The magnetic ground state of the Tm^{3+} site in $TmMn_2Si_2$

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The magnetic ground state of the Tm^{3+} site in $TmMn_2Si_2$ is investigated using ^{169}Tm-Mössbauer spectroscopy and bulk specific heat and magnetisation measurements. The results suggest a low-lying, pseudo-doublet ground state with $<\psi_0|J_z|\psi_1>$ close to the maximum allowed value of $J = 6$.

1. Introduction

Even though the transition metal sub-lattices of RCr_2Si_2 and RMn_2Si_2 (R = rare earth) order well above room temperature ($T_N \approx 700$ K and ≈ 500 K respectively [1, 2]), the R sub-lattices typically order much closer to liquid helium temperature. To a large extent, this suppression of magnetic order is linked with the fact that the rare earth and transition metal sub-lattices reside in separate layers and the interlayer interaction is weak. However, in the case of the thulium intermetallics, it has been proposed that the crystal field interaction favours a low-lying, non-magnetic singlet ground state for the non-Kramers Tm^{3+} ions, which further frustrates the R-R magnetic exchange process [1]. In this work the magnetic ground state of the Tm^{3+} site in $TmMn_2Si_2$ was investigated using ^{169}Tm-Mössbauer spectroscopy and bulk specific heat and magnetisation measurements.

2. Experimental details

The polycrystalline $TmMn_2Si_2$ specimen was prepared by repeated argon arc melting of stoichiometric proportions of Tm (99.9%) and Mn and Si (99.99+%). Rietveld analysis of the x-ray powder diffraction pattern confirmed that the specimen was predominantly single phase with less than 0.5 wt% $TmSi_2$ and Tm_2O_3 as impurity phases. The magnetic susceptibility and low temperature magnetisation measurements (B_{app} = 0.1 T and 7 T, respectively) were recorded using a SQUID magnetometer and the specific heat measurements were carried out in zero applied field using a Quantum Design PPMS. The ^{169}Tm-Mössbauer spectrum was recorded for the 8.4 keV transition ($I_g = 1/2$, $I_e = 3/2$) with the absorber ($\approx$ 10.5 mg $TmMn_2Si_2$ per cm^2) cooled to 2.8 K in a transmission geometry cryostat. The 10 mCi ^{169}Er source was a neutron activated foil of ^{168}Er(10 wt %)Al that was mounted externally at room temperature on a sinusoidal motion drive. The maximum drive velocity was calibrated against a standard TmF_3 absorber spectrum at 4.2 K.

3. Results and discussion

3.1 Magnetisation measurements

The inverse magnetic susceptibility data recorded for $TmMn_2Si_2$ powder are shown in Fig. 1(a) as a function of temperature where solid and open symbols represent increasing and decreasing temperature, respectively. An expanded view of the low temperature data is presented in the inset. These low temperature data are in excellent agreement with the earlier data of Okada *et al*. [3] (open diamonds) which were recorded for a specimen consisting of sub-micron single crystals. Okada *et al*. also reported susceptibility data for $LuMn_2Si_2$ that were negligible (at least 2 orders of magnitude smaller) when compared with the susceptibility data for $TmMn_2Si_2$. Given that the filled 4f shell of the Lu^{3+} ion is not magnetic, this means that the contribution of the antiferromagnetic Mn sub-lattice can be ignored and that the data in Fig. 1(a) can be attributed solely to the Tm sub-lattice. Below 16 K the data extrapolate to a Curie temperature of $T_C \approx 5.1$ K and the gradient corresponds to local effective moments of $p_{eff} \approx 6.39$ and $6.56\ \mu_B$ for decreasing and increasing temperature, respectively. This is only 15% less than the Tm^{3+} free ion effective moment of $g_J\sqrt{J(J+1)}$ = $7.56\ \mu_B$. The small jump in inverse susceptibility with increasing temperature at about 150 K is believed to be an artefact of the measurement technique.

