Abstract. The rare earth tetraborides REB$_4$ with RE = Ho, Er, Tm, crystallize in a tetragonal lattice where the positions of the RE ions can be mapped to a Shastry Sutherland lattice. We have investigated the magnetic properties by means of magnetisation and specific heat experiments in a magnetic field. All compounds are anisotropic, with RE = Er, Tm they are strong Ising magnets, for RE = Ho we find xy anisotropy. In magnetic field we find complex behaviour with a number of different phases as a function of applied field, field direction and temperature. Remarkable is the observation of fractional magnetisation plateaux for magnetic field || (001) in HoB$_4$ and TmB$_4$.

1. Introduction

The rare earth tetraborides REB$_4$ crystallize in a tetragonal lattice (SpGrp. 147). The chemical and crystallographic properties of these compounds are very similar for RE = Ho, Er, Tm… . One of the three valence electrons goes to the conduction band, therefore the tetraborides are good metals and the RKKY interaction is thought to be relevant. The RE lattice topology maps to a Shastry Sutherland (SS) lattice: It is formed from a regular array of squares and triangles (fig. 1a), the latter are here – accidentally – almost equal sided (fig 1b). So far, only few examples for that lattice are known, the most prominent probably is SrCu$_2$(BO$_3$)$_2$. The magnetic properties of the SS magnets have attracted attention first because an exact solution was provided by SS [1]. Later, unexpected by theory, it was found that the magnetization in SS magnets exhibits fractional magnetization plateaux that recently were explained in analogy to the fractional quantum Hall effect of a 2D electron gas for the case of SrCu$_2$(BO$_3$)$_2$ [2]. In contrast to SrCu$_2$(BO$_3$)$_2$, the tetraborides show long range order in zero field. We have constructed the
Fig. 1: In fig 1a we show the SS lattice as suggested in [1]. Fig. 1b gives the RE positions in the tetraborides system in the (a,b) plane and the interaction paths \( J_1 \) (on the triangular bonds) and \( J_2 \) (on square diagonals) chosen different from the SS case by us. Fig 1c shows the zero field phase diagram for Ising spins. The resulting structure is indicated with blue and red circles denoting the up/down spins.

The zero field phase diagram shown in fig. 1c as a function of \( J_1 \) and \( J_2 \) (c.f. fig. 1b) by diagonalisation of the interaction matrix for 8 Ising spins. Apart from the ferromagnetic structure, it consists of three different antiferromagnetic (af) phases with ferro- and af coupling between the SS dimers. The energy of the phases AF1, AF2 and AF3 is proportional to \(-J_1-2J_2\), \(-J_1-J_2\) and \(-3J_1+2J_2\), respectively and to \(5J_1+2J_2\) for the FM state. Similar to \( \text{SrCu}_2(\text{BO}_3)_2 \), the tetraborides show fractional magnetization plateaus in applied field \([3,4,5,6]\).

Here, we discuss our magnetization and susceptibility data for RE = Ho, Er, Tm. Based on the magnetization data we estimate parameters for the anisotropy and the interactions.

2. Experimental

The samples were prepared by an inductive, crucible free melting method. For the magnetization experiments oriented single crystals with approximate dimensions \(1^*1^*1\) mm\(^3\) were cut from larger samples. Magnetization data were measured in commercial PPMS and MPMS systems, the magnetic field was oriented within \(2^\circ\) with respect the crystal axis. Low temperature data on the ac susceptibility were obtained using a MPMS system at FZ Dresden - Rossendorf. For the data analysis of the magnetization experiments a demagnetization correction was applied, the absolute change to the data does not exceed 10% of the measured data.

3. Results and Discussion

3.1 High temperature susceptibility: The high temperature susceptibility was derived from magnetization data measured in a field of 50 mT. The paramagnetic Curie Weiss temperature \(\Theta\) differs significantly for \(B \parallel (001)\) and \(B \perp (001)\) (fig. 1). That can be understood by crystal field anisotropy. The susceptibility was analysed similar to the work of Yosida [7] which takes an anisotropy \(H_{\text{anis}} = D S^2_j\) into account. In TmB\(_4\) and ErB\(_4\) a strong Ising anisotropy is found, HoB\(_4\) has a small xy like anisotropy. All interaction integrals indicate af order. The effective moment \(\mu_{\text{eff}}\) for RE = Ho, Er, Tm obtained from the Curie Weiss

