Magnetic and thermal properties of novel TmPt₂B

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Abstract.

Ternary TmPt₂B crystallizes in the hexagonal CePt₂B-type structure (space group P6_22). Magnetic and specific heat measurements reveal long range magnetic order at 12.5 K. Field dependent results of both quantities clearly evidence a predominant ferromagnetic phase. The total angular momentum associated with the Tm³⁺ electronic configuration becomes split by crystalline electric field effects. The overall splitting turns out to be larger than 170 K.

Ternary rare earth (alkaline earth) - noble metal - metalloid (B,Si,Ge) systems have been extensively explored, evidencing a variety of interesting ground states: among them is heavy fermion superconductivity in absence of inversion symmetry in CePt₃Si [1], BCS superconductivity without inversion symmetry in BaPtSi₃ [2] or a diversity of magnetically ordered states in RE₂Pd₁₅B₅ [3]. In order to extend the knowledge on such materials, novel REPt₂B compounds (RE = Tm, Yb, Lu) have been prepared which are isostructural to the hexagonal CePt₂B type [4]. In a previous study [5] we have shown that CePt₂B orders antiferromagnetically at T_N ≈ 2.1 K. Besides the RKKY interaction, responsible for long range magnetic order, Kondo and crystalline electric field (CEF) effects determine the ground state properties.

The aim of the present work is a characterization of the physical properties of TmPt₂B by X-ray, magnetisation and heat capacity measurements. This allows to specify the magnetic properties and moreover assigning the electronic configuration of Tm in this compound, which, sometimes, fluctuates between the 4f¹² and the 4f¹³ state. LuPt₂B will provide information on the lattice dynamics of this family of compounds.

Polycrystalline samples were synthesized by argon arc-melting from high purity elemental ingots on a water-cooled copper hearth. The samples were re-melted several times in order to improve the homogeneity. The crystal structure was determined from X-ray single crystal data and found to be isostructural with the hexagonal CePt₂B type with a non-centrosymmetric space group P6_22 (RE in 3c (1/2,0,0), Pt in 6i (x,2x,0) and B in 3d (1/2,0,1/2)). Lattice and atom parameters and residual value for TmPt₂B are a = 0.52630(2) nm, c = 0.78705(3) nm, x_Pt = 0.15145(5), R₁₁ = 0.026 and for LuPt₂B are a = 0.52417(2) nm, c = 0.78583(4) nm, x_Pt = 0.15146(6), R₁₁ = 0.028, respectively. The crystal structure of {Tm, Lu}Pt₂B is shown in Fig. 1. The structure of {Tm, Lu}Pt₂B consists of hexagonal metal layers REPt₂ parallel to the ab-axes [Fig. 1(a)], forming rows of unfilled and boron-filled Archimedian antiprisms RE₄Pt₄ [Fig. 1(b)]. Distances are d_{Tm-B}=0.2940 nm, d_{Pt-B}=0.2064 nm, but no boron-boron contacts.
Figure 1. TmPt₂B structure: (a) projection along c-axis; b - arrangement of filled and unfilled Archimedian antiprisms [Tm₄Pt₄] and unfilled tetragonal pyramids [Tm₃Pt₂].

exist in the structure.

Measurements of various physical properties were carried out with standard techniques; details of which can be found in [6].

Temperature dependent magnetization measurements on TmPt₂B were performed at 1.98 mT, 0.013 T, 0.1 T, 1 T and 3 T external magnetic fields; results are summarized in Fig. 2(a). A distinct upturn of the magnetization curve around 12.6 K in the 1.98 mT measurement (inset in Fig. 2(a)) clearly indicates the onset of long range magnetic order. With an increase of the magnetic field, the magnetic phase transition becomes smooth and slightly shifts to higher temperatures. Also, a small hysteresis is observed for FC and ZFC at the transition temperatures for fields < 1 T. This together with the reduced moment of 4.35 µB/f.u. at 3 K and 6 T with respect to the moment of Tm³⁺ indicates a rather complex ferrimagnetic ordering in the presence of CEF splitting.

Further inspection of the low temperature data measured at 1.98 mT reveals a small anomaly around 6 K indicating the possibility of an reorientation of the magnetic moments as an order-to-order transition. Fig. 2(b) shows the temperature dependent magnetic susceptibility χ plotted as 1/χ vs. T for TmPt₂B. Data were taken at μ₀H = 1 T. Runs performed at different field values scale in an M/H vs. T plot, indicating that the sample is free from magnetic impurities.