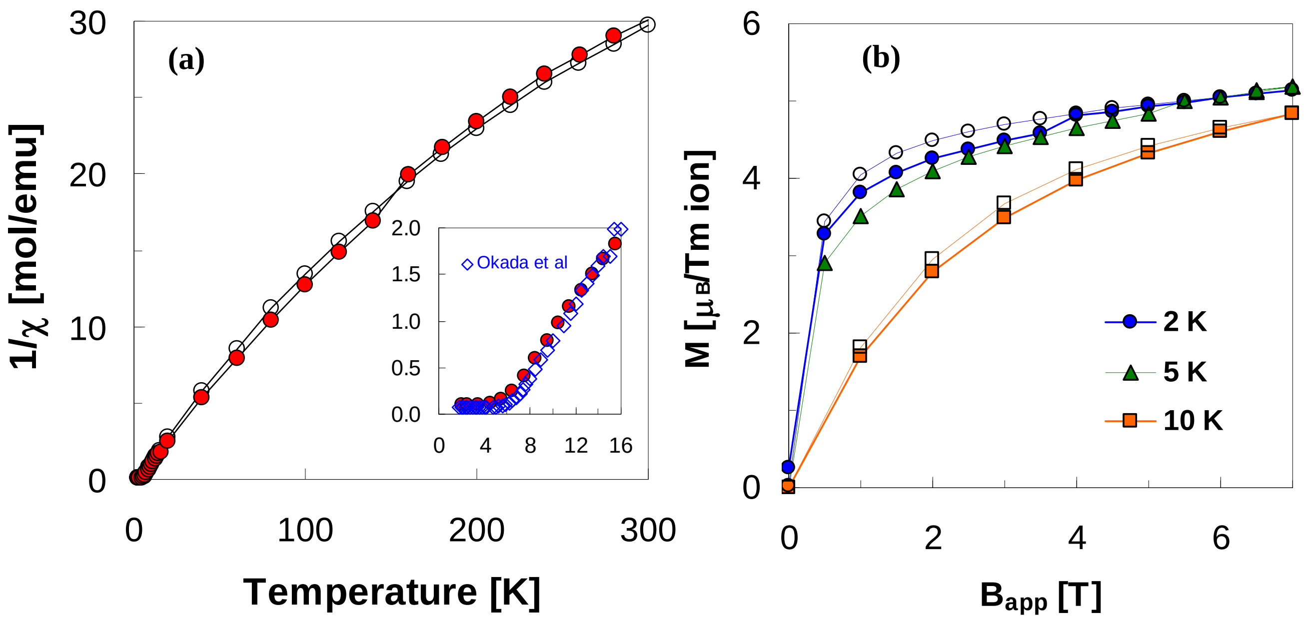

Fig. 1. (a) Inverse magnetic susceptibility, $1/\chi$, recorded for polycrystalline $TmMn_2Si_2$ with an external applied field of B_{app} = 0.1 T. Solid (open) symbols are for increasing (decreasing) temperature. In the inset, the low temperature data are compared with data from Okada *et al.* [3]. (b) Magnetisation versus applied field, B_{app}, for $TmMn_2Si_2$ at 2, 5 and 10 K where solid and open symbols represent increasing and decreasing B_{app}, respectively. Note that the 5 K data were recorded only for increasing B_{app}.

In Fig. 1(b) the magnetisation data are shown as a function of applied field up to 7 T for temperatures of 2, 5 and 10 K. The steep initial rise in the data for the two lower temperatures is further indication of a ferromagnetic Tm sub-lattice with $T_C \approx 5.1$ K. This result is in line with the neutron diffraction work of Leciejewicz *et al.* [4] who reported a ferromagnetic rare earth sub-lattice for $ErMn_2Si_2$, where Er and Tm are neighbours in the lanthanide series. The magnetisation approaches an intermediate saturation value of $\mu \approx 5$ μ_B/f.u. ($\approx$ 71% of the free ion moment of $g_J J = 7\ \mu_B$) as the external field is increased. It is interesting that the magnetisation data do not show strong hysteresis even at 2 K (which is below T_C) whereas significant residual magnetisations were measured for the data of $DyMn_2Si_2$ and $ErMn_2Si_2$ [2]. In this current set of data there are small jumps in the magnetisation with increasing applied field at $B_{app} \approx 3.8$ T for the 2 K data and at $B_{app} \approx 5.3$ T for the 5 K data. As for the case of the inverse susceptibility data, these features are believed to be an artefact of the measurement technique.

