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Journal of Alloys and Compounds 252 (1997) 16–19

Journal of ALLOYS AND COMPOUNDS

Magnetic ordering of $TbNi_3Ga_2$ studied by neutron diffraction and magnetic measurements

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Received 1 August 1996

Abstract

The magnetic and crystallographic properties of the compound $TbNi_3Ga_2$ have been studied by neutron diffraction and magnetic measurements. From magnetic measurements it is derived that $TbNi_3Ga_2$ orders ferromagnetically below about 14 K. Refinement of the neutron diffraction data obtained in the paramagnetic regime showed that $TbNi_3Ga_2$ adopts the hexagonal YCo_3Ga_2 type structure, but with a different distribution of the 3d atoms and Ga atoms over the three non-rare earth sites available in this structure type. Analysis of the neutron data obtained in the magnetically ordered regime shows that the magnetic structure is essentially ferromagnetic, the preferred direction of the Tb moments being perpendicular to the *c* direction. The Tb moment at the 2c site (3.9 μ_B) is substantially lower than that at the 1a site (8.3 μ_B).

Keywords: Rare earth nickel gallides; Crystal structure; Terbium moment; Magnetic structure; Neutron diffraction

1. Introduction

The compound $TbNi_3Ga_2$ has been reported by Fremy et al. [1] to crystallise with the hexagonal (h18) YCo_3Ga_2 type structure (space group $P6/mmm$; $a = 0.8735$ nm, $c = 0.4174$ nm, $Z = 3$). The rare earth and Co atoms occupy two sites each. The Y atoms are located on the 1a sites at (0,0,1/2) and on the 2c sites at (1/3,2/3,0). The 3d atoms occupy the sites 3g (1/2,0,1/2) and 6m (x,2x,1/2) with $x = 0.1799(4)$. The Ga atoms were found to occupy only a single site, 6j (x,0,0) with $x = 0.2895(7)$. Although no structural data were presented, the same site occupations were also reported in a later investigation of RNi_3Ga_2 compounds by Routsi et al. [2].

In a more recent investigation [3], we have used neutron diffraction to study the crystallographic and magnetic properties of the compound $CeCo_3Ga_2$, which had also been reported to crystallise with YCo_3Ga_2 structure type [1]. In fact, stuctural refinement of the neutron data obtained for this compound confirmed the YCo_3Ga_2 structure type proposed by Fremy et al., but revealed a different 3d atom and Ga atom site occupation than obtained by these authors. In the present investigation we have studied the compound $TbNi_3Ga_2$ in order to determine how far the site occupation found by us for $CeCo_3Ga_2$ is a more general one and present also in other compounds for which the YCo_3Ga_2 structure type had been reported. Included in this investigation is the determination of the magnetic structure of $TbNi_3Ga_2$, because it can be suspected that the two different coordinations associated with the two rare earth sites will lead to a different moment behaviour when the rare earth component carries a magnetic moment.

2. Experimental

The compound $TbNi_3Ga_2$ was prepared by arc melting stoichiometric proportions of the constituent metals (purity at least 99%) in a protective argon gas atmosphere. The sample, wrapped in Ta foil, was annealed for about three weeks at 900 °C in an evacuated quartz tube. The X-ray diffraction diagram taken from the annealed sample showed that it is approximately single phase, and that the YCo_3Ga_2 type structure had formed with lattice constants $a = 0.8714$ nm and $c = 0.4124$ nm. The magnetic properties of the $TbNi_3Ga_2$ compound were determined in fields up to 6 T on a SQUID magnetometer.

Neutron diffraction experiments were carried out on a

0925-8388/97/$17.00
PII S0925-8388(96)02613-8

powder sample of $TbNi_3Ga_2$, in the high temperature (HT) paramagnetic state at 30 K and the low temperature (LT) magnetically ordered state for temperatures of 1.5 and 8 K. The data were collected with the D1A (double axis multicounter diffractometer) at the facilities of the ILL in Grenoble using a wavelength of 1.908 Å. The step increment of the diffraction angle 2Θ was 0.1°. The data were corrected for absorption and evaluated by the Fullprof program [4].

3. Experimental results

3.1. Magnetic properties

Results of the magnetic measurements are displayed in Fig. 1. From the temperature dependence of the magnetisation shown in Fig. 1(a) it is derived that $TbNi_3Ga_2$ orders ferromagnetically at about 14 K. Above this temperature the Curie–Weiss law is followed, as shown in the inset to the figure. From the slope of the temperature dependence of the reciprocal susceptibility, we derive an effective moment of 9.80 μ_B per Tb atom, which is very close to the free ion value of 9.72 μ_B per Tb atom. Fig. 1(b) shows the field dependence of the magnetisation at 5 K. Saturation is seen to be not yet completely reached in the highest field strength applied, which is indicative of substantial anisotropy in the ordered state. The moment in 5.5 T equals 6.7 μ_B per Tb atom, which is considerably below the free ion value for the ordered moment (9 μ_B per Tb atom).

