Solid State Communications 152 (2012) 1027–1029

Contents lists available at SciVerse ScienceDirect

Solid State Communications

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

Antiferromagnetism of $ThCr_2Si_2$

A. Szytuła [a,*], B. Penc [a], M. Hofmann [b], J. Przewoźnik [c]

[a] M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland
[b] Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Technische Universität München, 85747 Garching, Germany
[c] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Kraków, Poland

ARTICLE INFO

Article history:
Received 20 December 2011
Received in revised form
28 February 2012
Accepted 5 March 2012
by C. Lacroix
Available online 30 March 2012

Keywords:
A. $ThCr_2Si_2$
D. Magnetic structure
E. Neutron diffraction

ABSTRACT

Neutron diffraction measurements indicate that the magnetic moments of chromium atoms in the $ThCr_2Si_2$ compound show long-range order. The Cr magnetic moment equal to $1.20(25)\mu_B$ at 1.5 K lie in the basal plane and form magnetic structure AFI-type.

1. Introduction

In the last four decades there has been a growing interest in the investigations of the RT_2X_2 group compounds, where R is the rare earth or actinide metals, T is the transition metal and X is the main group element. These compounds crystallize in a body-centered tetragonal structure (space group $I4/mmm$) [1,2]. The magnetic moments of the rare earth atoms form an enormous variety of magnetic structures. In RMn_2X_2 compounds the Mn sublattice orders anti- or ferromagnetically below 500 K. In contrast, in RT_2X_2 compounds with other transition metals (T=Fe, Co, Ni, X=Si, Ge) no magnetic order of the T moments is observed [3].

Magnetization data reported for the series RCr_2Si_2 (R=Gd, Tb, Dy, Ho, Er and Tm) indicate that the R ion moments order at very low temperatures [4]. Magnetization measurements for the mixed series $RFe_{2-x}Cr_xSi_2$ [5] have shown the presence of antiferromagnetic interactions for Cr rich compounds with ordering temperatures up to 700 K, whilst low ordering temperatures were observed for Fe rich compounds. In addition neutron diffraction measurements have provided direct evidence for antiferromagnetic order in the Cr sublattice in the Cr rich series $RFe_{2-x}Cr_xSi_2$ [6], $HoCr_2Si_2$ [7] and (R=Tb, Ho and Er) [8] with Néel temperatures well above ambient temperatures.

$ThCr_2Si_2$ also crystallizes in the body-centered tetragonal structure with space group $I4/mmm$ [1]. Earlier measurements [9] of the temperature dependence of the magnetic susceptibility in the temperature interval 100–570 K have not shown any evidence of a magnetic phase transition. In this study a paramagnetic Curie temperature of $\theta_p = -1700$ K and an effective magnetic moment of the chromium atom of $2.18\mu_B$ were determined [9].

Recently calculations based on first-principles resulted, besides presenting data on elastic constant, bulk, shear and Young's modulus and compressibility, in new evidence for spin ordering of the magnetic ground state [10]. In this work also partial and total densities of states were calculated. Within the light of this study we report results of X-ray and neutron diffraction measurements of $ThCr_2Si_2$ to clarify the magnetic properties. The neutron diffraction data enabled the magnetic structure of $ThCr_2Si_2$ to be determined.

2. Experimental

A detailed procedure for the sample preparation is given elsewhere [11]. X-ray powder diffraction confirm that the sample has the body centered tetragonal structure with the lattice parameters a=0.40414(2) nm and c=1.05879(6) nm in good agreement with those reported earlier [1,11,12]. Small impurities of ThO_2 and other unindexed phase were also observed. Neutron diffraction patterns were recorded using the E6 diffractometer at the Berlin Neutron Scattering Center of the Helmholtz Center Berlin for Materials and Energy. The data were collected at several temperatures between 1.5 and 395 K in the 2θ range 24–104° using an incident neutron wavelength of 0.244 nm.

