9)	-0.3(1)			

magnetic ordering inside these nets, Fig. 2. The G, S, C nets and their centrosymmetrical counterparts G', S', C', are stacked along y in the following way:

$$G\,S\uparrow\;\; C\uparrow S\uparrow G\cdot G'\,S\uparrow'\;\; C\uparrow' S\uparrow' G'$$
$$\qquad\quad |\qquad\qquad\qquad\quad |$$
$$m_{y=1/4}\quad \bar{1}\qquad\qquad m_{y=3/4}$$

G is a germanium, almost square, net at $y = 0.04$ and 0.45, like Nd_3 in Fig. 2.

S is a Nd net (Fig. 2), consisting of squares and triangles at $y \approx 0.11$ and 0.39; thus, stacking of the S nets results in deformed cubes of Nd (with Nd_3 in their center) and in trigonal prisms in the lower half of the cell, which are separated from their centrosymmetric neighbors by the two (G and G') germanium layers.

Table 2. A part of the integrated, calculated and observed neutron intensities of Nd_5Ge_4 at 4.2 K, including the powder multiplicity and Lorentz factor

h k l	I_{nuc}	I_{mag}	I_{tot}	I_{obs}	h k l	I_{nuc}	I_{mag}	I_{tot}	I_{obs}
0 1 0	-	0	0	87	1 5 0	-	3	3	3
0 0 1	-	0	0	17	2 0 2	9713	563	10276	11250
1 0 0	-	571	571	735	2 1 2	3792	92	3884	3748
0 2 0	348	8	355	725	0 4 2	8116	3666	11781	11645
0 1 1	21	7	27	30	2 4 0	8437	1636	10073	10077
1 1 0	-	892	892	910	1 5 1	7566	1012	8578	7890
1 0 1	294	460	753	775	0 0 3	-	0	0	0
0 2 1	-	3	3	4	2 2 2	4694	53	4747	5485
1 2 0	-	110	110	200	3 0 0	-	357	357	412
1 1 1	3	2549	2553	3017	0 1 3	4106	692	4797	5439
0 3 0	-	0	0	364	1 4 2	4936	1428	6364	6270
1 2 1	725	601	1326	1002	3 1 0	-	109	109	107
0 3 1	0	749	749	888	2 4 1	12888	2011	14899	14556
1 3 0	-	192	192	157	0 6 0	10512	2537	13049	13218
0 0 2	255	971	1226	1264	1 0 3	465	285	750	759
2 0 0	628	0	628	847	0 2 3	-	34	34	34
0 1 2	-	54	54	90	3 0 1	8447	120	8568	8561
2 1 0	0	4	5	5	1 1 3	14776	2004	16780	17102
0 4 0	288	2903	3191	3268	3 2 0	-	96	96	99
1 3 1	1822	4606	6429	6443	3 1 1	6625	120	6745	7354
1 0 2	34	789	822	1371	2 3 2	235	390	624	659
2 0 1	509	1335	1845	2090	0 5 2	-	83	83	60
0 2 2	156	1988	2144	2415	0 6 1	-	18	18	13
2 2 0	0	58	58	64	1 6 0	-	182	182	129
1 1 2	506	3916	4423	4610	2 5 0	3311	369	3680	2614
2 1 1	27	940	967	986	1 2 3	227	107	334	250
0 4 1	-	395	395	522	3 2 1	7	13	20	21
1 4 0	-	33	33	122	0 3 3	385	449	834	1066
1 2 2	23	386	409	866	3 3 0	-	272	272	368
2 2 1	4363	64	4428	4500	1 5 2	2328	124	2453	3445
1 4 1	241	67	308	285	1 6 1	198	13	211	284
0 3 2	-	9	9	8	2 5 1	129	189	318	418
2 3 0	1715	680	2395	2167	1 3 3	355	124	479	493
0 5 0	-	0	0	924	2 4 2	18	216	233	242
1 3 2	20699	5518	26216	26105	3 3 1	1319	104	1423	1405
2 3 1	12255	2036	14291	14128	2 0 3	645	52	697	695
0 5 1	362	289	651	863	3 0 2	4724	560	5284	5148

