Magnetic Structure and Phase Diagram of TmB$_4$

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Magnetic structure of single crystalline TmB$_4$ has been studied by magnetization, magnetoresistivity, and specific heat measurements. A complex phase diagram with different antiferromagnetic phases was observed below $T_{N1} = 11.7$ K. Besides the plateau at half-saturated magnetization ($1/2\,M_S$), also plateaus at $1/9$, $1/8$ and $1/7$ of M_S were observed as a function of applied magnetic field $B \parallel c$. From additional neutron scattering experiments on TmB$_4$, we suppose that these plateaus arise from a stripe structure which appears to be coherent domain boundaries between antiferromagnetic-ordered blocks of 7 or 9 lattice constants. The received results suggest that the frustration among the Tm^{3+} magnetic ions, which maps to a geometrically frustrated Shastry–Sutherland lattice, leads to a strong competition between antiferromagnetic and ferromagnetic order. Thus, stripe structures in intermediate field appear to be the best way to minimize the magnetostatic energy against other magnetic interactions among the Tm ions combined with very strong Ising anisotropy.

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1. Introduction

Rare earth tetraborides REB$_4$ crystallize in a tetragonal structure with the space group $P4/mbm$, where the RE ions map to a Shastry–Sutherland type geometrically frustrated lattice (SSL) in the c-plane. It was shown that all heavy REB$_4$ (RE = Tb, Dy, Ho, Er, Tm) exhibit a strong Ising-like anisotropy which orients the RE magnetic moments along the c-axis, and complex phase diagrams below T_N(TbB$_4$) = 43 K, T_{TN}(DyB$_4$) = 20.3 K, T_{TN}(HoB$_4$) = 7.1 K, T_{TN}(ErB$_4$) = 15.4 K and T_{TN}(TmB$_4$) = 11.7 K [1–5]. Moreover, in the ordered antiferromagnetic (AF) state of TmB$_4$, the magnetization M for $B \parallel c$ reaches saturation M_S at about 4 T accompanied by plateaus at $1/8\,M_S$ and $1/2\,M_S$.

On the other hand, for $B \perp c$ the $1/2$ M_S state and the saturation of M were observed only at much higher field above 30 T [6]. Such behavior may result from the combined effect of the crystal electric field (CEF) and the magnetic frustration attributed to the SSL formed by the Tm^{3+} ions.

The aim of this work is to confirm and extend recent studies of the magnetic structure of TmB_4 by investigations of macroscopic physical quantities like magnetization, resistivity and specific heat.

2. Experimental details

A large single crystal of TmB_4 was prepared by a floating zone melting technique. The c-axis and a-axis of the crystal were determined by Laue photographs. Oriented small samples were cut parallel to these directions. The temperature and field dependence of magnetization, $M(T, B)$, up to 14 T, and in a temperature range from 1.8 K to 300 K was measured using a vibrating sample magnetometer of Quantum Design (PPMS). DC resistivity measurements between 1.5 K and 300 K, $\rho(T, B)$, were carried out in a ^{4}He flow cryostat with a 7 T magnet using the standard four-terminal method. Specific heat measurements down to 0.3 K and up to 5 T, $C(T, B)$, were made by the relaxation method in a ^{3}He cryostat of Oxford Instruments (Kelvinox).

3. Results and discussion

TmB_4 shows a strong anisotropy in the temperature dependence of the susceptibility $\chi(T)$ for $B \parallel c$ and $B \perp c$ (see inset Fig. 1a). The Néel temperatures $T_{N1} = 11.7$ K and $T_{N2} = 9.8$ K are the same for both field directions, and the effective moment value is close to that of a free Tm^{3+} ion, $\mu_{\text{eff}}(B \parallel c) = 6.5$ and $\mu_{\text{eff}}(B \perp c) = 6.7$. However, the paramagnetic Curie temperature θ_P is positive, $\theta_P = 45.9$ K, for $B \parallel c$, whereas it is negative, $\theta_P = -57.6$ K, for $B \perp c$. Most interesting is the $M(B)$ dependence for $B \parallel c$, where besides the plateau at half-saturated magnetization ($1/2$ M_S) in high field also plateaus of $M(B)/M_S = 1/9$, $1/8$ and $1/7$ are observed in fields around $B = 1.6$ T at low temperature (Fig. 1a). In addition, $\chi(T)_{B \perp c}$ has a broad maximum around 85 K which likely comes from the CEF splitting. For $B \perp c$, just above T_{TN1}, the magnetization plateaus are seen as a function of temperature. The plateau magnetization depends linearly on the applied field which suggests a quadratic Zeeman effect with a splitting of 14 meV between ground and first excited state.

