Journal of Magnetism and Magnetic Materials 324 (2012) 657–659

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Letter to the Editor

Magnetic structure of $TmCu_2Ge_2$

B. Penc [a,*], S. Gerischer [b], A. Hoser [b], A. Szytuła [a]

[a] M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland
[b] BENSC, Helmholtz–Zentrum Berlin, Hahn–Meitner–Platz 1, D-14 109 Berlin, Germany

ARTICLE INFO

Article history:
Received 25 July 2011
Received in revised form
16 September 2011
Available online 29 September 2011

Keywords:
Magnetically ordered material
Magnetic structure
Neutron diffraction

ABSTRACT

$TmCu_2Ge_2$ compound crystallizes in the tetragonal $ThCr_2Si_2$-type crystal structure. The neutron diffraction reveals the presence of an incommensurate antiferromagnetic order below $T_N=2.5$ K. The Tm magnetic moment of 5.0(1) μ_B at 0.47 K is parallel to the *c*-axis. The order is described by the propagation vector $\boldsymbol{k}=[k_x, k_x, 0]$, where $k_x=0.117(3)$. The increase of the values of the components k_x near the Néel temperature is observed.

1. Introduction

Ternary RCu_2Ge_2 compounds (R is a rare earth element) crystallize in the tetragonal $ThCr_2Si_2$-type structure [1]. An antiferromagnetic order described by the propagation vector $\boldsymbol{k}=$ (½, 0,½) was found in some of these compounds with the heavy rare earth elements [2–5]. $TmCu_2Ge_2$ compound was reported to be paramagnetic down to 4.2 K [6]. ^{169}Tm Mössbauer investigation of the $TmCu_2Ge_2$ compound indicates more significant influence on the crystal field interaction at the rare-earth site [7]. The ^{197}Tm Mössbauer spectroscopy data for $TmCu_2Ge_2$ do not show the magnetic order up to 4.2 K. The new magnetic and specific heat data give the anomaly connected with the phase transition para–antiferro magnetic at 3.8 K [8]. This work reports the results of the temperature dependence of the neutron powder diffraction data for a polycrystalline sample of $TmCu_2Ge_2$ in order to determine the magnetic structure of this compound.

2. Experimental details

The sample was obtained by arc melting of the constituent elements taken in the stoichiometric ratio 1:2:2. The purity was 3 N (Tm), 4 N (Cu) and 5 N (Ge). The melting was performed in a purified argon atmosphere. The sample was subsequently vacuum annealed at 800 °C for 1 week. Next the sample was examined by X-ray powder diffraction at room temperature on a Philips PW-3710 X'PERT diffractometer using CuKα radiation. Neutron diffraction patterns were recorded with the use of an E6 diffractometer located at the Berlin Neutron Scattering Center in the Helmholtz Center Berlin for Materials and Energy. The incident neutron wavelength was 2.45 Å. The powder sample was enclosed in a cylindrical copper container with a diameter of 8 mm. For a better thermal contact a small amount of the deuterated methanol–ethanol mixture was dropped into the container. The data were collected at several temperatures between 0.47 K and 4.17 K, using an ILL-type cryostat with a ^{3}He insert in it. The 2Θ range was $3.4^\circ - 122.6^\circ$.

The neutron diffraction data were analyzed with the use of the Rietveld-type program FULLPROF (version 4.60—March 2009) [9].

3. Results

The X-ray diffraction data collected at room temperature as well as the neutron diffraction data recorded at 4.17 K (see Fig. 1) unambiguously confirmed that $TmCu_2Ge_2$ crystallizes in a tetragonal unit cell of $ThCr_2Si_2$-type (space group I4/mmm; no. 139). In this structure the atoms are located at the following sites;

2 Tm atoms at 2(a): 0,0,0;
4 Cu atoms at 4(d): 0, ½, ¼; ½, 0, ¼;
4 Ge atoms at 4(e): 0, 0, *z*; 0, 0, $-z$
+ the body centering translation.