3.2 Specific heat measurements

The specific heat data for $TmMn_2Si_2$ are shown in Fig. 2 as solid circles. It appears that a magnetic transition with ordering temperature of approximately 5 K is superimposed on

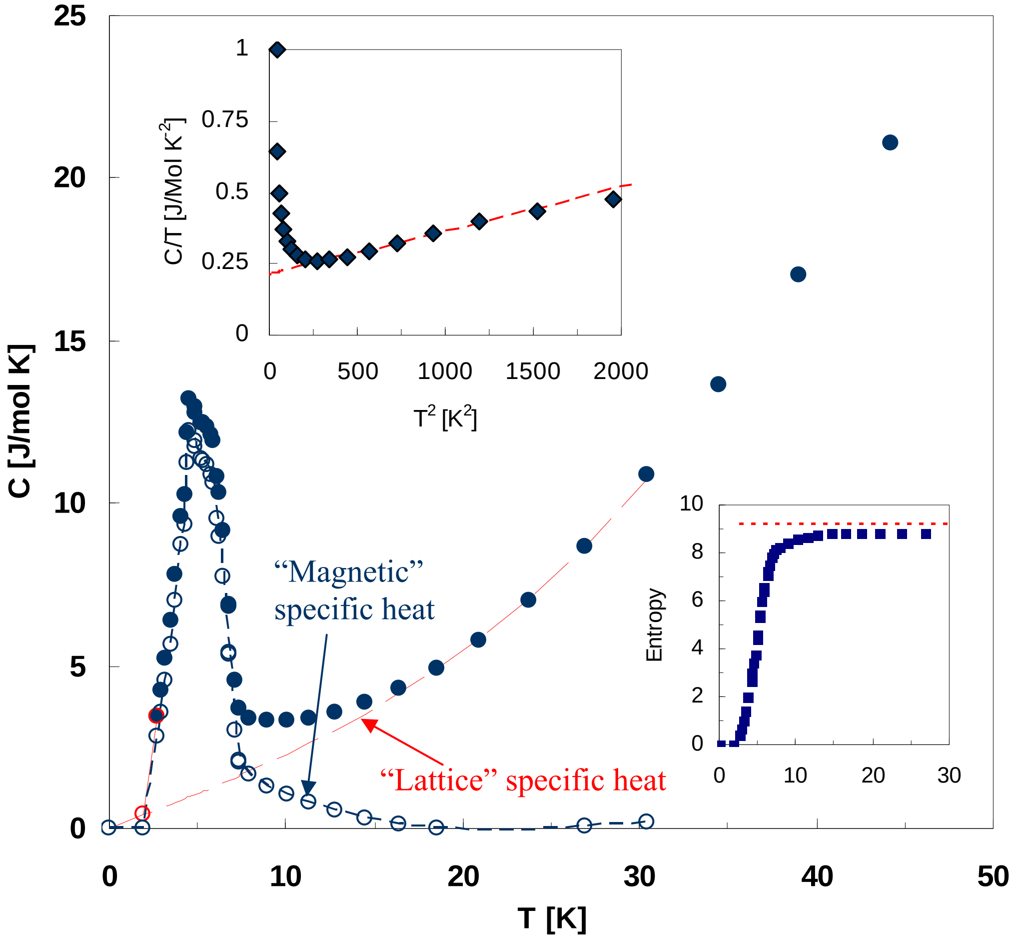

Fig. 2. Specific heat data for $TmMn_2Si_2$ (solid circles). The open circles represent the magnetic specific heat after subtraction of the lattice specific heat. The top-left inset is a plot of C/T against T^2 and the bottom right inset is a plot of entropy versus temperature.

a broader Schottky feature. As a first approximation, it was assumed that the low temperature specific heat for 17 < T < 38 K is predominantly due to the lattice and can be described by $C \approx \gamma T + \beta T^3$. This behaviour is supported by the linear dependence of the plot of C/T versus T^2 in the top-left inset of Fig. 2. The linear analysis yields an electronic coefficient of $\gamma \approx 211.7$ mJ mol^{-1} K^{-2}, a phonon coefficient of $\beta \approx 0.151$ mJ mol^{-1} K^{-4}, and a Debye temperature of $\Theta \approx 234$ K. The values of γ and β were then used to strip the lattice specific heat contribution and arrive at the magnetic contribution to the low temperature specific heat. The bottom-right inset of Fig. 2 shows the associated magnetic entropy calculated as a function of increasing temperature. The total magnetic entropy is ≈ 8.9 J mol^{-1} K^{-1}, which corresponds to 2 to 3 crystal field levels. Based on this result, in combination with the results from the magnetisation measurements, we propose that there is most likely a low-lying, 2-singlet ground state with $<\psi_0|J_z|\psi_1>$ close to the maximum allowed value of $J = 6$.

