High Field Magnetization of Tm$_2$AlB$_6$, an AlB$_2$-type Analogue Compound

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Abstract. The high field magnetization of Tm$_2$Al$_{11}$B$_6$ was measured up to 140 kOe. Tm$_2$Al$_{11}$B$_6$ was previously observed to show an interesting magnetic field dependence wherein one of the two transitions, $T_{N1}$, showed little magnetic field dependence from 20 kOe to 70 kOe in the specific heat. A kink in the high field magnetization at ~3 K is observed even up to 140 kOe, indicating the antiferromagnetic-like nature of the transition, and the high field state’s extreme stability (steep phase boundary) versus magnetic field. Even at the highest fields the saturation magnetization takes a small value (~ 3.3 μ$_B$/Tm) only about half that expected for a trivalent thulium ion. It is likely that only one Tm ion among the two crystallographic sites in Tm$_2$Al$_{11}$B$_6$ is ordering, while the other has a non magnetic singlet ground state.

Introduction

Boron forms various compounds in combination with metal atoms. We are particularly interested in the rare earth borides, of which many novel and varied compounds have been discovered within the past decade, and in which the shell of $f$ electrons supplies attractive physical properties [1].

The magnetism of well known borides like tetraborides RE$_4$B$_4$ (RE = rare-earth metal), hexaborides REB$_6$, and dodecaborides REB$_{12}$ has been a topic of great interest over the years [2-4]. Interesting magnetic behavior has also been observed in higher borides which contain the B$_{12}$ icosahedra as a structural building block. Magnetism in these higher borides varies from one-dimensional dimer-like magnetic transition in REB$_{50}$ and REB$_{44}$Si$_2$ [5-7], two-dimensional spin-glass behavior in REB$_{17}$CN, REB$_{22}$C$_2$N, and REB$_{28.5}$C$_4$ [8,9] to three-dimensional long-range order in GdB$_{18}$Si$_5$ [10]. Although these are magnetically dilute $f$-electron insulators, surprisingly strong magnetic coupling has been observed (e.g. $T_N = 17$ K for TbB$_{50}$[5], peak of ZFC susceptibility $T_f = 29$ K for HoB$_{17}$CN[8,9]).

The rare-earth metal aluminoboride system REAlB$_4$ has been attracting increasing attention with recent discoveries. Multiple magnetic transitions were reported to occur at low temperatures below an antiferromagnetic transition temperature $T_N$ in the YCrB$_4$-type structure [11] compound TmAlB$_4$ [12]. The origin of this behaviour was discovered to be due to an intrinsic tiling variation (building defects) in the crystals due to the presence of the closely related ThMoB$_4$-type structure [13] (space group Cmmm) [14]. Both structures have similarities to the AlB$_2$-type structure (AlB$_2$-type analogue compounds), with a planar boron network built of pentagonal and heptagonal rings having differently sized rare-earth and aluminum atoms. The difference between the YCrB$_4$-type and ThMoB$_4$-type structures is in the orientation of the pairs of condensed pentagonal rings, i.e. tiling. Crystals with both structure types were obtained from the same flux for YbAlB$_4$ and LuAlB$_4$ [15], with one of the
compounds; the ThMoB$_4$-type YbAlB$_4$ reported to exhibit heavy fermion superconductivity at 80 mK [16].

The discovery that intrinsic tiling building defects may be the origin of multiple magnetic anomalies in TmAlB$_4$ is striking because there are more than a hundred compounds reported with this type of structure, and it is possible that such phenomenon is actually ubiquitous [14].

We have recently been successful in synthesizing a new thulium layered compound Tm$_2$AlB$_6$ which is another AlB$_2$-type analogue compound (Y$_2$ReB$_6$-type structure [17]) with pentagonal, hexagonal, and heptagonal rings [18]. The structures of the two compounds are shown for comparison in Figs. 1(a) and (b). Tm$_2$AlB$_6$ is closer to the AlB$_2$-type structure compared to TmAlB$_4$. Incidentally, the AlB$_2$-type structure compound TmB$_2$ was recently synthesized and discovered to be ferromagnetic [19]. Therefore, for the REB$_2$: TbB$_2$, DyB$_2$, HoB$_2$, ErB$_2$, and TmB$_2$ are ferromagnetic while YbB$_2$ is antiferromagnetic.

The Tm$_2$AlB$_6$ system was found to have two antiferromagnetic transitions, with the higher temperature $T_{N1}$, exhibiting an unusual magnetic field dependence. In this work, the high field magnetic properties of a Tm$_2$AlB$_6$ compound were investigated up to 140 kOe to further investigate and elucidate this phenomenon.

**Experimental details**

Synthesis of Tm$_2$Al$_{11}$B$_6$ was carried out in the following way. First of all, stoichiometric amounts of thulium powder and $^{11}$B boron powder were well mixed together with an excess of aluminum powder [Tm]/[Al]= 1/9. The mixture was compacted with a hand press into a pellet of approximately 1 cm$^3$. The pellet was reacted at 1500°C for 10 hours to form a single phase polycrystalline sample. Characterization was done by using X-ray powder diffraction (XRD) measurements with Cu K$_\alpha_1$ radiation ($\lambda= 1.54060 \ \text{Å}$) on a RINT-ULTIMA diffractometer. High field measurements of the magnetization under fields of up to 140 kOe were performed using a PPMS magnetometer at the Helmholtz Centre in Berlin.

**Results and Discussion**

First we review the previously reported basic physical properties of Tm$_2$Al$_{11}$B$_6$ [18].

