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CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE OF $TbGe_2$

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Summary

Results of a structure determination based on X-ray diffraction and neutron diffraction are reported for $TbGe_2$. The crystal structure is orthorhombic (space group *Cmmm*) and the lattice constants are $a = 4.114$ Å, $b = 29.873$ Å and $c = 4.005$ Å. Results of magnetic measurements and neutron diffraction are reported which show that $TbGe_2$ orders antiferromagnetically below $T_N = 41$ K. The magnetic structure is a collinear antiferromagnetic arrangement of the terbium moments with the same unit cell as the chemical unit cell. The terbium moments are oriented parallel to the *c* direction.

1. Introduction

Recently we studied the properties of $TbGe_x$ alloys in the concentration range $1.55 \leqslant x \leqslant 1.72$ and found that the stoichiometry of the intermetallic phase in this range corresponds to Tb_3Ge_5 [1]. This compound has an orthorhombic structure with $a = 5.7424$ Å, $b = 17.2271$ Å and $c = 13.6943$ Å and details of the neutron diffraction analysis showed that the structure of Tb_3Ge_5 derives from the defect α-$ThSi_2$ structure. During this investigation we found that X-ray diagrams of samples of a more germanium-rich composition than Tb_3Ge_5 contained an additional set of lines not belonging to the Tb_3Ge_5 pattern. The occurrence of a compound $TbGe_2$, which is close in composition to Tb_3Ge_5, has been reported by several authors [2 - 4]. We were not able, however, to index the additional set of lines which we observed on the basis of the various structure types suggested for $TbGe_2$. This prompted us to prepare $TbGe_2$ and study its crystal structure in more detail.

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2. Experimental details

Various rare earth germanium samples were prepared by arc melting in an atmosphere of purified argon gas. The purity of the starting materials was 99.9% for terbium and 99.99% for germanium. After arc melting the samples were vacuum annealed for 3 weeks at 800 °C. After annealing the samples were powdered and examined by standard X-ray diffraction using Cu Kα and Cr Kα radiation. The neutron diffraction data were collected on a powder sample of $TbGe_2$ (λ = 1.713 Å) with the DMC (double axis multi counter system) at the Saphir Reactor, Würenlingen. The step increment of the diffraction angle 2θ was 0.10°. The data were corrected for absorption and evaluated by the line profile analysis method [5]. The magnetic properties of the compound $TbGe_2$ were studied in the range 4.2 - 300 K on a home-built σ–T recorder based on the Faraday method.

3. Magnetic properties

The results of the magnetic measurements are shown in Fig. 1. It is seen that $TbGe_2$ has a Néel-type transition at T_N = 41 K. Above this temperature the reciprocal susceptibility follows Curie–Weiss behaviour. From the slope and the horizontal intercept we derived the values μ_{eff} = 10.0 μ_B (Tb atom)$^{-1}$ and θ_p = −50 K. These values are in good agreement with those reported by Sekizawa *et al.* for $TbGe_2$ [2].

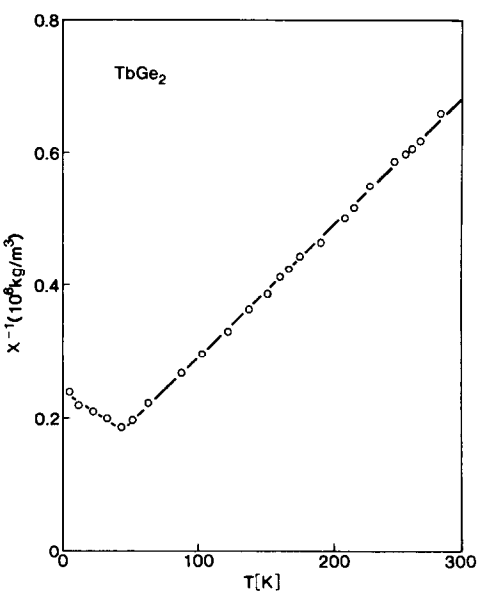

Fig. 1. Temperature dependence of the reciprocal susceptibility (χ^{-1}) for the compound $TbGe_2$.