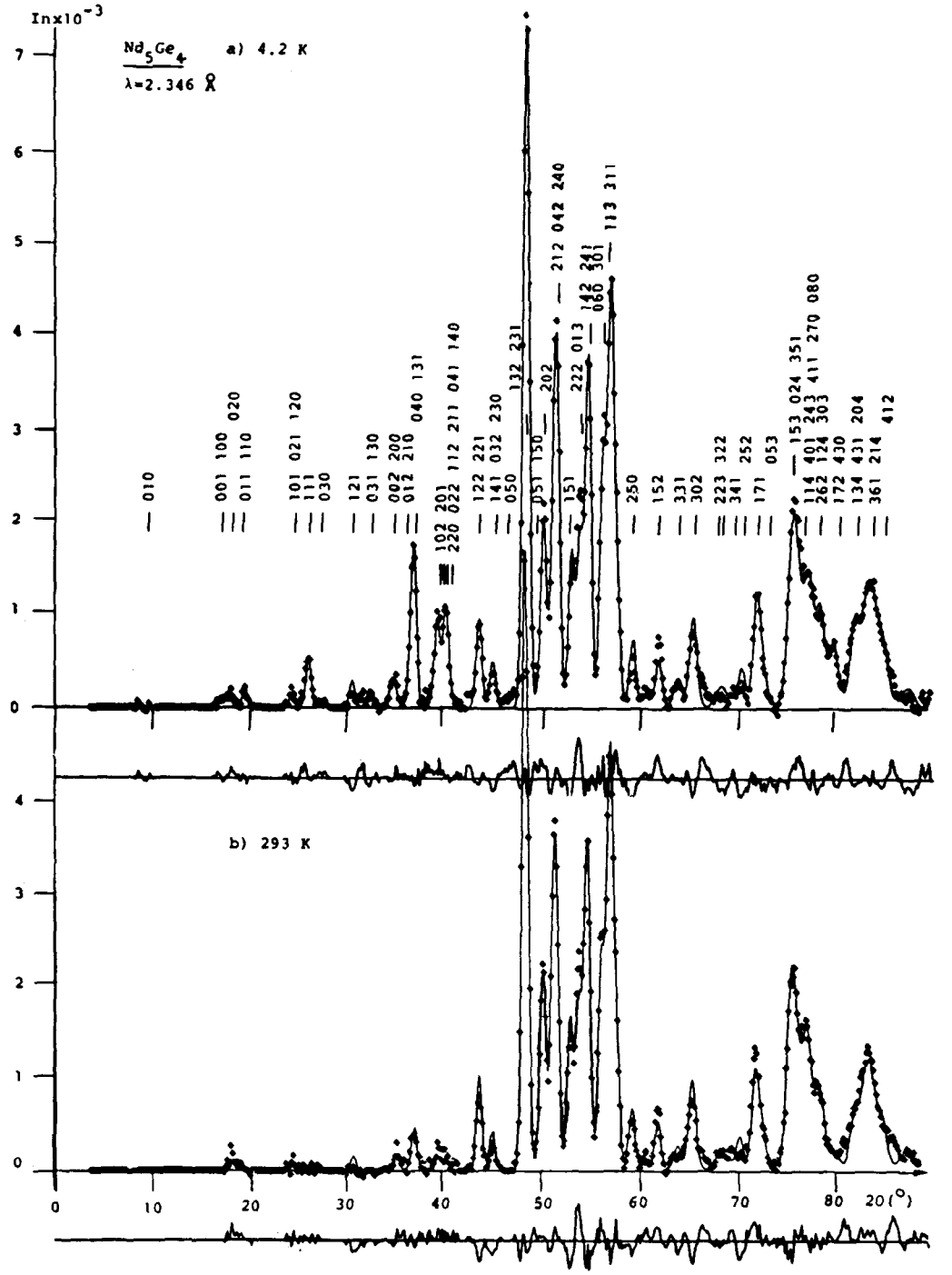

Fig. 1. Neutron diffraction patterns from (a) ordered (4.2 K) (b) paramagnetic (293 K) Nd_5Ge_4. The full curve is the calculated profile and the points are the observed intensities. The difference diagram is below. For clarity only the strongest lines are indexed.

