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# Magnetic order and structural properties of $Tb_2Fe_2Si_2C$

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ABSTRACT

The structural and magnetic properties of $Tb_2Fe_2Si_2C$ have been investigated by bulk measurements (magnetisation and specific heat), X-ray diffraction, neutron powder diffraction and $^{57}$Fe Mössbauer spectroscopy over the temperature range 3 K–300 K $Tb_2Fe_2Si_2C$ is antiferromagnetic with a Néel temperature $T_N$ of 44(2) K. The magnetic structure can be described with a propagation vector $\mathbf{k} = [0\ 0\ \frac{1}{2}]$ with the Tb magnetic moments ordering along the *b*-axis. We also observed strong magnetoelastic effects in particular along the *a*- and *c*-axes associated with the antiferromagnetic transition. The $^{57}$Fe Mössbauer spectra show no evidence of magnetic splitting down to 10 K, indicating that the Fe atom is non-magnetic in $Tb_2Fe_2Si_2C$.



## 1. Introduction

The $R_2Fe_2Si_2C$ (R = rare-earth) series of compounds were discovered by Paccard and Paccard [1]. These quaternary compounds crystallise in the monoclinic $Dy_2Fe_2Si_2$ C-type structure with the $C2/m$ (#12) space group. An extensive range of compounds with R = Y, La–Nd, Sm, Gd–Tm and Lu has been synthesised and studied [1–3]. The R, Fe and Si atoms occupy 4*i* sites with the *m* point symmetry, generated by (*x*,0,*z*), while the C atom occupies the 2*a* site at (0,0,0) with the 2/*m* point symmetry.

These compounds are antiferromagnetic, with Néel temperatures ($T_N$) ranging from $T_N$ ~ 45 K for $Tb_2Fe_2Si_2C$ to $T_N$ ~ 2.7 K for $Tm_2Fe_2Si_2C$ [2,4]. No magnetic order was observed for $Y_2Fe_2Si_2C$, $Pr_2Fe_2Si_2C$ and $Lu_2Fe_2Si_2C$ down to 2 K. Based on magnetisation studies, the magnetism of $R_2Fe_2Si_2C$ was attributed solely to the R atoms, *i.e.* the Fe atom was reported to be non-magnetic. The magnetic structures of $Nd_2Fe_2Si_2C$ and $Tb_2Fe_2Si_2C$ were first reported by Le Roy et al. [5] who proposed a doubled antiferromagnetic structure along the *c*-axis ($\mathbf{k} = [0\ 0\ \frac{1}{2}]$) with both the R and Fe sublattices being magnetically ordered, almost perpendicular to each other. Recently, we used neutron diffraction on $Gd_2Fe_2Si_2C$ and $Ho_2Fe_2Si_2C$ to show that the Gd and Ho sublattices order antiferromagnetically along the *b*-axis with a propagation vector $\mathbf{k} = [0\ 0\ \frac{1}{2}]$ and on the basis of $^{57}$Fe Mössbauer spectroscopy we found that the Fe atom carries no magnetic moment in these compounds [6,7].

In this paper, we present the results of our re-examination of the magnetic and structural properties of $Tb_2Fe_2Si_2C$ using x-ray diffraction, magnetisation, specific heat measurements, neutron powder diffraction and $^{57}$Fe Mössbauer spectroscopy. Our main interest arises from the inconsistent results between magnetic studies which suggest that the Fe atom is non-magnetic [4] and the neutron diffraction study of Le Roy et al. [5] who proposed magnetic order in both the Tb and Fe sublattices. Our findings reveal that while our neutron diffraction refinements cannot definitively confirm or rule out the existence of magnetic order of the Fe sublattice, no magnetic splitting is observed in the $^{57}$Fe Mössbauer spectra collected below $T_N$, thus establishing the absence of magnetic ordering of the Fe sublattice in this compound. In addition, our low temperature x-ray diffraction measurements show large magnetoelastic effects with a magnitude of ~$5 \times 10^{-3}$ (at 20 K) associated with the antiferromagnetic transition below $T_N = 44(2)$ K, with the effects being prominent along the *a* and *c* directions.