4. The crystal structure of $TbGe_2$

It proved possible to index most of the diffraction lines observed in the X-ray diagram of $TbGe_2$ on the basis of an orthorhombic unit cell with the lattice constants $a = 4.114$ Å, $b = 29.873$ Å and $c = 4.005$ Å. Systematic extinctions led to space group *Cmmm* (number 65). A computer program [6] was used to generate a trial structure. After refinement the realiability factor was equal to 11%. The corresponding atomic position parameters are listed in Table 1. The relatively small number of reflection lines that were excluded from this analysis could be shown to belong to a more germanium-rich phase than $TbGe_2$. In the system $TbGe_x$ the intensity of this set of lines was found to increase strongly for samples in which x was larger than two. In the X-ray diagram of $DyGe_2$, for which we also performed a structure determination, the additional sets of lines were absent. The 70 K neutron data shown in Fig. 2 were used for the refinement of the nuclear structure. All

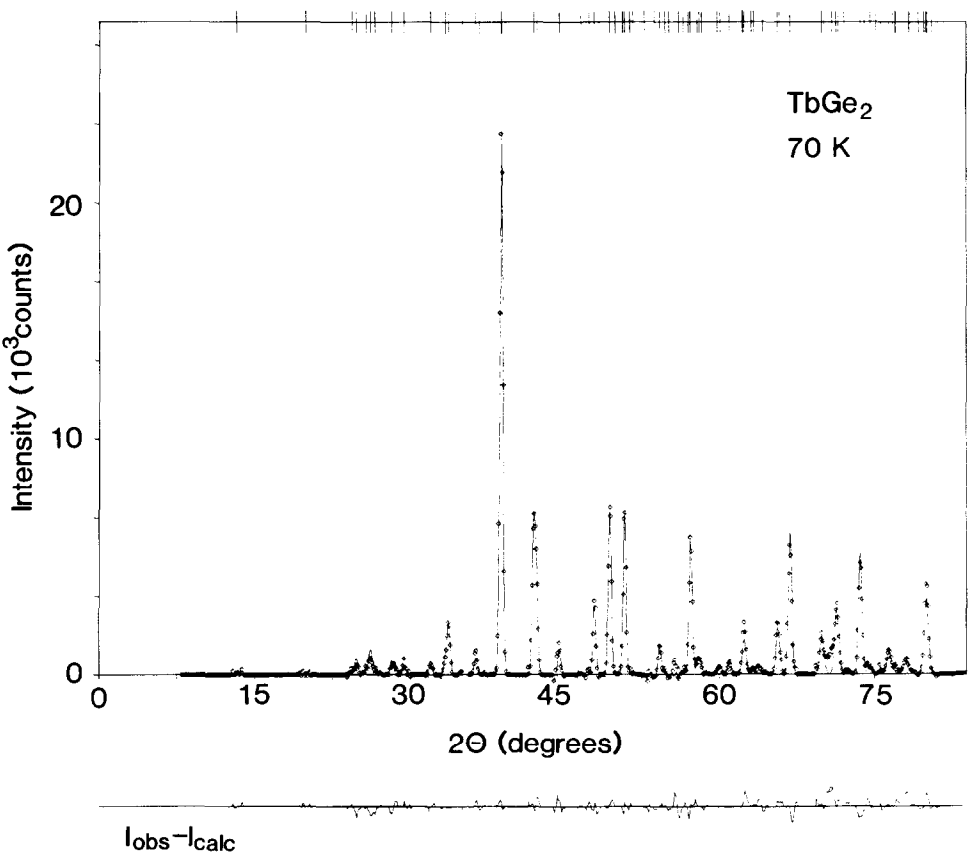

Fig. 2. Neutron diffraction pattern of $TbGe_2$ in the paramagnetic state (70 K). The points represent the observed intensitiies corrected for absorption and the background and the lines of the germanium-rich impurity phase described in the text. The trace represents the profile calculated by least-squares fitting.