| Table 1: Results of the susceptibility data. See the text for a discussion. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | \(\mu_{\text{eff}} (\mu_\text{B})\) | \(\Theta_\perp (\text{K})\) | \(\Theta_\parallel (\text{K})\) | \(T_{N1} (\text{K})\) | \(T_{N2} (\text{K})\) | \(\sum J_a (\text{K})\) | \(D (\text{K})\) |
| HoB\(_4\)      | 9.2             | -12.7           | -6.1            | 7.4             | 6.3             | -1.3            | 0.3             |
| ErB\(_4\)      | 8.4             | -22.7           | 12.9            | 15.3            | -               | -1.4            | -4.6            |
| TmB\(_4\)      | 6.6             | -63             | 40.3            | 11.7            | 9.8             | -4.8            | -6.4            |
fit is almost independent on the field direction and agrees within error with the free ion value. For field along the c-axis, HoB₄ and TmB₄ show two transitions in zero field at slightly higher Néel temperature $T_N$ than found e.g. by Kim [6]. Also, the Curie Weiss temperatures, in particular for HoB₄, differ from that work. An explanation could be the strong dependence of $\Theta$ and $T_N$ on the magnetic field orientation.

With knowledge of the magnetic structure the interaction constants of our $J_1, J_2$ model (c.f. Fig. 1b) can be determined from the interaction integral and the Néel temperature. For TmB₄ the AF3 type structure is the zero field ground state [5]. The $T_N, \Theta$ data lead to interactions $J_1 = 0.85$ K and $J_2 = 0.3$ K which is consistent with the AF1 phase and structural elements of that phase are indeed stable in high magnetic field [5]. ErB₄ has been reported to show the type AF1 structure [8]. The high temperature susceptibility data for ErB₄, however, give a large negative value for $J_2$ which is not consistent with our model. One possible reason is that the 8 ion lattice used here is too small for type AF1 structures. Finally, for HoB₄ so far no reliable structure model has been established. The structure appears to be incommensurate in zero field [9] with moments mainly in the tetragonal plane. A small field of 0.2 Tesla lifts the incommensuration and then our preliminary data indicate a type AF1 structure.

3.2: Magnetisation plateaux: One of the most striking observations in SS magnets is the emergence of fractional magnetisation plateaux. All compounds discussed here show in high magnetic field a plateau that is stable over a large field area. For Er- and TmB₄ we find $M/M_{Sat}=1/2$, for HoB₄ a $1/3$ plateau is observed. At low temperature well below $T_N$, TmB₄ exhibits additional plateaux as a function of magnetic field where fractional values of $M/M_{Sat}=1/6$ up to $1/12$ have been observed. For some of these plateau values the magnetic structure was suggested as stripe structures similar to domain boundaries [5]. In contrast, ErB₄ does not show any additional plateaux and seems to be a metamagnet due to the strong anisotropy.

Here we like to concentrate on HoB₄. At a temperature of 2K the magnetisation data indicate additional plateaux at $M/M_{Sat}=4/9$ and 3/5 for magnetic field parallel to the c–direction. However, they are not very pronounced and this could be attributed to the relatively high temperature when comparing to $T_N = 7.4$ K. It seems that plateaux get more stable at low temperature, this idea is supported when comparing with TmB₄ and also with SrCu₂(BO₃)₂. There magnetisation plateaux are seen only at low temperature [2, 5]. Therefore, it was natural to extend the characterization of HoB₄ to low temperatures and we have investigated the magnetisation and ac susceptibility down to 65 mK. Looking at Fig. 3 it is obvious that the magnetization plateau at $M/M_{Sat} = 1/3$ is reproduced by static magnetisation and ac methods, independent on temperature.
Fig. 3: Magnetization as a function of magnetic field with B||(001). The left figure gives the magnetization at 2 K (from quasistatic MPMS), the saturation moment corresponds to 6 \(\mu_B/\text{Iion}\). The right figure shows the ac susceptibility at 500 mK (from a 16 Hz ac MPMS system). The magnetization is obtained by integration of the susceptibility data assuming that in high field (B=5Tesla) saturation is achieved.

In addition, the ac susceptibility data show a series of maxima which may well be associated with fractional values of the magnetisation. The fact that they are not reflected in the magnetization integral could well be due to the ac measuring method: Fractional states may be very close in energy, but very different in their spatial order and thermal equilibrium may need time scales beyond the experimental scale available here. The strong hysteresis in “up” and “down” sweeps of the magnetic field supports this, together with sample orientation effects that can also be the reason for differences to the work of Kim [8].

4. Conclusions
We have derived interaction and anisotropy parameters from high temperature magnetization data for a number of tetraborides. Fractional magnetization plateaux are observed in TmB\(_4\) and HoB\(_4\). They appear for magnetic field parallel to the c – axis both for Ising like TmB\(_4\) and the xy - like HoB\(_4\) and are subject to strong hysteresis. The fact that the plateaux are more prevalent at low temperature may indicate they are stabilized more by quantum fluctuations rather than thermal fluctuation.

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