* Corresponding author. Tel.: +48 12 6635546; fax: +48 12 6337086.
E-mail address: szytula@if.uj.edu.pl (A. Szytuła).

0038-1098/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ssc.2012.03.015

The neutron diffraction data were refined using the Rietveld-type program FULLPROF [13].

In purpose to determine the critical temperature of the magnetic order the additionally magnetic measurement was performed using a vibrating sample magnetometer (VSM), option of the Quantum Design PPMS.

3. Results

Fig. 1 shows the neutron diffraction patterns of $ThCr_2Si_2$ measurements in the temperature range 1.5–295 K. The observed reflections obey the condition $h+k+l=2n$ typical for the nuclear reflections in the $ThCr_2Si_2$ structure-type. $ThCr_2Si_2$ crystallizes in a body-centered tetragonal structures with two formula units per unit cell [1,11,12] with the atomic positions Th:2a (0,0,0), Cr:4d $(0,\frac{1}{2},\frac{1}{4})$ and Si:4e (0, 0, z). The structure of $ThCr_2Si_2$ can be described as a sequence of Th sheets and [Cr_2Si_2] blocks consisting of [$CrSi_4$] tetrahedrons: … Th[Cr_2Si_2] Th[Cr_2Si_2] ….

Fig. 2 gives the intensities of the strongest nuclear and magnetic peaks 101, 110 and 103 intensities at 1.5 and 295 K.

The magnetic contribution to the intensities of (101) and (103) lines are characteristic of the occurrence of an antiferromagnetic component within (001) Cr planes. Numerical analysis of the neutron diffraction pattern at 1.5 K indicates that the magnetic structure is of AFI-type with the following sequence of the sign$+--+$of Cr moments in position $\frac{1}{2}0\frac{1}{4}$, $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$ and $0\frac{1}{2}\frac{3}{4}$. In this magnetic structure each [Cr_2Si_2] block consists of chains of parallel Cr moments that are coupled antiferromagnetically. Adjacent [Cr_2Si_2] blocks order in an antiferromagnetic arrangement along the c-axis. The refined magnetic moment of $1.20(15)\mu_B$ is parallel to the a-axis ($R_{mag}=8.3\%$). A possible arrangement with Cr moments parallel to the c-axis observed in isostructural $R$$Cr_2Si_2$ compounds [7,8] yields a smaller value of the magnetic moment of $0.96(10)\mu_B$ and a considerably higher value of $R_{mag}=12.0\%$. The magnetic structure of $ThCr_2Si_2$ with moments parallel to the a-axis is presented in Fig. 3.

A comparison of the calculated nuclear and magnetic intensities with the observed intensities for the diffraction data of $ThCr_2Si_2$ at 1.5 K is shown in Fig. 4.

The thermal evolution of the refined values of the magnetic moment and lattice parameters a and c are given in Fig. 5. This data suggests that the Néel temperature is considerably higher at 300 K similar to the transition temperatures observed in other isostructural 1:2:2 compounds [8]. Temperature dependence of

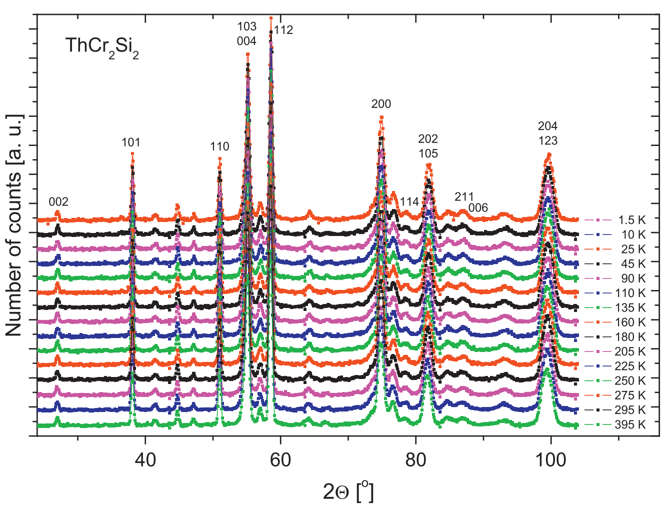

Fig. 1. (Color online) Neutron diffraction patterns of $ThCr_2Si_2$ in the temperature range 1.5–295 K.