TABLE 1

The refined parameters from the 70 K (nuclear data) and 4.2 K (magnetically ordered data) of $TbGe_2$ compared with 293 K X-ray data

Cmmm Orthorhombic	*70 K neutron*			*4.2 K neutron*				*293 K X-ray*		
Atom site	*x*	*y*	*z*	*x*	*y*	*z*	μ_z (Tb) (μ_B)	*x*	*y*	*z*
Tb1 4(i)	0.0	0.4234(4)	0.0	0.0	0.4263(3)	0.0	9.45(8)	0.0	0.4249(3)	0.0
Tb2 4(j)	0.0	0.3077(5)	0.5	0.0	0.3098(3)	0.5	7.55(7)	0.0	0.3091(5)	0.5
Ge1 2(a)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ge2 2(c)	0.5	0.0	0.5	0.5	0.0	0.5	—	0.5	0.0	0.5
Ge3 4(i)	0.0	0.1572(5)	0.0	0.0	0.1573(7)	0.0	—	0.0	0.1538(6)	0.0
Ge4 4(i)	0.0	0.2384(3)	0.0	0.0	0.2393(5)	0.0	—	0.0	0.2424(6)	0.0
Ge5 4(j)	0.0	0.1053(4)	0.5	0.0	0.1087(6)	0.0	—	0.0	0.1016	0.5
a (Å)		4.1000(4)			4.0964(3)				4.114(1)	
b (Å)		29.832(3)			29.834(4)				29.873(2)	
c (Å), B_{of} (Å^{-2})		3.9915(4), 0.95			3.9877(4), 0.75				4.005(2)	
R_n, R_m, R_{wp}, R_{exp}%		9.5, —, 15, 5.5			7.7, 5.1, 12.8, 8.1				11%	

nuclear lines have been indexed with the same orhtorhombic C-centred cell as derived from X-ray data ($a = 4.114$, $b = 29.873$, $c = 4.005$). Also the nuclear diffraction pattern contained the set of additional impurity lines discussed above. These were left out of consideration in the refinement. However, some more overlapping lines might still be hidden under the peaks since the R factors did not decrease on further refinement ($R_n = 9.5\%$, $R_{wp} = 15\%$). The refined parameters are compared in Table 1 with the X-ray results.

5. The magnetic structure of $TbGe_2$

Figure 3 displays the chemical structure when viewed along [001]. This structure consists of a paired-layer stacking of trigonal prisms of terbium atoms which are all centred by germanium atoms. This kind of stacking has been observed in α-$ThSi_2$ (shown in the bottom part of the figure) as well as in the orthorhombic distorted modification ($GdSi_2$). The prism axes are in the (010) plane and point in the a or b direction. Between two successive layers the prism axis is rotated by 90°. Besides the orthorhombic deformation the difference with the α-$ThSi_2$ structure is that there are only three paired-layers instead of four, followed by a germanium layer at the mirror plane m_y ($y = 0, \frac{1}{2}$).

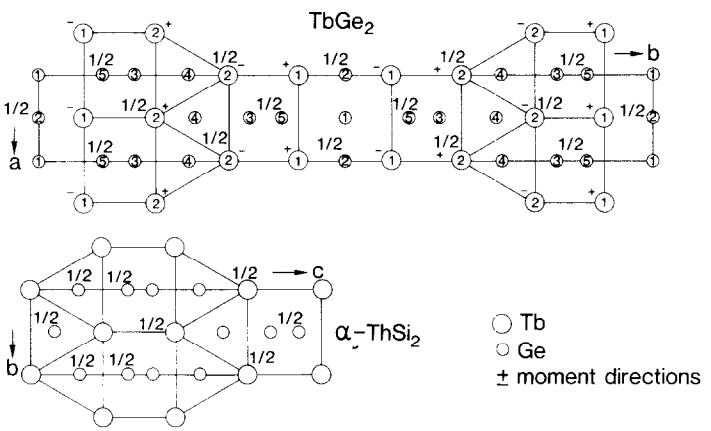

Fig. 3. Atomic and magnetic moment arrangements in the $TbGe_2$ structure when viewed along the [001] direction, showing its relation to the α-$ThSi_2$ structure. The ± signs refer to the relative direction of the terbium moments.