The values of the lattice parameters and the free positional parameter *z* determined from the x-ray data at room temperature and neutron diffraction data at 0.47 and 4.17 K are listed in Table 1.

In the neutron diffraction pattern at $T=0.47$ K additional peaks of the magnetic ordering are observed. (see Fig. 1) These peaks are indexed by the propagation vector $\boldsymbol{k}=(0.117(3), 0.117(3), 0)$. The intensities of the magnetic peaks were calculated using the FullProf program [9]. The best fit was obtained for a sine modulated magnetic structure (Fig. 2). The magnetic moment distribution is

* Corresponding author.
E-mail address: ufpenc@cyf-kr.edu.pl (B. Penc).

0304-8853/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2011.09.033

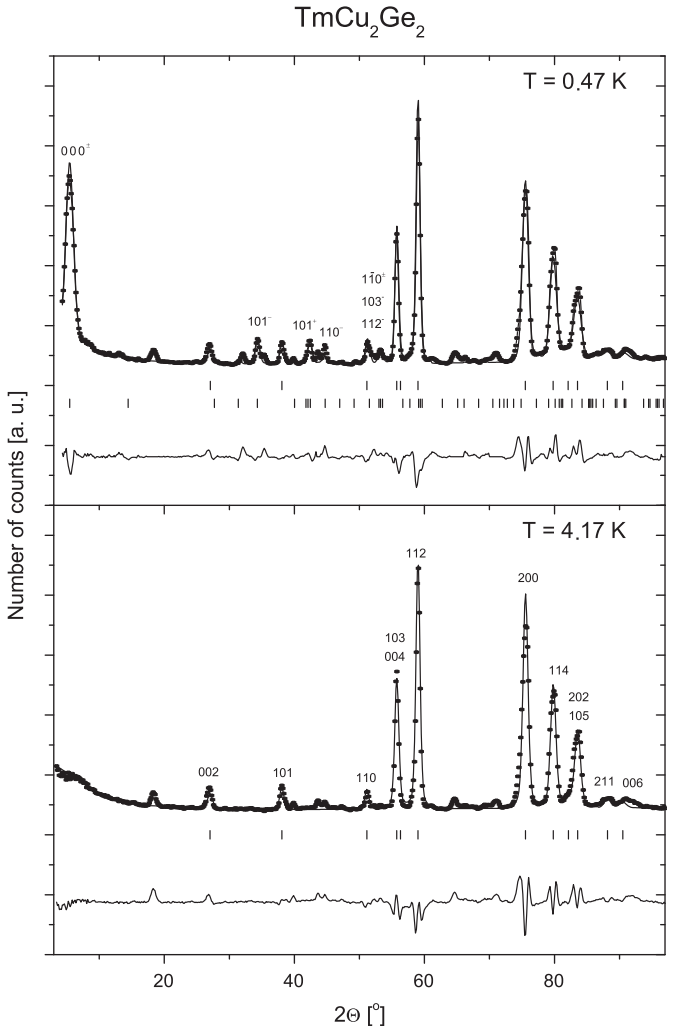

Fig. 1. Neutron diffraction pattern of $TmCu_2Ge_2$ collected at 0.47 and 4. 17 K. The squares represent experimental points; the solid curves are the calculated profiles for the model crystal and magnetic structures described in the text and the difference between observed and calculated intensities (at the bottom of diagram). The vertical bars indicate the Bragg peaks of nuclear and magnetic origin. The peaks at 2Θ equal to 64.5° and 74.2° are connected with the cryostat (Al). The other peaks of small intensities are connected with the unknown impurity phase.

Table 1
Lattice parameters a and c, unit cell volume, a/c ratio, Ge positional parameter z and magnetic data of $TmCu_2Ge_2$ derived from the X-ray data at room temperature and the neutron diffraction data collected at 0.47 and 4.17 K.

