Journal of Alloys and Compounds, 187 (1992) 73–80
JALCOM 311

Magnetic ordering of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ studied by neutron diffraction and magnetic measurements

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(Received February 19, 1992)

Abstract

The magnetic properties of the compounds $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ were studied by magnetic measurements and neutron diffraction. Neutron diffraction experiments made in the paramagnetic temperature range confirmed the $CeNiSi_2$ structure reported earlier for these compounds. Refined atomic position parameters for both compounds are given. Neutron diffraction measurements performed in the magnetically ordered regime showed that the rare earth moments in $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ order antiferromagnetically below $T_N = 16$ K and $T_N = 39$ K respectively. The preferred moment direction is along the c axis in both cases. Antiferromagnetic ordering was also found from magnetic measurements.

1. Introduction

Ternary silicides and germanides of the type $RMSi_2$ and $RMGe_2$ are fairly common and have been reported to exist for most rare earth elements R and for several transition metals M [1]. Their crystal structure is of the $CeNiSi_2$ type [2] which is related to both the AlB_2 type and the α-$ThSi_2$ type.

In previous studies we have investigated the magnetic properties of several silicides of the type $RNiSi_2$ and showed that antiferromagnetic ordering occurs when R is a heavy rare earth element [3] while ferromagnetism is found for light rare earth elements [4]. In the present investigation we have focused our attention on two germanides of the same series. These germanides are formed only when the M concentration is lower than would correspond to a full occupation of the nickel sites in the $CeNiSi_2$ structure [1], although x in RM_xGe_2 depends on the nature of the M component.

2. Experimental procedures and results

Samples of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ were prepared by arc melting from starting materials of at least 99.9% purity, followed by vacuum annealing

0925-8388/92/$5.00

at 800 °C for about 4 weeks. X-ray diffraction showed that after this treatment the samples were approximately single phase, the reflection lines being indexed on the basis of the orthorhombic $CeNiSi_2$ structure type [1].

The temperature dependence of the magnetization of these two compounds were studied by means of a superconducting quantum interference device magnetometer in the temperature range 4.2–350 K in magnetic field strengths

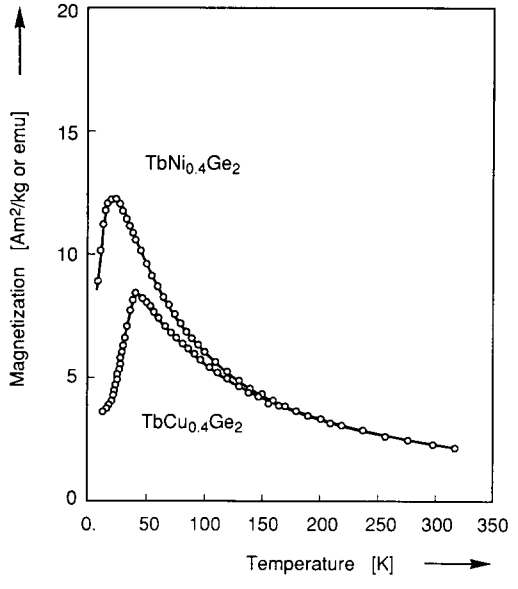

Fig. 1. Temperature dependences of the magnetization of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$.

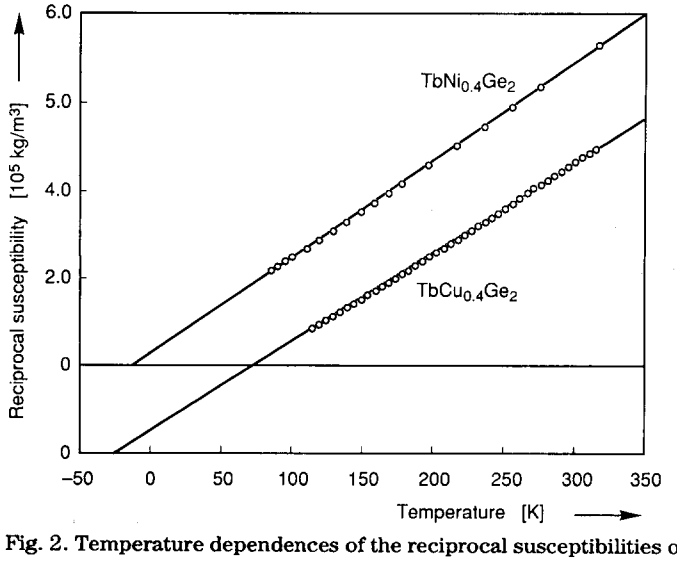

Fig. 2. Temperature dependences of the reciprocal susceptibilities of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$.