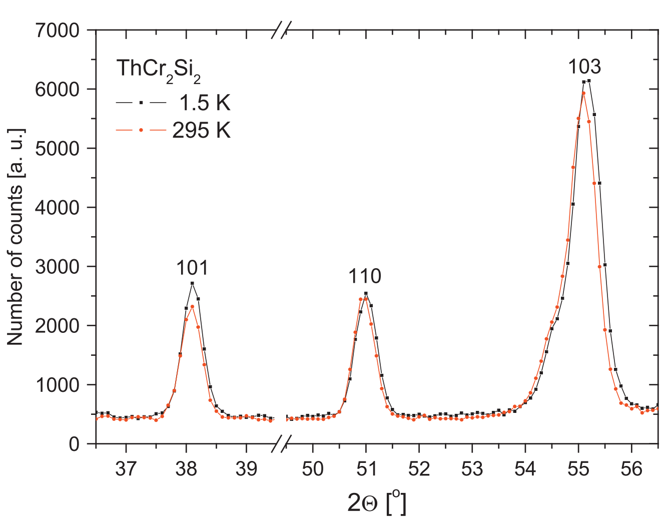

Fig. 2. (Color online) The nuclear and magnetic peaks 101, 110 and 103 intensities at 1.5 and 295 K.

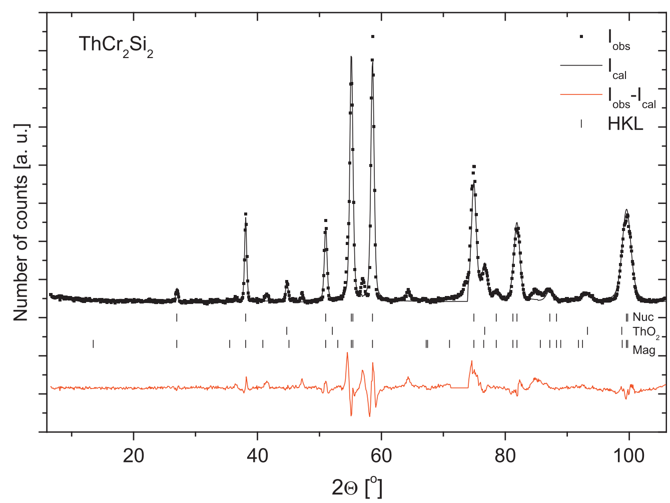

Fig. 3. (Color online) Observed and calculated neutron diffraction patterns of $ThCr_2Si_2$ at 1.5 K. The squares represent the experimental points; the solid curves are the calculated profiles for the refined crystal and magnetic structures described in the text. The difference between the observed and calculated intensities is shown at the bottom of diagram. Tick marks indicate the positions of the Bragg peaks of nuclear and magnetic origin and the ThO_2 impurity. The other reflections correspond to the unidentified impurity phase.

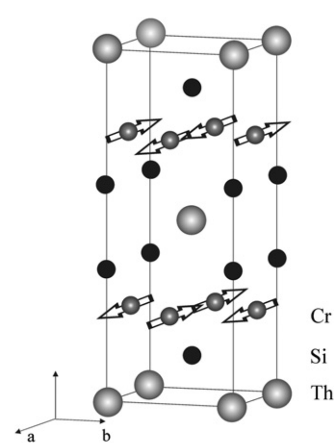

Fig. 4. Magnetic structure of $ThCr_2Si_2$.