The magnetic phase diagram (see Fig. 1b) was constructed from the peak positions of numerically calculated $d\chi(T)/dT$ and $dM(B)/dB$, and shows tree phases (II, III, and IV) below T_{N1} with one triple point at $(T_t, B_t) \approx (8.6$ K, 2.2 T).

Preliminary results of the neutron scattering experiments of TmB_4 reveal a simple AF structure of the uu-dd type in zero magnetic field. The ferrimagnetic high field phase (phase IV) seems to consist of large blocks with a size of 8 chemical
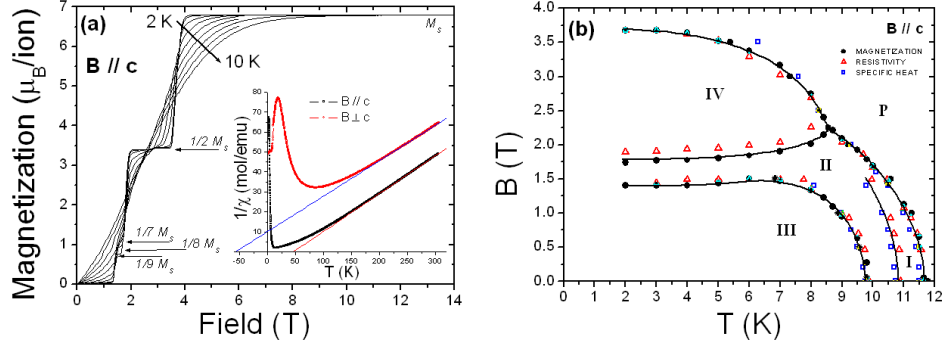
Fig. 1.   Magnetization data (a) and the final $B-T$ phase diagram (b) of TmB$_4$ for $B \parallel c$.

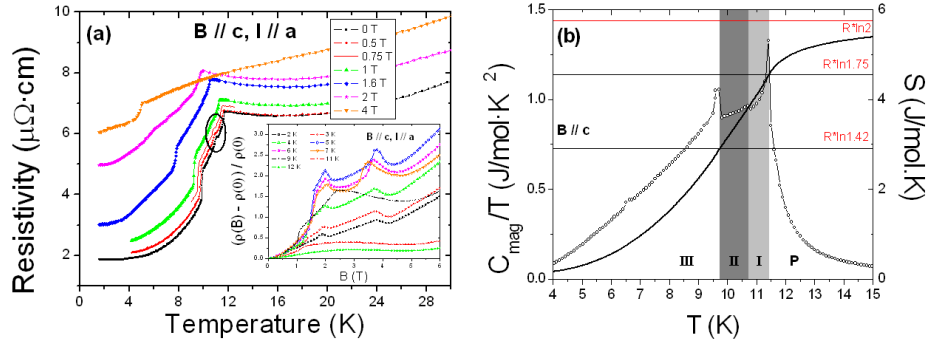
Fig. 2.   Magnetoresistivity (a) and magnetic specific heat (b) of TmB$_4$ for $B \parallel c$.

unit cells. The data suggest that AF correlations between the dimers (Tm^{3+}–Tm^{3+}) are dominant in the c-plane and ferromagnetic (FM) interactions along the c-axis. The properties of the intermediate phase (II) are more complex and show hysteresis effects both as a function of temperature and magnetic field. We suppose that the magnetization plateaus at $M(B)/M_{\mathrm{S}} = 1/7$ and $1/9$ seen in intermediate field arise from a magnetic *stripe structure* as was suggested for TbB$_4$ in [2]. In essence, the stripes appear to be coherent domain boundaries between AF-ordered blocks of 7 or 9 lattice constants.