up to 20 kOe. The results are shown in Fig. 1. Néel-type transitions are seen to occur at around 23 K and 38 K for $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ respectively. The results displayed in Fig. 2 show that in the range well above T_N the reciprocal susceptibility χ^{-1} behaves very closely according to the Curie–Weiss law. The corresponding effective moments $9.89\mu_B$ for $TbNi_{0.4}Ge_2$ and $10.40\mu_B$ for $TbCu_{0.4}Ge_2$ are close to the free-Tb^{3+}-ion value.

Neutron diffraction data were obtained from $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ with the double-axis multicounter system at the SAPHIRE reactor, Würenlingen, using $\lambda = 0.17059$ nm and step increments of the diffraction angle 2θ of 0.10°. Measurements were made in the paramagnetic range as well as in the magnetically ordered range. All data were corrected for absorption and evaluated by means of the line profile analysis method [5, 6]. The scattering lengths and magnetic form factor used for the various elements are from ref. 7 and ref. 8 respectively.

The neutron diffraction data obtained in the paramagnetic regime are shown in Figs. 3(a) and 4(a). They confirm the $CeNiSi_2$ type of structure [1]. Refine structural parameters are given for both compounds in Tables 1 and 2.

The low temperature neutron diffraction patterns of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$ were collected with a counting rate twice that used for the nuclear data. The results are shown in Figs. 3(b) and 4(b). It can be seen from Figs. 3 and 4 that all magnetic reflections appear at reciprocal-lattice positions of the chemical unit cell.

In addition to the main magnetic reflections, one observes in the small-angle 2θ region in the $TbNi_{0.4}Ge_2$ pattern a wavy and broad intensity contribution at around $2\theta = 20°$, which might indicate the presence of short-range order effects. One may also discern four further weak magnetic contributions at 2θ values of 9.09°, 17.28°, 20.16° and 21.45°. The last two reflections are not well resolved from the wavy background. Although the first two peaks could be indexed as $(\frac{3}{2}00)$ and $(02\frac{1}{2})$, which would correspond to a cell doubling in the a and c directions, they may not belong to the ordered $TbNi_{0.4}Ge_2$ main phase. There are two arguments supporting this assumption: (a) the presence of foreign contributions in the nuclear pattern shown in Fig. 4 and (b) the difference in temperature dependence between the intensities of the two reflections mentioned and the magnetic reflections of the main phase.

The latter fact may be seen from Fig. 5 which shows that these contributions and the short-range order persist above the Néel temperature $T_N = 16$ K where the magnetic contribution of the main (020) reflection has completely disappeared already (see also Fig. 6). As already mentioned, this behaviour suggests that these contributions have to be attributed to an impurity phase. For this reason, not much importance was attributed to them and they were excluded from the refinement.

From the absence of the allowed magnetic (001) reflection with structure factor $i\ (1-1+1-1)$ and from the strong intensity of the (020) reflection