T (K)	300	4.17	0.47
a (Å)	3.9914(2)	3.9785(12)	3.9853(12)
c (Å)	10.3277(5)	10.3056(37)	10.3394(42)
V (Å^3)	164.53(3)	163.12(16)	164.22(16)
a/c	2.5875(2)	2.590(2)	2.594(2)
z	0.3821(2)	0.3822(6)	0.3801(6)
R_{Bragg} (%)	3.5	2.9	2.8
R_{prof} (%)	2.9	2.6	2.5
z	0.3821(2)	0.3822(6)	0.3801(6)
μ (μ_B)			5.0(1)
k_x			0.117(3)
R_{mag} (%)			4.1

then described by

$$\mu(\mathbf{r}) = \mu_0 \cos(2\pi \mathbf{k}.\mathbf{r})$$

where μ_0 denotes the amplitude of modulation, $\boldsymbol{k}$ is a propagation vector, $\boldsymbol{r}$ is a vector pointing from the origin of the coordinate system.

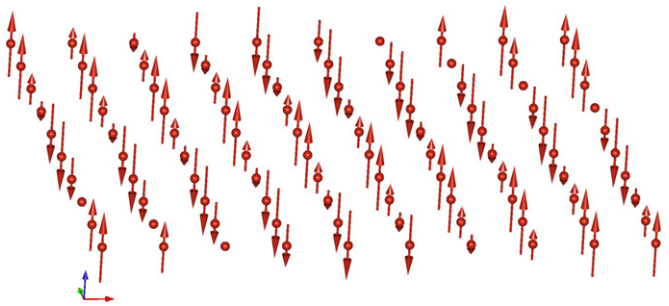

Fig. 2. Magnetic structure of $TmCu_2Ge_2$. Distribution of the magnetic moments basal plain a-a.

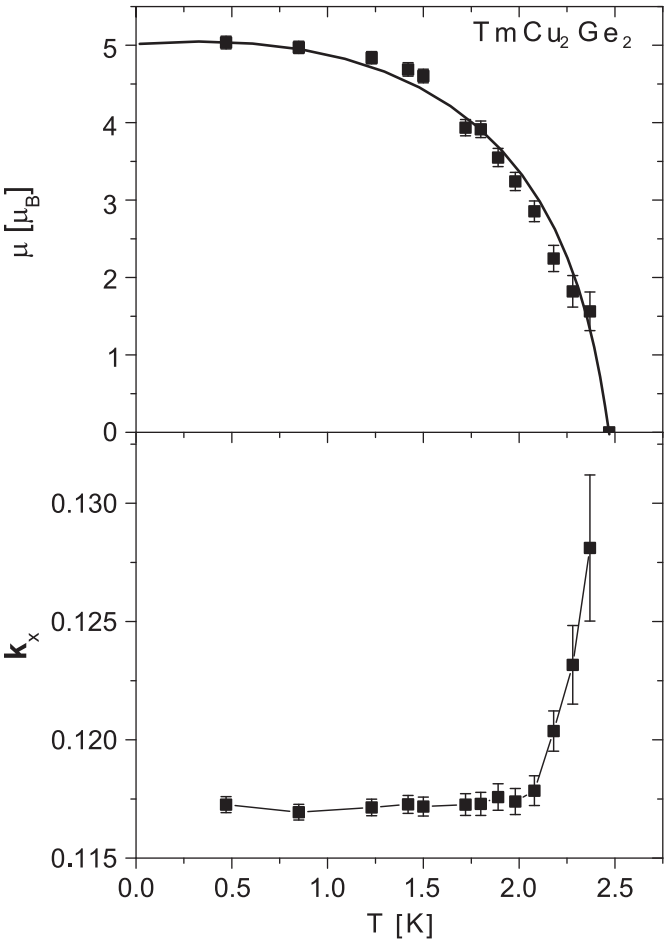

Fig. 3. Temperature dependence of the Tm magnetic moment μ and k_x component of the propagation vector for $TmCu_2Ge_2$.

The best fit was found for the magnetic moments equal to 5.0(1) μ_B at 0.47 K parallel to the c-axis. The temperature dependence of the (000) $\pm$ magnetic satellite indicates the Néel temperature to be equal to 2.5 K. The analysis of the magnetic part of neutron diffraction pattern as a function of temperature indicates that the value of the propagation vector is constant in the temperature range 0.47–2.08 K and next increases up to the Néel temperature (see Fig. 3).