3.3 ^{169}Tm-Mössbauer spectroscopy

The ^{169}Tm-Mössbauer spectrum for $TmMn_2Si_2$ that was recorded at 2.8 K is shown in Fig. 3. As expected for $T < T_C$, a magnetically split ''sextet'' is observed. At 2.8 K, the fitted theory curve corresponds to a magnetic hyperfine field of $B_{hf} = 586(6)$ T and an electric field gradient of $V_{zz} = 46(1) \times 10^{21}$ V m^{-2} acting at the ^{169}Tm nucleus. In the case of the electric field gradient, a small part of the reduction in magnitude will be due to an opposing lattice contribution. The experimental values are only moderately less than the free ion values of B_{hf} = 663 T and V_{zz} = 69 x 10^{21} V m^{-2}, respectively [5], which supports the magnetisation measurements in that there is only moderate crystal field quenching from the free ion properties.

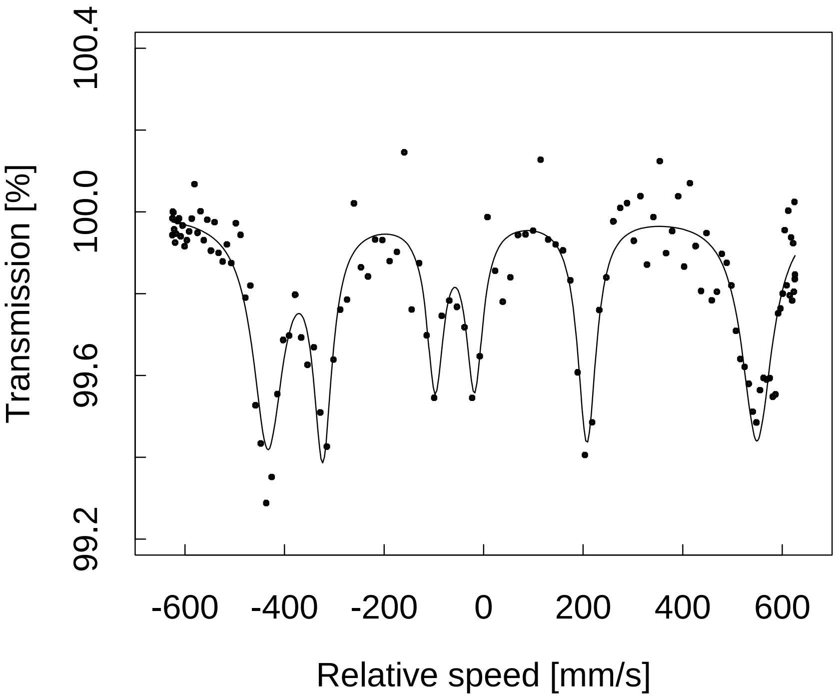

Fig. 3. ^{169}Tm Mössbauer spectrum for $TmMn_2Si_2$ at 2.8 K

4. Conclusion

In this work the magnetic ground state of the Tm^{3+} site in $TmMn_2Si_2$ was investigated using ^{169}Tm-Mössbauer spectroscopy and bulk specific heat and magnetisation measurements. The results are consistent with a low-lying, 2-singlet, ground state with $<\psi_0|J_z|\psi_1>$ close to the maximum allowed value of $J = 6$. A full investigation of the crystal field scheme, based on inelastic neutron scattering results for $ErMn_2Si_2$ and the temperature dependence of the ^{169}Tm quadrupole interaction strength for $TmMn_2Si_2$, is currently underway.

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References

[1] Moze O, Hofmann M, Cadogan J M, Buschow K H J, and Ryan D H 2003 *Eur. Phys. J. B* **36** 511

[2] Szytula A and Szott I 1981 *Solid State Commun.* **40** 199

[3] Okada S, Kudou K, Mori T, Iizumi K, Shishido T, Tanaka T and Rogl T 2002 *J. Crystal Growth* **244** 267

[4] Leciejewicz J, Siek S and Szytula A, 1984 *J. Magn. Magn. Mater.* **40** 265

[5] Stewart G 1994 *Mater. Forum* **18** 177