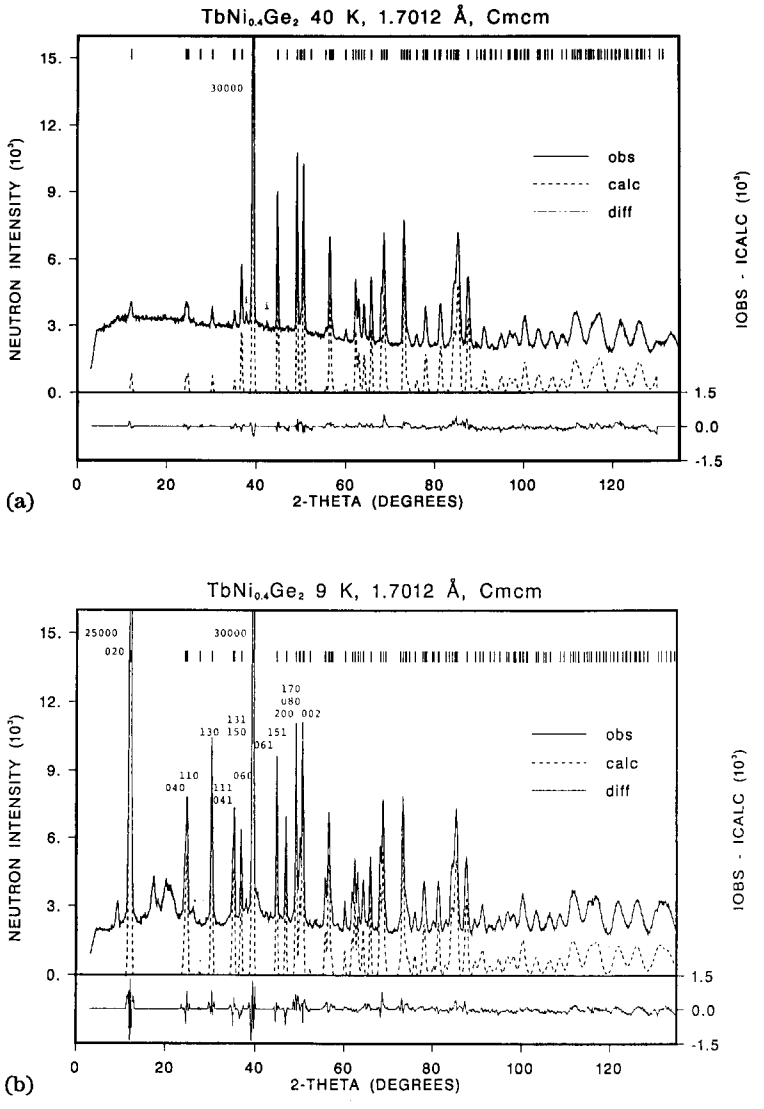

Fig. 3. (a) Neutron diffraction pattern of the compound $TbNi_{0.4}Ge_2$ in the paramagnetic range (40 K) showing observed intensities (——) and calculated intensities (– – –): i, foreign contributions. (b) Data obtained in the magnetically ordered regime (9 K). The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of the figure (right-hand scale).

with structure factor $i\,(0.97-0.97+0.97-0.97)$ in $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$, one may derive that the easy-magnetization direction is along the c axis. The refinement has converged to collinear magnetic structure with the terbium moments oriented along the c axis for both compounds. The corresponding magnetic space group is $Cm'cm$ (Sh_{63}^{459}) which allows for the 4c symmetry position only an antiferromagnetic mode of the type Gz $(+-+-)$.