3.2. Nuclear structure of $TbNi_3Ga_2$

The neutron diffraction pattern collected in the HT paramagnetic state at 30 K is shown in Fig. 2(a). The refined parameters are given in Table 1. These results confirm the YCo_3Ga_2 type structure [1], except for the Ni/Ga distribution. The latter was found to be identical with the Co/Ga distribution reported previously by us for $CeCo_3Ga_2$ in Ref. [3].

3.3. Magnetic structure of $TbNi_3Ga_2$

The 1.5 K (LT) data are displayed in Fig. 2(b). Comparison with the data given in part (a) shows that there is predominantly an enhancement of the nuclear intensities, as usually expected for ferromagnetic ordering. The refinement of the magnetic intensities leads to a collinear moment arrangement at the Tb(1) and Tb(2) sites, with the moments confined to the (001) plane, as is shown in Fig. 3. This arrangement corresponds to a symmetry reduction to the $C112/m$ ($P2/m$) monoclinic space group. Since the Tb(1) atom is situated on a 2_z axis, with its moment normal to it, the magnetic space group is $P2'/m'$.

It can be seen in Table 1 and Fig. 3 that there is a large

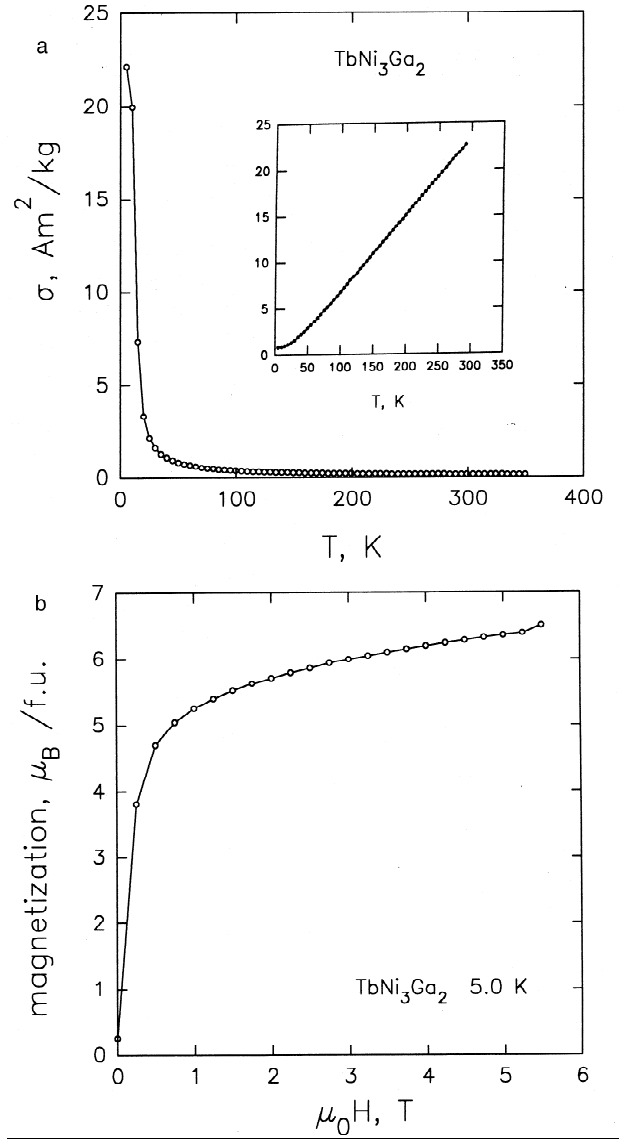

Fig. 1. (a) Temperature dependence of the magnetisation for $TbNi_3Ga_2$ measured in a field of 0.1 T. The inset shows the temperature dependence of the reciprocal susceptibility ($m^3\,mol^{-1}$) using magnetisation values measured in a field of 3 T. (b) Field dependence of the magnetic moment at 5 K.