## 2. Experimental methods

The $Tb_2Fe_2Si_2C$ samples were prepared by arc-melting the high purity elements (at least 99.9 wt%) under an argon atmosphere. The

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ingots were turned and re-melted several times to ensure homogeneity. X-ray powder diffraction (XRD) patterns were collected at various temperatures between 300 K and 20 K using a PANalytical Empyrean diffractometer (Cu-$K_\alpha$ radiation) equipped with an Oxford Instruments Phenix closed-cycle refrigerator.

Magnetisation and zero field specific heat data were measured using a Quantum Design Physical Property Measurement System (PPMS). Magnetisation data were collected in the temperature range between 2 K and 300 K in an applied field $\mu_0 H = 1$ T, while the specific heat measurement was performed using a relaxation method between 2 K and 300 K. The ordering temperature was determined from the peak of the temperature derivatives of magnetisation and specific heat data.

Neutron diffraction experiments were carried out on the Echidna high resolution powder diffractometer [8] at the OPAL reactor in Sydney, Australia with an incident neutron wavelength of 2.4395(5) Å. Short duration neutron diffraction patterns were collected at various temperatures between 3 K and 60 K to provide overall insight into the structural and magnetic behaviour over this temperature range. Long duration patterns were obtained at 3 K and 60 K – below and above the antiferromagnetic transition $T_N$ = 44(2) K – for more detailed investigations. All diffraction patterns were corrected for absorption effects and were refined by the Rietveld method using the FullProf/Winplotr software [9,10].

$^{57}$Fe Mössbauer spectra were collected in standard transmission mode using a $^{57}$Co–Rh source. The spectrometer was calibrated with an $\alpha$-Fe foil at room temperature and the sample temperature was varied from 10 K to 80 K using a vibration-isolated, closed-cycle refrigerator. All spectra were fitted using the Recoil software [11].

## 3. Results

### 3.1. Crystal structure

Refinement of the X-ray diffraction pattern collected at room temperature confirmed the formation of the monoclinic $Dy_2Fe_2Si_2C$-type structure with impurity phases (identified as $TbC_{0.33}$ (terbium carbide) and unreacted silicon) present in the total amount of ~3 wt%. The refined pattern is shown in Fig. 1. The lattice parameters of $Tb_2Fe_2Si_2C$ obtained from this refinement are $a$ = 10.628(1) Å, $b$ = 3.9362(4) Å, $c$ = 6.7701(6) Å and $\beta$ = 129.32(1)°, in good agreement with the values reported by Paccard and Paccard [1].

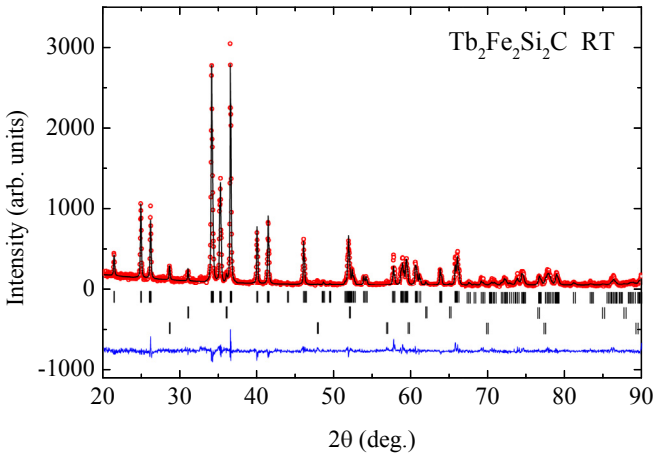


**Fig. 1.** Rietveld refinement of the X-ray diffraction pattern of $Tb_2Fe_2Si_2C$ collected at room temperature (Cu-$K_\alpha$ radiation). The Bragg markers from top to bottom represent $Tb_2Fe_2Si_2C$, $TbC_{0.33}$ and Si, respectively.