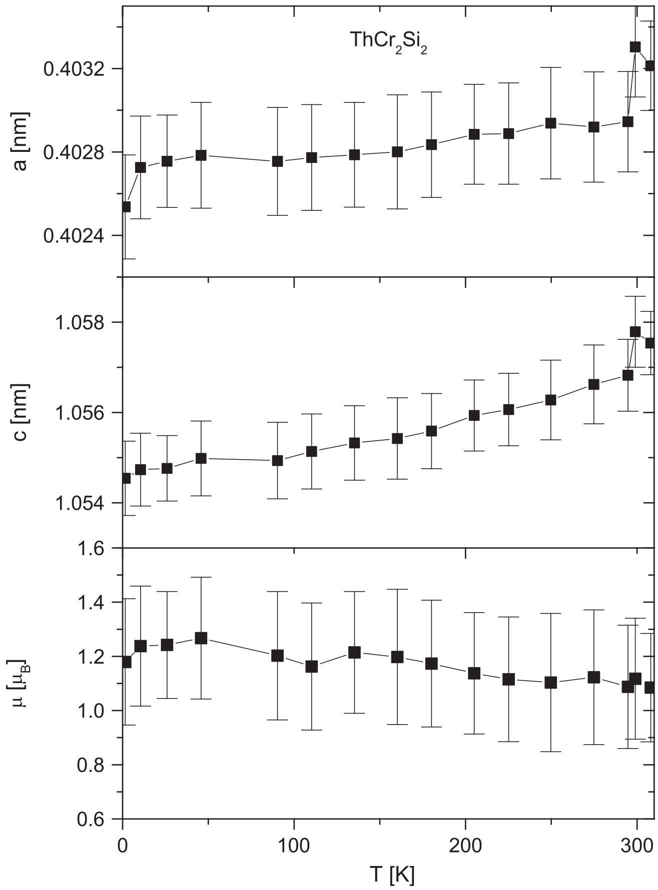

Fig. 5. Temperature dependence of the lattice parameters *a* and *c* and the Cr magnetic moment of $ThCr_2Si_2$.

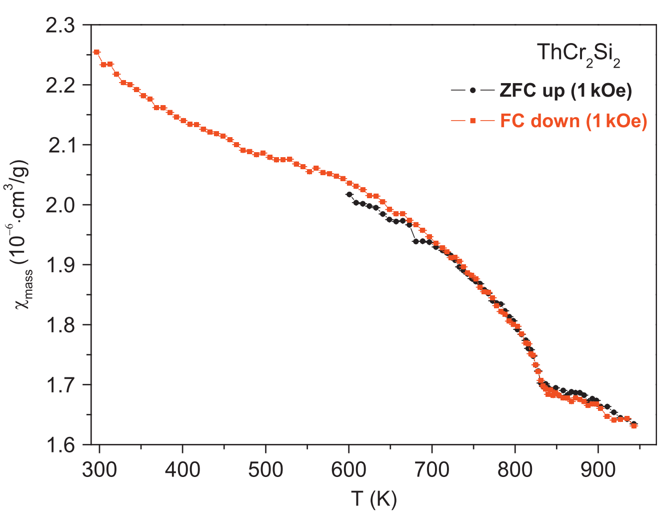

Fig. 6. (Color online) Temperature dependence of the magnetic susceptibility of $ThCr_2Si_2$.

the DC magnetic susceptibility measurement in the temperature range 300–950 K at zero magnetic field (ZFC) and field ($H=1$ kOe) cooling (FC) is shown in Fig. 6. This data indicate anomaly at 830 K, which is probably critical temperature of the magnetic order of Cr moments.