C is a mixed net of G (with Nd instead of Ge squares) and S (with Ge instead of Nd squares and triangles) at $y = 1/4$. The germanium S nets are turned by 90° compared to those of neodymium.

The arrows symbolize the direction of the resulting ferrimagnetic moment. The moment of Nd_1 points along the common edge of the squares and triangles, while Nd_2 points towards the square diagonal, and Nd_3 has an intermediate angle between Nd_1 and Nd_2.

The ordered moment values at 4.2 K, namely 2.6, 3.1 and 2.4 μ_B for the three Nd positions, are below the saturation value ($gJ = 3.27\ \mu_B$) of the free Nd^{3+} ion. This could be caused by crystal field effects. On the other hand, the moment values are larger than the spontaneous

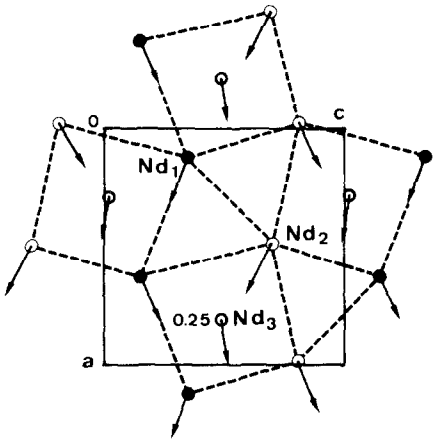

Fig. 2. The magnetic structure of the characteristic S layer (Nd_1, Nd_2 at $y = 0.11$) of Nd_5Ge_4 at 4.2 K (*Pnm'a'* space group) with the Nd_3 atoms ($y = 0.25$) projected on S.

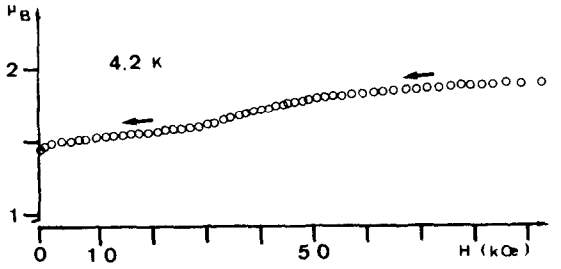

Fig. 3. Magnetization in μ_B/Nd vs effective field of polycrystalline Nd_5Ge_4 at 4.2 K. An external field of 95 kOe had been applied on cooling the powder sample through the Curie point down to 4 K.

average moment, 1.49 μ_B extrapolated from the magnetization curve (Fig. 3) for zero field. The incomplete saturation, $\mu = 1.92\ \mu_B$ for an effective field of 92 kOe is probably due to the anisotropy and to the polycrystalline sample.

From the temperature dependence of the strongest magnetic line 131 (Fig. 4), which has contributions from all magnetic atoms, we assume that they order altogether at $T_c = 52$ K and that no other phase transition is visible for the temperature interval $T \leq T_c$.

The difference of the Nd_5Ge_4 structure compared to those of Ho and Tb is that the moment direction does not change on inversion through the symmetry center, and

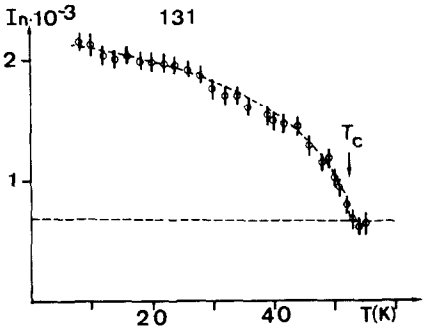

Fig. 4. The temperature dependence of the strongest magnetic reflection 131 of Nd_5Ge_4.

thus the structure has a large ferromagnetic component. This may be due to a sign change in the exchange integral created by the larger Nd^{3+} ion. The common characteristic of the three isomorphic compounds examined is the anisotropic behaviour and the relation of the plane of easy magnetization (010) to the layered nature of the chemical structure.

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