4. Discussion

The magnetic ordering determined in the case of $TmCu_2Ge_2$ is different from those observed in other RCu_2Ge_2 compounds,

which is similar to that observed in isostructural $TmCu_2Si_2$ [10,11].

The ordering observed in both $TmCu_2X_2$ (X=Si, Ge) compounds can be visualized as the (110) ferromagnetic plane with a sine modulation along the [110] direction. This type of magnetic structure can be described by the two exchange integrals considering nearest (J_1) and next nearest neighbors (J_2) exchange between atoms belonging to the same (001) plane of the form [12]: $J(k)=2J_1(\cos 2\pi k_x+\cos 2\pi k_y)+4J_2(\cos 2\pi k_x+\cos 2\pi k_y)$.

The incommensurate structure with $\boldsymbol{k}=(k_x, k_x, 0)$ corresponding to the $TmCu_2X_2$ (X=Si, Ge) compounds is stable for $J_1>0$, $J_2<0$ and $|J_1|\sim|J_2|$.

For $TmCu_2Ge_2$ the value of the k_x component of the propagation vector equals 0.117(3), near the value for isostructural $TmCu_2Si_2$, which is equal to 0.147 [10,11]. Also the value of the Tm magnetic moment, equal to 5.03(8) μ_B, is close to the value for $TmCu_2Si_2$ (5.10(3) μ_B) [11]. The large discrepancy between the Néel temperatures: experimental equals 2.5 K and calculated on the basis of the de Gennes formula (scaling for $GdCu_2Ge_2$, $T_N=12$ K) gives $T_N=0.9$ K, indicates the influence of the crystal electric field.

The relevant Hamiltonian for the crystalline electric field of the tetragonal symmetry D_{4n} of Tm^{3+} ion in the present crystal is given by $H_{CEF}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4$ where O_l^m are the Stevens equivalent operators expressed by the angular momentum J_x, J_y and J_z and B_l^m are the CEF parameters. The 4f multiple of Tm^{3+} ($J=6$) splits into seven singlets and three doublets. The values of the B_l^m parameters for $TmCu_2Si_2$ determined by the different methods are presented in Refs. [11,13–16]. The results of these investigations indicate that the B_2^0 parameter is negative, which in the prediction Greedan and Rao [17] suggests that the magnetic moment is parallel to the *c*-axis. This is in good agreement with the experimental result. The CEF levels consist of a singlet ground state, a singlet first excited state at 6.1 K, a doublet second excited state at 79.6 K and so on [11]. Temperature dependences of the quadrupole splittings are similar for both $TmCu_2X_2$ (X=Si, Ge) compounds [7]. This suggests similar influence of the crystal electric field. The small difference between the magnetic parameters of both Tm compounds with X=Si and Ge indicates the small change of the CEF parameters with the change of X element.

The relatively small values of the magnetic moments in both compounds near 5 μ_B might be due to the reduction of $\langle J_z\rangle$ value of the CEF ground state [16].

The increase of the lattice parameters a and c at 0.47 K is probably connected with the magnetostriction effect and/or the alignment of the quadrupole moment of thulium charge distribution in the electric field gradient of the noncubic lattice sites for the tetragonal $ThCr_2Si_2$ structure. Increases of the lattice constants at low temperatures are observed in isostructural $TmCu_2Si_2$ and RCu_2Si_2 (R=heavy rare earth element) compounds with $L\neq 0$ [18]. The data from the ^{169}Tm Mössbauer spectra for $TmCu_2X_2$ (X=Si, Ge) compounds give the large increase of the quadrupole splitting at low temperatures [11,12,15].

The Difference in values of critical temperatures of the magnetic order observed in this work and in Ref. [8] result probably because the investigated samples are of different compositions. The data in Ref. [19] indicate six compounds with the stoichiometry 1:2:2, 2:1:6, 3:4:4, 1:1.24:0.76, 1:1:1 and 5:1:10.