Figure 4 displays the neutron pattern in the ordered state at 4.2 K, the calculated and observed intensities are given in Table 2. The Néel temperature 42 ± 1 K derived from the temperature variation shown in Fig. 5 for the neutron peak having the strongest magnetic intensity (040) is in good agreement with the susceptibility measurements shown in Fig. 1. All observed magnetic reflections in Fig. 4 can be indexed with the same unit cell

TABLE 2

Some of the observed and calculated integrated neutron intensities of $TbGe_2$ at 4.2 K with wave vector $k = 0$

$h\ k\ l$	I_{nuc}	I_{mag}	I_{tot}	I_{obs}	*ESD*
0 2 0	509	3449	3958	3987	128
0 4 0	15	33557	33572	33941	215
1 1 0	50	468	518	524	90
0 0 1	346	0	346	207	66
0 2 1	110	650	762	550	62
1 3 0	564	8964	9528	9300	116
0 8 0	248	694	942	1006	73
0 4 1	366	20	386	604	96
1 5 0	178	3240	3420	3442	108
0 6 1	302	948	1248	1494	104
0 10 0	189	403	593	594	66
1 7 0	1152	2288	3442	3554	48
1 1 1	100	3560	3656	3872	108
1 3 1	284	1008	1292	1608	80
0 8 1	34	670	704	356	72
1 5 1	9476	424	9900	9920	144
1 9 0	458	42	500	490	8
0 10 1	2538	2134	4672	4548	96
1 7 1	1460	460	1916	1896	80
1 11 0	646	2196	2842	3062	104
1 9 1	8	4792	4804	5060	114
0 14 0	0	683	684	897	66
0 12 1	1476	62	1538	1836	84
2 0 0	3097	0	3097	2997	90
2 2 0	18	72	90	80	62
1 13 0	130	30	160	210	38
0 0 2	2937	0	2937	3355	80
0 2 2	18	2	20	20	0
2 4 0	2	2690	2392	2802	74
1 11 1	8	220	228	256	56
0 4 2	2	166	168	354	86
2 6 0	4	102	104	82	64
0 14 1	612	40	652	654	64
0 16 0	159	221	380	313	59
0 6 2	4	14	16	48	56
2 0 1	146	0	146	210	62
2 2 1	48	1992	2044	1996	72
2 8 0	116	188	304	278	14
1 1 2	20	20	40	40	0
1 13 1	908	8	920	910	5
1 15 0	1498	1330	2828	2832	66
2 4 1	188	20	208	172	32
1 3 2	248	480	728	592	48
0 8 2	112	38	150	38	52
1 5 2	92	248	340	504	56
2 6 1	184	704	892	1020	64
0 16 1	172	632	804	832	62
2 10 0	132	154	276	280	34
0 10 2	120	44	164	120	40
1 7 2	736	260	996	1032	60
2 8 1	24	452	476	532	64