The magnetoresistivity measurements, $\rho(T, B)$, as shown in Fig. 2a, detect the additional phase (phase I) between paramagnetic and ordered phase II. The value of residual resistivity ratio $RRR \approx 114$ indicates the high quality of the sample. The analysis by spin wave scattering formula $\rho(T) \propto T^x \exp(-\Delta_{\mathrm{sw}}/k_{\mathrm{B}}T)$ below T_{N2} gives the parameter $x \approx 2$, typical of FM ordering, and spin wave activation energy $\Delta_{\mathrm{sw}} \approx 2.4$ meV, which decreases down to ≈ 1 meV with increasing magnetic field. The temperature dependence of the specific heat $C(T)$ up to 5 T confirms the existence of phase I. In the paramagnetic state the magnetic part of

specific heat, $C_{\mathrm{mag}}(T, B)$, can be very well fitted by a Schottky anomaly with a parameter $T_{\max} \approx 48$ K and gap energy $\Delta E \approx 9.9$ meV. The magnetic entropy at zero field was calculated from C_{mag}/T vs. T dependence and is shown in Fig. 2b. The total molar entropy below $T_{\mathrm{N}1}$ is $Rln1.75$ and the contribution below $T_{\mathrm{N}2}$ being only $Rln1.42$, similar as for HoB$_4$ [1]. The site symmetry of the Tm^{3+} ion is mm and the CEF can therefore lift all the degeneracy of the $^3H_6$ ground state of Tm^{3+}. The fact that the entropy of TmB$_4$ in ordered state is less than $Rln2$ makes it possible that Tm^{3+} has a ground state of two closely lying singlets, nevertheless, the magnetization data suggest a doublet ground state with $J_m = 6$.

In summary, TmB$_4$ exhibits a strong Ising-like anisotropy. The combination of the CEF anisotropy and of magnetic frustration leads to strong competition between AF and FM order. Consequently, complex magnetic structures are found in the various magnetic phases of TmB$_4$. The stripe structure in intermediate field appears to be the best way to minimize the magnetostatic energy against other magnetic interactions between Tm ions combined with the very strong Ising anisotropy. Interestingly, this leads to intermediate stripe phases based on odd integers (1/7, 1/9) when the sample history favors AF order, the even occurrence (1/8) is found for the opposite FM case.

Acknowledgments

References

[1] Z. Fisk, M.B. Maple, D.C. Johnston, L.D. Woolf, *Solid State Commun.* **39**, 1189 (1981).

[2] S. Yoshii, T. Yamamoto, M. Hagiwara, T. Takeuchi, A. Shigekawa, S. Michimura, F. Iga, T. Takabatake, K. Kindo, *J. Magn. Magn. Mater.* **310**, 1282 (2007).

[3] R. Watanuki, G. Sato, K. Suzuki, M. Ishihara, T. Yanagisawa, Y. Nemoto, T. Goto, *J. Phys. Soc. Jpn.* **74**, 2169 (2005).

[4] S. Michimura, A. Shigekawa, F. Iga, M. Sera, T. Takabatake, K. Ohoyama, Y. Okabe, *Physica B* **378-380**, 596 (2006).

[5] F. Iga, A. Shikegawa, Y. Hasegawa, S. Michimura, T. Takabatake, S. Yoshii, T. Yamamoto, M. Hagiwara, K. Kindo, *J. Magn. Magn. Mater.* **310**, e443 (2007).

[6] S. Yoshii, T. Yamamoto, M. Hagiwara, A. Shigekawa, S. Michimura, F. Iga, T. Takabatake, K. Kindo, *J. Phys* **.**, 51 (2059)06.