Multiple antiferromagnetic-like transitions were found at $T_{N1} = 3.5 \ \text{K}$ and $T_{N2} = 2.8 \ \text{K}$ at zero field. The Curie-Weiss fit of the magnetic susceptibility at relatively high temperature ($T > 30 \ \text{K}$) yielded an effective magnetic moment of $\mu_{\text{eff}} = 7.0 \ \mu_B/\text{Tm}$ and a Curie-Weiss temperature $\theta = -2.9 \ \text{K}$. The value of $\mu_{\text{eff}}$ is close to the theoretical value for the $^3H_4$ multiplet of the free trivalent thulium ion (7.56 $\mu_B$). The Curie-Weiss temperature agrees well with the energy scale of the transition temperatures.

The magnetic field dependence of the two transitions, $T_{N1}$ and $T_{N2}$, differed sharply. A low field of 4 kOe suppressed the low temperature transition, whereas $T_{N1}$ initially decreased with applied field but then exhibited a robustness versus the magnetic field above 20 kOe with the peak temperature hardly shifting up to 70 kOe from specific heat results. The high field magnetization was measured in this work to investigate this further.

The temperature dependence of the high field magnetization $M$ of Tm$_2$Al$_{11}$B$_6$ is plotted for magnetic fields from 1 kOe to 140 kOe in Fig. 2. The low field data is consistent with the previous report. Considering the higher field data, it can be observed that despite showing behaviour which might be interpreted as saturation at low temperatures, the magnetization continues to increase with increasing

![Figure 1. Views of crystal structures of (a) Tm$_2$AlB$_6$ (b) TmAlB$_4$ (YCrB$_4$-type).](image)
Figure 2. $M$-$T$ curves of Tm$_2$Al$_{11}$B$_6$.

Figure 3. Tm$_2$Al$_{11}$B$_6$ $M$-$T$ (a) 20 kOe (b) 140 kOe.

Figure 4. Phase diagram of Tm$_2$Al$_{11}$B$_6$.

fields. Saturation is further excluded because in the approximation of noninteracting magnetic moments ($\theta$ is small for Tm$_2$Al$_{11}$B$_6$),

$$M = Ng\mu_B B J_B(x),$$

where $B_J(x)$ is the Brillouin function, $g = 7/6$ and $J = 6$ for a trivalent thulium ion, $x$ for 20 kOe, for example, is too small for $M$ to show such a saturation behaviour.

This behaviour is rather indicated to be due to an antiferromagnetic-like transition at ~3 K which persists even up to high fields, namely, $T_N$, which was observed in the specific heat up to 70 kOe. The individual $M$-$T$ curves given in Figs 3(a) and (b) show that there is a kink below 3 K indicative of an antiferromagnetic-like transition (saturation behaviour is excluded for the reasons given above). The remarkable stability of this transition versus magnetic field is notable. The temperature of the transition $T_N$ is virtually field dependent above 20 kOe up to at least 140 kOe. We add the present results to the phase diagram of Tm$_2$Al$_{11}$B$_6$ (Fig. 4). The present result further reveals the antiferromagnetic-like nature of this transition (a downward kink in the magnetization) at high fields, which was not clear from specific heat results.

To explain the robust high field phase boundary, a crystallographic transition can be imagined, however, the symmetry of the Tm site in Tm$_2$Al$_{11}$B$_6$ is already quite low and it is not obvious how such a transition can be driven in conjunction with magnetic ordering of the thulium ions. The observed antiferromagnetic-like behaviour of the $M$-$T$ curves also indicates this to be unlikely.

Another interesting result is the relative small values of the magnetization. $M$ for 140 kOe only approaches a maximum value of $M \sim 3.3 \mu_B$/Tm. This is about half of that which would be expected for a trivalent thulium atom. There are two Tm sites in Tm$_2$Al$_{11}$B$_6$. The present results may indicate that only one Tm ion in Tm$_2$Al$_{11}$B$_6$ orders, whereas the other has a non magnetic singlet ground state. This is also supported by the previously observed low values of magnetic specific heat (entropy) [19].
The origin of this complex magnetic behaviour in Tm$_2$Al$_{11}$B$_6$ remains to be solved. As noted above, complex behaviour in the related AlB$_2$-type analogue compound of TmAlB$_4$ has previously been observed but was able to be attributed to intrinsic tiling building defects [14]. However, such tiling defects are not likely to be able to explain the anomalous behaviour of Tm$_2$Al$_{11}$B$_6$, i.e. extremely steep phase boundary and small magnetization value. Tm$_2$Al$_{11}$B$_6$ is different from TmAlB$_4$ in that the two thulium ions occupy different sites in the lattice, thus the crystal field splitting could vary between the Tm sites and cause intricate behaviour.

Conclusions
High field magnetization was investigated for Tm$_2$Al$_{11}$B$_6$, which is an AlB$_2$-type analogue compound, previously observed to have an unusual field dependence. The high field magnetization data support the extreme stability (steep phase boundary) of a high field state which was previously indicated from specific heat measurements. The present results reveal that the magnetic stability persists up to the high magnetic field of 140 kOe. Furthermore, the $M$-$T$ curves reveal the antiferromagnetic-like nature of this transition (a downward kink in the magnetization) despite its extreme independence to magnetic field at high fields.

The magnetization for the highest field 140 kOe only approaches a maximum value of $M \sim 3.3 \mu_B$/Tm. This is about half of that which would be expected for a trivalent thulium atom and possibly indicates that only one of the two crystallographic thulium site magnetically orders while the other has a non magnetic singlet ground state.

Further investigations using neutron scattering measurements will be done to make the phases and complex behavior in this layered compound clearer.

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