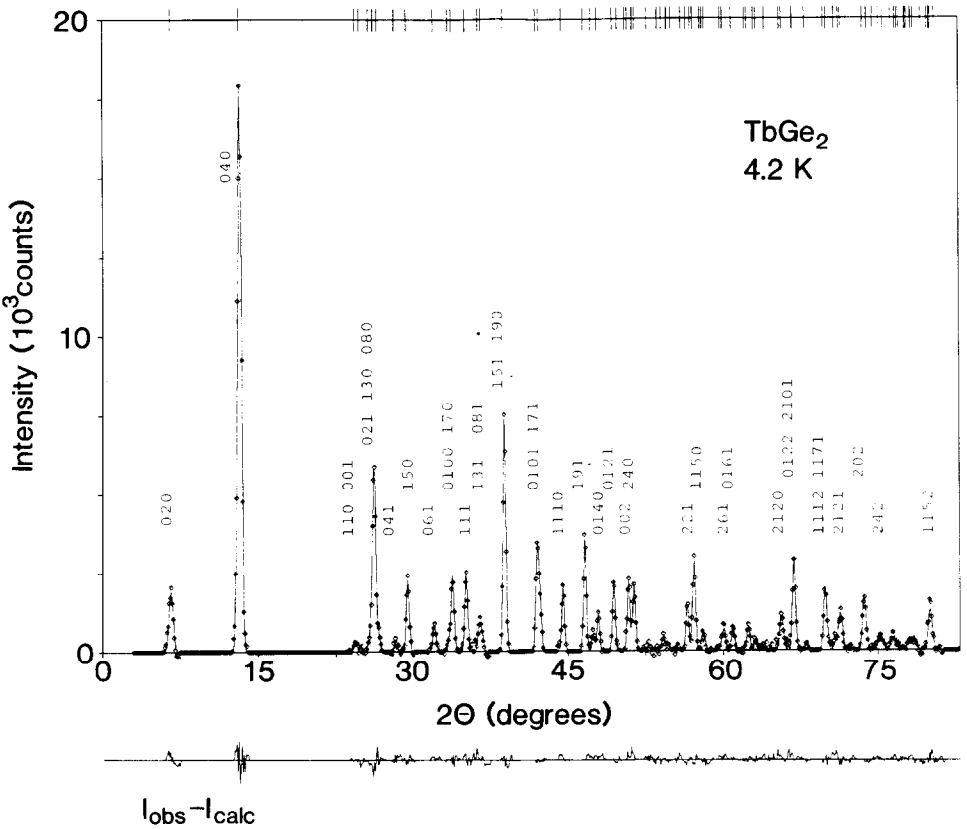

Fig. 4. Neutron diffraction pattern of $TbGe_2$ in the magnetically ordered state (4.2 K). The points represent the observed intensities corrected for absorption and the background and for the lines of the germanium-rich impurity phase described in the text. The trace represents the profile calculated by the least-squares fitting.

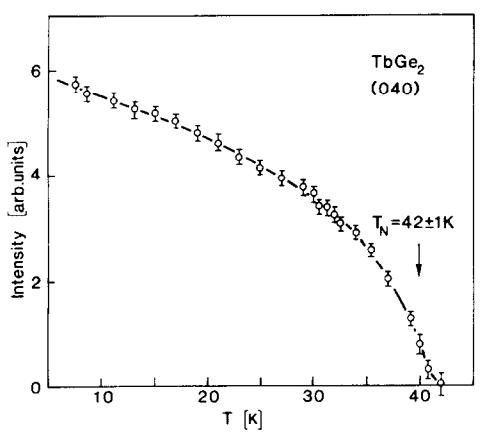

Fig. 5. Temperature dependence of the integrated neutron intensity of the magnetic reflection (040) of $TbGe_2$.

as found for the nuclear reflections ($k = 0$). The terbium atoms are distributed into two special symmetry positions corresponding to 4(i) with the parameters (0, 0.426, 0.) and to 4(j) with the parameters (0, 0.309, 0.5). These positions are located at the intersection of two mirror planes and a two-fold axis $m2m$, and would only allow for a moment arrangement parallel to the x axis. However, the refinement of the magnetic intensities has shown that the magnetic structure has a lower symmetry than the crystallographic structure and can be described by the monoclinic space group Cm_y with a collinear antiferromagnetic arrangement parallel to the c axis. The two terbium positions have their moment directions antiparallel. The magnetic mode describing the uniaxial arrangement is G_z (+ − + −), the signs referring to the atoms enumerated for C_{1m1} in a sequence corresponding to the International Tables. The moment values found from the refinement procedure are 9.4 μ_B and −7.7 μ_B for the terbium atoms at 4(i) and 4(j) respectively. These values are close to the free ion value of Tb^{3+} ($gJ\mu_B = 9\ \mu_B$). In Fig. 3 we have assigned a ± sign to the μ_z moment direction of the terbium atoms. The uniaxial moment arrangement in $TbGe_2$ can be seen as an alternating + − + − ... stacking of ferromagnetic terbium layers with the terbium moments perpendicular to the longest orthorhombic axis b. This corresponds, in principle, to the same kind of arrangement as found in the compound $TbGe_{1.67}$, the only difference being the moment direction which in the latter compound is parallel to the longest axis c (tetragonal).