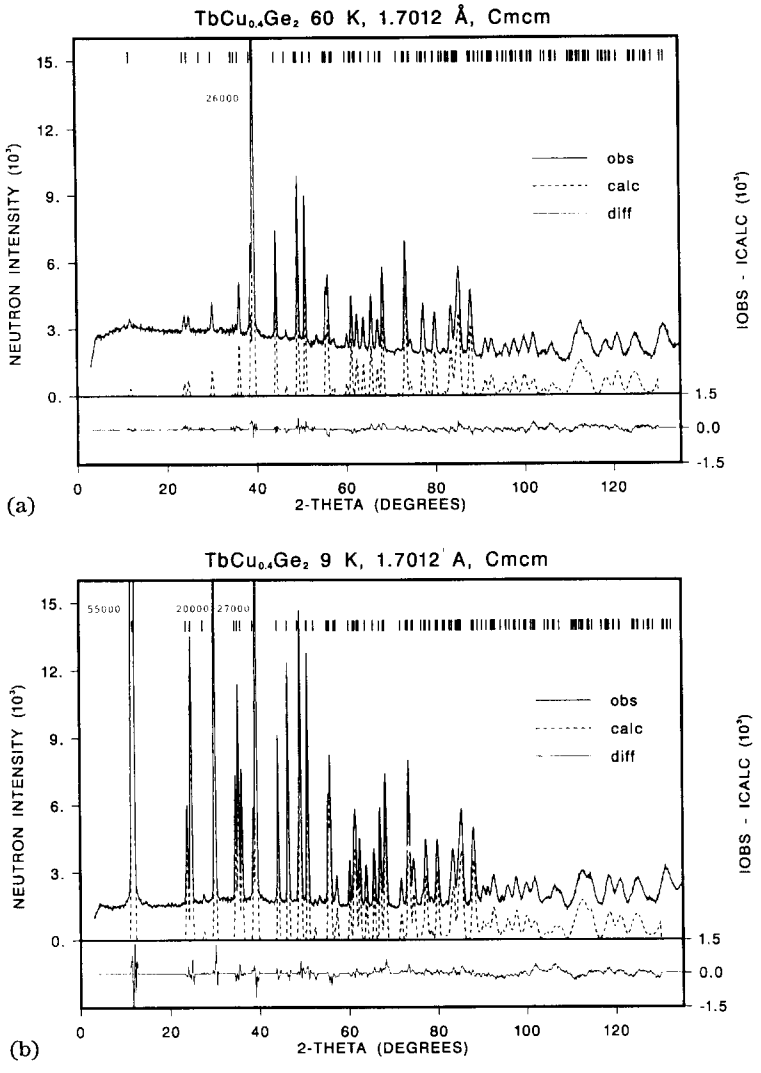

Fig. 4. (a) Neutron diffraction pattern of the compounds $TbCu_{0.4}Ge_2$ in the paramagnetic range (60 K) showing observed intensities (——) and calculated intensities (– – –). (b) Data obtained in the magnetically ordered regime (9 K). The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of the figure (right-hand scale).

3. Concluding remarks

The results obtained in the course of the present investigation have shown that the magnetic ordering temperatures of RM_xGe_2 compounds depend strongly on the nature of the M component. In going from M≡Ni to M≡Cu the magnetic ordering temperature more than doubles its value although the magnetic structures remain the same.

TABLE 1

Refined parameters for the neutron data of $TbNi_{0.4}Ge_2$ (space group, *Cmcm* (No. 63); all atoms at 4c (0, y, ¼))

Parameter	Value at the following temperatures	
	40 K	9 K
y, Tb	0.1047(1)	0.1068(2)
y, Ni	0.3117(3)	0.3197(2)
y, Si(1)	0.4508(1)	0.4601(6)
y, Si(2)	0.7489(2)	0.7507(5)
μ_z (μ_B)	–	5.60(3)
a (nm)	0.40891(2)	0.40861(3)
b (nm)	1.61422(9)	1.61508(11)
c (nm)	0.39807(2)	0.39779(3)
B_{of} (nm^2)	0.0065(2)	0.0068(1)
R_n	8.5	5.12
R_{wp} (%)	10.15	10.04
R_m	–	6.4
R_{exp} (%)	4.9	3.6

TABLE 2

Refined parameters for the neutron data of $TbCu_{0.4}Ge_2$ (space group, *Cmcm* (No. 63); all atoms at 4c (0, y, ¼))

Parameter	Value at the following temperatures	
	60 K	9 K
y, Pr	0.1063(2)	0.1047(2)
y, Ni	0.3180(3)	0.3192(6)
y, Si(1)	0.4531(2)	0.4538(2)
y, Si(2)	0.7479(2)	0.7484(2)
μ_z (μ_B)	–	8.82(5)
a (nm)	0.40929(2)	0.40901(2)
b (nm)	1.64764(10)	1.64881(10)
c (nm)	0.39663(2)	0.39624(2)
B_{of} (nm^2)	0.0049(2)	0.0009(1)
R_n	7.8	8.85
R_{wp} (%)	10.7	7.70
R_m	–	3.70
R_{exp} (%)	5.3	2.83

In the 9 K neutron diffraction pattern of $TbNi_{0.4}Ge_2$ we found some minor foreign magnetic contributions with a different thermal behaviour from that for the main reflection lines. We also found short-range order effects persisting to higher temperatures far above T_N, which in turn may be due to concentration fluctuations of the nickel atoms in $TbNi_{0.4}Ge_2$. For instance, it is not unlikely that the onset of long-range or short-range magnetic order