In order to get some quantitative information, least squares fits according to the modified Curie Weiss law, i.e., χ = χ₀ + C/(T − θₚ) were applied to χ(T) data above 50 K. Here, χ₀ represents a temperature independent Pauli-like susceptibility, C is the Curie constant, related to μ_eff and θₚ is the paramagnetic Curie temperature. The results of the fit yield an effective moment (μ_eff = 6.94 µB) and a paramagnetic Curie temperature θₚ = ±1 K. The value obtained for μ_eff is very close to the theoretical value of 7.17 µB associated with the Tm³⁺ state. A Tm²⁺ state as observed in some Tm-based intermetallics can thus be excluded in TmPt₂B. Since |θₚ| is small compared to the ordering temperature, simple ferromagnetic order can be ruled out again. The possibility of a negative value of θₚ in TmPt₂B hints towards antiferromagnetic correlations, in agreement with the proposed complex ferrimagnetic ordering.

The temperature dependent specific heat C_p of TmPt₂B and LuPt₂B plotted as C_p/T vs. T is shown in figure 3(a). A sharp λ-like anomaly at T = 12.6 K in TmPt₂B indicates a magnetic phase transition. LuPt₂B serves as a non-magnetic reference. A standard analysis (inset, Fig. 3(a)) reveals the Sommerfeld coefficient γ = 2.2 mJ/mol-K² and a low temperature Debye temperature θ_D² = 250 K for LuPt₂B.

The phonon contribution to the specific heat C_ph was analyzed by a model consisting of a combination of one Debye- and three Einstein functions. Considering 4 atoms per formula unit,
Figure 2. (a) Temperature dependent magnetization of TmPt$_2$B for different magnetic fields. The measurement at 1.98 mT is highlighted in the inset. (b) Temperature dependent magnetic susceptibility $\chi$ of TmPt$_2$B plotted as $1/\chi$ vs. $T$ for $\mu_0 H = 1$ T. The solid line represents a modified Curie Weiss law. The inset shows low temperature features of $\chi(T)$.

the phonon dispersion relation of LuPt$_2$B consists of 3 acoustic and 9 optical branches. Using equal weights for the Einstein modes reveals a reasonable fit of the experimental data (solid line in Fig. 3(a)) for a Debye temperature $\theta_D = 140$ K, Einstein temperatures $\theta_{E1} = 133$ K, $\theta_{E2} = 227$ K and $\theta_{E3} \approx 980$ K. It should be noted that the Debye temperature derived is determined by the acoustic modes only, whereas $\theta_{DT}^T$ evaluated from low temperature specific heat data is some averaged value over acoustic branches of the phonon dispersion, assuming the entire spectral weight. In order to incorporate the effect of optical branches, $\theta_D$ deduced from the summary fit must be multiplied with the factor $\sqrt{n} = 1.59$, where $n = 4$ is the number of atoms per formula unit.

The magnetic contribution to the specific heat $\Delta C_p$ of TmPt$_2$B is shown in Fig. 3(b). $\Delta C_p(T)$ is obtained by subtracting heat capacity data of the non-magnetic reference LuPt$_2$B from the measured $C_p$ values of TmPt$_2$B. The magnetic phase transition is evident at 12.6 K. The small kink at $T \approx 6$ K (arrow, Fig. 3) can be due to a re-orientation of magnetic moments.

In the paramagnetic temperature range, a broad Schottky maximum is observed, centered around 70 K. This contribution is a consequence of the thermal population of levels created by lifting the ground state degeneracy of the total angular momentum $j$ due to CEF effects. Specifically, non-Kramers ion Tm$^{3+}$ with $j = 6$ in the context the hexagonal unit cell of TmPt$_2$B causes the 13-fold degenerate state to split into non-magnetic singlets and magnetic doublets. The fact that TmPt$_2$B orders magnetically indicates that the ground state is a doublet.

Integrating $\Delta C_p(T)/T$ yields the magnetic entropy $S_{mag}$, shown as solid line in Fig. 3b. At low temperatures, magnetic ordering causes a splitting of the ground state doublet, liberating $S_{mag} = R \ln 2$ in the vicinity of the ordering temperature. The fact that a plateau-like structure right above the ordering temperature is missing indicates that exited levels are energetically near to the ground state. For example, $R \ln 4$ is reached around 50 K; the rather continuous
Figure 3. (a) Temperature dependent specific heat of TmPt$_2$B and LuPt$_2$B plotted as $C/T$ vs. $T$. inset shows $C/T$ vs. $T^2$ with a $\gamma + \beta T$ fit indicated by the solid line. (b) Magnetic contribution to the specific heat of TmPt$_2$B. The solid line represents the magnetic entropy and refers to the right axis.

increase of $S_{mag}$ observed above $T_N$ would favour 2 singlets as the CEF states above the split doublet. The magnetic entropy reached at $T = 170$ K, the highest temperature studied in case of TmPt$_2$B, amounts to about $R \ln 10$. Thus, the majority of CEF levels are already thermally populated at this temperature.

In conclusion, CEF effects due to hexagonal symmetry in TmPt$_2$B provide a magnetic doublet as ground state of the non-Kramers ion Tm$^{3+}$ ($j = 6$). Then, RKKY interactions generate a complex magnetically ordered phase below $T_C = 12.5$ K with predominant ferromagnetic character followed by a spin re-orientation below 6 K.

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