difference between the ordered moment values observed for Tb moments at the two sites. The moment value at the 1a site, $\mu_{Tb(1)} = 8.3\ \mu_B$, is close to the saturation value of the free Tb^{3+} ion, $gJ\ \mu_B = 9\ \mu_B$. By contrast, the moment value pertaining to the 2c site is reduced to less than half this value, $\mu_{Tb(2)} = 3.9\ \mu_B$. The weighted mean of the Tb moment is 5.4 μ_B/f.u., which is slightly lower than the value found from magnetisation measurements in the highest field applied. The (LT) refined pattern (Fig. 2(b)) shows the presence of some very weak magnetic peaks at reciprocal lattice positions different from those of the nuclear structure. Their presence is better shown in the difference diagram (Fig. 2(b)). It has been possible to

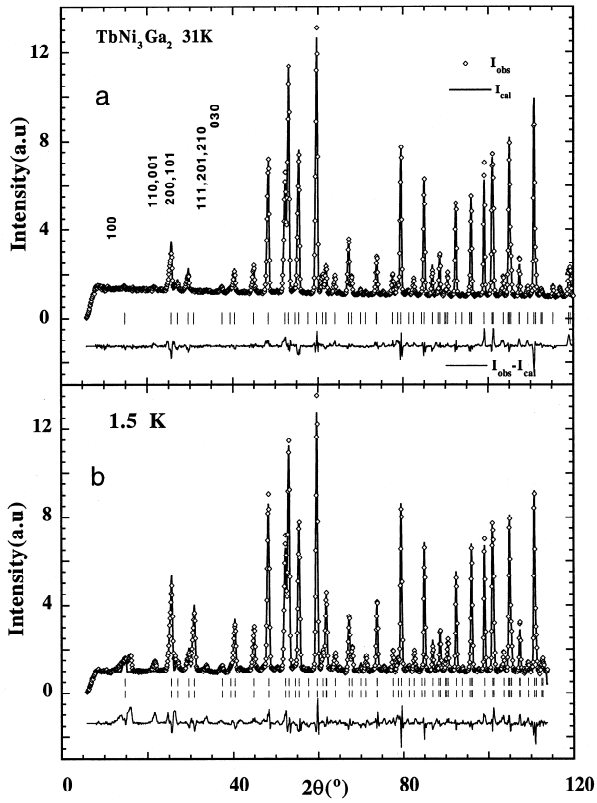

Fig. 2. Observed, calculated and difference neutron diagram of $TbNi_3Ga_2$ measured (a) at 30 K in the paramagnetic state and (b) in the magnetically ordered state at 1.5 K.

index those peaks with the help of several sets of wavevectors corresponding to cell enlargements of (2a,3b,2c) and (3a,3a,2c). No model is yet available for a quantitative analysis of the modulated part of the structure, which most probably concerns mainly the Tb(2) site. The 8 K refined data have shown only a minor change of the ferromagnetic moment values, $\mu_{Tb(1)} = 7.1(1)\ \mu_B$ and $\mu_{Tb(2)} = 3.4(1)\ \mu_B$, while the modulated part is almost absent.

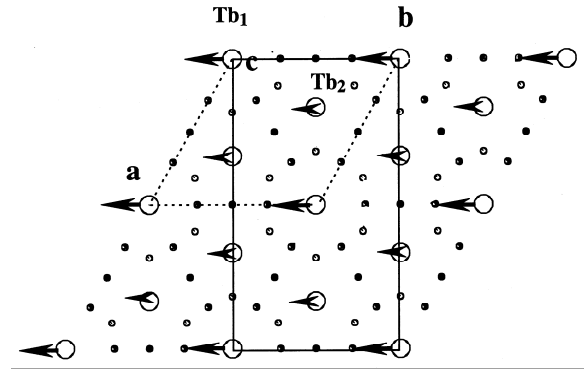

Fig. 3. Schematic representation of the ferromagnetic moment arrangement in $TbNi_3Ga_2$ when viewed along [001].

4. Discussion

The YCo_3Ga_2 type structure as proposed by Fremy et al. [1] is derived from the more simple hexagonal $CaCu_5$ type structure of YCo_5. The Co atoms occupy two different sites (3g and 2c) in the latter structure. The YCo_3Ga_2 type structure is formed by filling all 2c sites with Ga, leaving the 3g sites occupied by Co atoms. Because the Ga atoms are larger than the Co atoms, this leads to a shift of one third of the Y atoms to the $z = 1/2$ plane and some readjustment of the other atomic positions. This structural scheme is a most appealing one because there is a complete match between the site occupancies and the formula composition, the Ga atoms substituting exclusively into one of the two sites. Much to our surprise we found during a recent neutron diffraction study of the compound $CeCo_3Ga_2$ that the site occupancies are different, corresponding to a more equal substitution of Ga into the original 3g and 2c sites of the $CaCu_5$ type structure. This can also be seen in Table 2, where we have listed these site occupancies for $CeCo_3Ga_2$, bearing in mind that 2c ($CaCu_5$) corresponds to 6j (YCo_3Ga_2), and 3g ($CaCu_5$) corresponds to 6m and 3g (YCo_3Ga_2). This site relation-