The magnetic data are reported only for the 3:4:4 phase [20]. Specific heat data indicate two phase transitions at 2.1 and 2.8 K.

To explain the discrepancies, determination of magnetic properties of the other phases is planned.

Acknowledgments

This research project has been supported by the European Commission under the 6th Framework Program through the Key Action: Strengthening the European Research Area, Research Infrastructures, Contract no. RII3-CT-2003-505925 NMI3 and the Ministry of Science and Higher Education in Poland within the confines of the Grant no. N N202 201039.

References

[1] N. Rieger, E. Parthé, Monatshefte für Chemie 100 (1969) 444.
[2] H. Pinto, M. Melamud, M. Kuznietz, H. Shaked, Physical Review B 31 (1985) 508.
[3] P. Schobinger - Papamantellos, A. Niggli, P.A. Kotsanidis, J.K. Yakinthos, Journal of Physics and Chemistry of Solids 45 (1984) 645.
[4] P.A. Kotsanidis, J.K. Yakinthos, E. Roudaut, Solid State Communications 50 (1984) 413.
[5] D. Penc, S. Baran, D. Kaczorowski, A. Hoser, A. Szytuła, Journal of Alloys and Compounds 503 (2010) L18.
[6] P.A. Kotsanidis, J.K. Yakinthos, Solid State Communications 40 (1981) 1041.
[7] G.A. Stewart, P.W. Thompson, J.M. Cadogan, Hong Shuo Li, Hyperfine Interactions 99 (1994) 407.
[8] A.P. Pikul, Ł. Gondek, D. Kaczorowski, A. Szytuła, Journal of Physics: Conference Series 100 (2010) 032056.
[9] J. Rodriguez-Carvajal, Physica B 192 (1993) 55.
[10] Y. Allain, F. Bourée - Vigneron, A. Oleś, A. Szytuła, Journal of Magnetism and Magnetic Materials 75 (1988) 303.
[11] M. Kosaka, H. Onodera, K. Ohoyama, M. Ohashi, Y. Yamagushi, S. Nakemura, T. Goto, Journal of Physical Society of Japan 66 (1997) 2844.
[12] J.K. Yakinthos, E. Roudaut, Journal of Magnetism and Magnetic Materials 68 (1987) 90.
[13] G.A. Stewart, J. Żukrowski, in: P.P. Guertin, W. Suski, A. Żołnierek (Eds.), Crystalline Electric Field Effects in f-electron Magnetism, Plenum Press, New York, 1982, p. 319.
[14] A. Chatterji, S. Chatterjee, R. Chatterjee, Physica Status Solidi (b) 238 (2003) 180.
[15] S.J. Harker, B.D. van Dijk, A.M. Mulders, P.C.M. Gubbens, G.A. Stewart, C.F. de Vroege, K.H.J. Buschow, Journal of Physics: Condensed Matter 14 (2002) 2705.
[16] Nguyen D. Dung, Y. Ota, K. Sugiyama, T.D. Matsuda, Y. Haga, K. Kindo, M. Hagiwara, T. Takeuchi, R. Settai, Y. Ōnuki, Journal of Physical Society of Japan 78 (2009) 024712.
[17] J.E. Greedan, V.U.S. Rao, Journal of Solid State Chemistry 6 (1973) 0387 8 (1973) 368.
[18] W. Schlobitz, J. Baumann, G. Neumann, D. Flümacher, K. Regegntin, Crystalline Electric Field Effects in f-electron Magnetism, in: R.P. Guertin, S. Suski, Ż. Żołnierek (Eds.), Plenum Pres, New York, 1982, p. 289.
[19] L.O. Fedyna, O.I. Bodak, Ya.O. Tokaychuk, M.F. Fedyna, I.R. Mokra, Journal of Alloys and Compounds 367 (2004) 70.
[20] S. Baran, D. Kaczorowski, A. Szytuła, A. Gil, T. Hofmann, in: Abstract Book of the 5th European Conference on Neutron Scattering, Praha, 17–22 July 2011, p. 183.