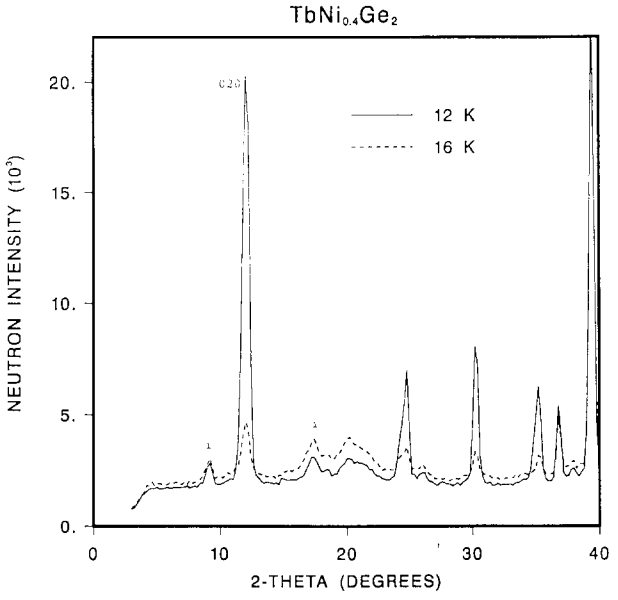

Fig. 5. Small-angle part of the neutron diffraction pattern of $TbNi_{0.4}Ge_2$ below T_N (——) and at $T_N = 16$ K (– – –): i, foreign magnetic contributions.

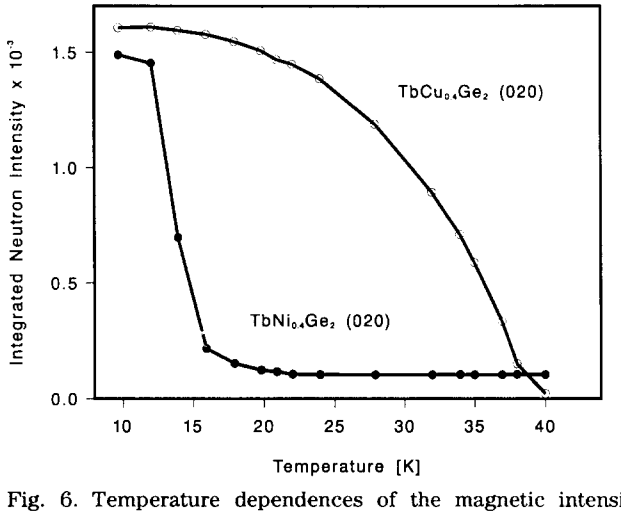

Fig. 6. Temperature dependences of the magnetic intensities of the (020) reflections of $TbNi_{0.4}Ge_2$ and $TbCu_{0.4}Ge_2$.

is strongly dependent on the nickel content and that long-range order persists only within a limited concentration region (effect of chemical pressure). Neutron diffraction studies of compounds of variable nickel concentration are needed to corroborate this interpretation and will currently be undertaken.

The refined parameters listed in Tables 1 and 2 lead to satisfactory agreement between observed and calculated diffraction patterns, as follows

from the corresponding R factors. The ordered magnetic moment value $5.70\mu_B$ of $TbNi_{0.4}Ge_2$ is lower than the value of the free ion Tb^{3+} ($gJ\mu_B = 9\mu_B$). This may be indicative of short-range order effects or of crystalline field effects. The ordered moment value for $TbCu_{0.4}Ge_2$ equals $8.82\mu_B$ which is close to the free-ion value.

The temperature dependence of the intensity of the main magnetic reflection is shown for both compounds in Fig. 6. The results show that both compounds order magnetically at quite different temperatures, 16 K for $TbNi_{0.4}Ge_2$ and 39 K for $TbCu_{0.4}Ge_2$. The transition for the nickel compound displays a more abrupt character, the difference from the T_N value derived from magnetization measurements again indicating magnetic short-range order effects.

References

1 M. François, G. Venturini, B. Malaman and B. Roques, *J. Less-Common Met., 160* (1990) 197, 215.
2 O. P. Bodak and E. I. Gladyshevskii, *Sov. Phys. Crystallogr., 14* (1970) 859.
3 P. Schobinger-Papamantellos and K. H. J. Buschow, *J. Less-Common Met., 171* (1991) 321.
4 P. Schobinger-Papamantellos and K. H. J. Buschow, *J. Alloys Comp., 217* (1992) 51.
5 H. M. Rietveld, *J. Appl. Crystallogr., 2* (1969) 65.
6 A. W. Hewat, *Rep. AERE-R7350*, 1973 (Atomic Energy Research Establishment Harwell).
7 V. Sears, *Methods Exp. Phys. A, 23* (1986) 521.
8 A. J. Freeman and I. P. Desclaux, *J. Magn. Magn. Mater., 12* (1979) 11.