### 3.2. Magnetic properties

In Fig. 2, we present the dc (molar) magnetic susceptibility of $Tb_2Fe_2Si_2C$ obtained with an applied field of $\mu_0 H = 1$ T. The antiferromagnetic transition at $T_N$ = 44 K is indicated by a cusp-like transition in the susceptibility data. This result is in excellent agreement with the previously reported ordering temperature of 45 K [4]. The Curie–Weiss fit to the inverse molar susceptibility (inset in Fig. 2), yields a paramagnetic Curie temperature of $\theta_P$ = +36(2) K and an effective magnetic moment of $\mu_{eff}$ = 9.76(4) $\mu_B$, which agrees well with the theoretical $\mu_{eff}$ of 9.72 $\mu_B$ expected for the $Tb^{3+}$ ion. Further, this result suggests that the Fe atom is non-magnetic in $Tb_2Fe_2Si_2C$.

In Fig. 3, we show the low temperature specific heat data, $C_P$, of $Tb_2Fe_2Si_2C$. It is clear that the specific heat shows a $\lambda$-type anomaly at 44 K which is consistent with the antiferromagnetic transition seen in the dc susceptibility at 44 K. From the $C_P$ data, we can also calculate the magnetic contribution to the entropy, $S_{mag}$, of $Tb_2Fe_2Si_2C$ by integrating $C_{mag}/T$, where $C_{mag}$ is the magnetic contribution to the specific heat. To this end, we used the specific heat of $Y_2Fe_2Si_2C$ as a non-magnetic background. The non-magnetic contribution is then removed, taking into account the molar mass difference between $Y_2Fe_2Si_2C$ and $Tb_2Fe_2Si_2C$, following the 'many-Debye' method of Bouvier et al. [12]. The normalised (mass corrected) $C_P$ data for $Y_2Fe_2Si_2C$ are also shown in Fig. 3. The calculated values of the magnetic entropy of $Tb_2Fe_2Si_2C$ are shown in the inset of Fig. 3. The magnetic entropy released at $T_N$ is 10.7 J mol$^{-1}$ K$^{-1}$ which is close to $R\ln(4)$ = 11.53 J mol$^{-1}$ K$^{-1}$ which suggests that the magnetic ground state consists of four levels.

### 3.3. Low temperature X-ray diffraction

In Fig. 4, we show the temperature dependence of the lattice parameters and the unit cell volume of $Tb_2Fe_2Si_2C$. This compound does not undergo a structural phase transition down to the lowest measurement temperature of 20 K. The lattice parameters and the unit cell volume decrease monotonically as the temperature is decreased to $T_N$ ~ 45 K, however anomalies are observed upon cooling below the Néel temperature. The *ac*-plane of the unit cell

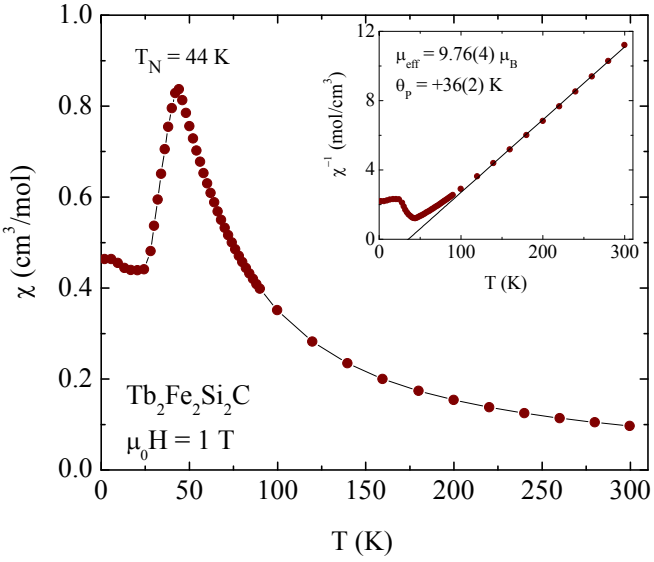


**Fig. 2.** DC susceptibility of $Tb_2Fe_2Si_2C$ obtained in field-cooled (FC) mode with an applied field of $\mu_0 H$ = 1 T. The inset shows the inverse susceptibility and a fit to the Curie–Weiss law.