Table 1
Refined structural parameters of the $TbNi_3Ga_2$ compound in the paramagnetic state at 30 K and in the magnetically ordered state at 1.5 K (only ferromagnetic contributions); space group $P6/mmm$

Atom	Site	Occupancy	1.5 K			30 K		
			x	*y*	*z*	*x*	*y*	*z*
Tb(1)	1a	1.0	0.0	0.0	0.5	0.0	0.0	0.5
Tb(2)	2c	1.0	0.3333	0.6666	0.0	0.3333	0.6666	0.0
Ni(1)	6m	1.0	0.1835(4)	0.3670(4)	0.5	0.1835(2)	0.3670(8)	0.5
Ni(2)	6j	0.5	0.2900(4)	0.0	0.0	0.2895(2)	0.0	0.0
Ga(1)	6j	0.5	0.2900(4)	0.0	0.0	0.2895(2)	0.0	0.0
Ga(2)	3g	1.0	0.5	0.0	0.5	0.5	0.0	0.5
μ_{Tb1}, μ_{Tb2} (μ_B)					8.3(2)	3.9(1)	—	—
a, *c* (nm)					0.86986(6)	0.41160(3)	0.87018(1)	0.41172(1)
Bof (nm^2)						0.0014(6)		0.0046(6)
R_n, R_m (%)					5.2	7.9	6.2	—
R_{wp}, R_{exp} (%)					15.6	4.0	10.9	3.4

Table 2
Site occupancies observed in ternary compounds RT_3Ga_2 of rare earths R, 3d elements T and gallium, crystallising in the YCo_3Ga_2 type structure; the site symbols given in square brackets refer to the sites in the basic $CaCu_5$ type structure

Atom	Site	YCo_3Ga_2 [1]	$CeCo_3Ga_2$ [3]	$TbNi_3Ga_2$ (present work)
R(1)	1a	1.0	1.0	1.0
R(2)	2c	1.0	1.0	1.0
T(1)	6m [3g]	1.0	1.0	1.0
T(2)	6j [2c]	0.0	0.5	0.5
Ga(1)	6j [2c]	1.0	0.5	0.5
T(3)	3g [3g]	1.0	0.0	0.0
Ga(2)	3g [3g]	0.0	1.0	1.0

ship has been indicated in Table 2, where the original $CaCu_5$ type sites are given in square brackets. It is seen from this table that one half of the original 2c sites and one third of the original 3g sites become occupied by Ga atoms. The remaining two thirds of the latter site form a new site in the YCo_3Ga_2 type, characterised by its exclusive occupation with Co atoms (6m), while the former one third form a site that is exclusively occupied by Ga atoms (3g).

It was mentioned already that a prominent change with respect to the $CaCu_5$ type structure of YCo_5 is that one third of the Y atoms are shifted to the $z = 1/2$ level in the YCo_3Ga_2 type structure. In the data presented in Table 1 this latter site (1a) is occupied by the Tb(1) atoms, the Tb(2) atoms occupying the 2c sites. The Tb(1) atoms have by far the more symmetric coordination shell. Using the atomic position parameters listed in Table 1, one finds that these Tb atoms have six nearest neighbours in the basal plane in the form of a regular hexagon, consisting exclusively of Ni atoms. There are 12 near neighbours in the form of two hexagons in the planes at 1/2c above and below the basal plane. These neighbour positions are statistically occupied by equal amounts of Ni and Ga atoms. Also, the Tb(2) atoms are coordinated by 18 neighbour atoms but the six neighbour atoms located in the same plane as the Tb(2) atoms consist of a statistical mixture of Ni and Ga atoms. The six neighbour atoms in the planes at 1/2c above and below the Tb(2) planes consist also of equal amounts of Ni and Ga atoms in the form of interpenetrating triangles of Ni and Ga atoms. By inspecting the projection of the structure onto the [001] plane shown in Fig. 3, it is easily verified that the number of near Tb neighbours and the corresponding Tb–Tb distances are also completely different for the two Tb sites. In view of the expected differences in molecular field and crystal field between the two Tb sites, it is not surprising that we found the corresponding ordered Tb moments to also show quite substantial differences.

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