4. Discussion

The results of the neutron diffraction measurements indicate that the Cr magnetic moments in $ThCr_2Si_2$ indeed show long-range order. The antiferromagnetic order of the Cr moment within the basal plane is similar to that observed in Mn sublattice in $CaMn_2Ge_2$ and $BaMn_2Ge_2$ [14]. This type of order is labeled as AFM3 in Ref. [10] and corresponds to the minimum energy. The observed direction of Cr moments is different to those found in isostructural RCr_2Si_2 (R=rare earth) compounds where the Cr moments align parallel to the *c*-axis. This indicates a change of the direction of the magnetic moment due to the exchange of rare earth by chromium atoms in the crystal structure. The value of the Cr magnetic moment of 1.20(15)μ_B is smaller than those observed in RCr_2Si_2 (R=Tb, Ho, Er) compounds which are between 1.35(7) and 1.62(2)μ_B [8].

The interatomic Cr–Cr distance in $ThCr_2Si_2$ is equal 0.2858 nm and is thus near to distances typically observed in RMn_2X_2 compounds whereas in the rare earth compounds RCr_2Si_2 it is shorter between around 0.2765 nm and 0.2754 nm [8]. In RMn_2X_2 (X=Si, Ge) compounds the exchange interactions are very sensitive to the interlayer distance [15] with makes it probable that a similar dependence is also likely to be observed in RCr_2Si_2 compounds.

The determined value of the Néel temperature of the $ThCr_2Si_2$ compound is probably 830 K and is similar to those found in the isostructural RCr_2Si_2 equal 758 K (R=Tb), 718 K (R=Ho) and 692 K (R=Er) [7,8], refuting the very high value of the Neel temperature of about 1770 K reported in Ref. [9]. According to [9] this value corresponds to the paramagnetic Curie temperature which is incorrect as it was determined from the data in the ordered and not in the paramagnetic state.

Acknowledgments

Financial support by the BENSC for participation in the neutron diffraction experiment is gratefully acknowledged.

References

[1] Z. Ban, M. Sikirica, Acta Crystallogr. 18 (1964) 594;
Z. Ban, M. Sikirica, Croat. Chim. Acta 36 (1964) 51.
[2] O.S. Zarchnyuk, P.I. Kripyakevich, E.J. Gladyshevskii, Sov. Phys.-Crystallogr. 8 (1964) 477;
O.S. Zarchnyuk, P.I. Kripyakevich, E.J. Gladyshevskii, Sov. Phys.-Crystallogr. 9 (1964) 706.
[3] A. Szytuła, J. Leciejewicz, Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics, Chemical Rubber Company Press, Boca Raton, FL, 1994.
[4] A. Domman, F. Hulliger, Ch. Baerlocher, J. Less-Common Met. 147 (1998) 97.
[5] I. Ijjaali, G. Venturini, B. Malaman, J. Alloys Compd. 279 (1998) 102.
[6] I. Ijjaali, G. Venturini, R. Welbter, J. Toboła, B. Malaman, in: Proceedings of the 13th International Conference on Solid Compounds of Transition Elements, Stresa, Italy, 4–7 April, 2000, p. P-B17.
[7] O. Moze, M. Hofmann, K.H.J. Buschow, J. Alloys Compd. 308 (2000) 60.
[8] O. Moze, M. Hofmann, J.M. Cadogan, K.H.J. Buschow, D.H. Ryan, Eur. Phys. B 39 (2003) 511.
[9] L. Omejec, Z. Ban, Z. Anorg. Allg. Chem. 380 (1971) 111.
[10] I.R. Shein, A.L. Ivanovskii, Solid State Commun. 151 (2011) 1165.
[11] J. Leciejewicz, S. Siek, A. Szytuła, J. Less-Common Met. 144 (1988) L9.
[12] M. Marazza, R. Ferro, G. Rambaldi, G. Zaniecchi, J. Less-Common. Met. 53 (1977) 193.
[13] J. Rodriguez-Carvajal, Physica B 192 (1993) 55.
[14] B. Malaman, G. Venturini, R. Welter, E. Ressouche, J. Alloys Compd. 210 (1994) 209.
[15] A. Szytuła, J. Alloys Compd. 178 (1992) 1.