6. Concluding remarks

We have confirmed the results reported already by several other authors that there exists a compound of the stoichiometry $TbGe_2$ [2 - 4]. By contrast, we did not confirm any of the crystal structures proposed for this compound in the literature. Instead we found that $TbGe_2$ crystallizes in a novel type of structure that has been determined in the course of the present investigation. We have shown that the $TbGe_2$ structure bears some similarity to the α-$ThSi_2$-type of structure which is also the basic structure of the $TbGe_{1.67}$ compound [1]. It is of interest to note, that in spite of the structural similarity, there is a remarkable influence of the stoichiometry on the magnetic properties. Besides the change of the magnetic moment direction the Néel temperature decreases by more than 55% ($T_N = 41$ K for $TbGe_2$ while $T_N = 17$ K for $TbGe_{1.67}$) for a change in germanium concentration of only 5 at.%.

Chourasia *et al.* [7, 8] studied compounds of the type RGe_2 by means of extended X-ray absorption fine structure (EXAFS) Although these authors prepared their samples with 1:2 stoichiometry, they did not give any details regarding the crystal structure of RGe_2 but assumed that these materials crystallize in the α-$ThSi_2$ type. By means of EXAFS measurements the following bond lengths were determined: $d_{Ge-Ge} = 2.25 \pm 0.01$ Å and $d_{Tb-Ge} = 2.99 \pm 0.01$ Å. These values do not compare favourably with the

TABLE 3

Interatomic separation between two germanium atoms and between terbium and germanium (in Å) in the crystal structure of $TbGe_2$; only distances below 4 Å were considered

Ge(4)—Ge(4)	2.171 ± 0.004	Tb(2)—Ge(4)	2.880 ± 0.012
Ge(3)—Ge(5)	2.532 ± 0.012	Tb(1)—Ge(5)	2.996 ± 0.005
Ge(4)—Ge(3)	2.426 ± 0.017	Tb(2)—Ge(3)	3.056 ± 0.007
Ge(1)—Ge(2)	2.871 ± 0.000	Tb(1)—Ge(1)	3.077 ± 0.009
Ge(1)—Ge(5)	3.729 ± 0.010	Tb(1)—Ge(3)	3.167 ± 0.014
Ge(2)—Ge(5)	3.758 ± 0.010	Tb(2)—Ge(5)	3.314 ± 0.015

bond distances shown in Table 3, calculated on the basis of our structure determination for $TbGe_2$. In these calculations we have restricted ourselves to nearest and near neighbour distances within a sphere of 4 Å from the central atom (germanium or terbium) considered. Inspection of the distances given in Table 3 shows that the value $d_{Ge-Ge} = 2.25$ Å reported by Chourasia *et al.* [7, 8] would correspond to our value for the Ge(4)—GE(4) separation while their value $d_{Tb-Ge} = 2.99$ Å would correspond to the distance between the atoms Tb(1) and Ge(5). But both distances (Ge(4)—Ge(4) and Tb(1)—Ge(4)) can hardly be regarded as average Ge—Ge and Tb—Ge bond distances representative of $TbGe_2$.

It is of interest to study in how far the structure type found in the course of the present investigation occurs in other R—Ge systems. We mentioned already that this is the case for $DyGe_2$. Preliminary investigations furthermore showed that RGe_2 compounds with the same structure are also found for R ≡ Ho and Er but not for the light rare earth elements. A similar change in crystal structure for compounds of the RGe_2 stoichiometry has already been reported by Sekizawa [2]. In fact, there are several reasons that make us believe that the compounds with orthorhombic structure found by the latter author are the same as those studied by us. There is an almost perfect match between the magnetic properties determined for $TbGe_2$ by Sekizawa and those presented in Section 3. There is a simple relation between the lattice constants proposed by Sekizawa (a^*, b^*, c^*) and those associated with the crystal structure described above (a, b, c), namely $a^* \approx 2c$, $b^* \approx 2a$ and $c^* \approx \frac{1}{2}b$. Using the results of both investigations one may draw the conclusion that compounds of the RGe_2 stoichiometry adopt the tetragonal α-$ThSi_2$ structure when R is a light rare earth element whereas the orthorhombic $TbGe_2$ type is found when R is a heavy rare earth element.

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