Journal of Solid State Chemistry **154,** 223–228 (2000)
doi:10.1006/jssc.2000.8839, available online at http://www.idealibrary.com on IDEAL®

Specific Heat of Antiferromagnetic-like $TbB_{41}Si_{1.2}$, a B_{12} Icosahedral Boron-Rich Compound

Takao Mori[1] and Takaho Tanaka

National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received September 9, 1999; in revised form February 3, 2000; accepted February 15, 2000

A detailed measurement of the specific heat of the B_{12} icosahedral compound $TbB_{41}Si_{1.2}$ was made. $TbB_{41}Si_{1.2}$ crystals were grown by the floating zone method. Magnetic susceptibility measurements indicated that an antiferromagnetic-like transition occurs at 18 K in these crystals. TbB_{50} and isostructural $TbB_{41}Si_{1.2}$ are the first higher borides in which a magnetic transition was observed to occur. A hump in the specific heat is observed below 20 K, supporting the conclusion that a magnetic transition occurs in this system. An interesting magnetic field dependence was observed. Near the metamagnetic critical field of 31 kG, determined from magnetization measurements, the hump shifts to lower temperatures approaching 0 K. At 40 kG no hump is apparent. However, on further increasing the magnetic field to 55 and 70 kG, a new hump in the specific heat appears, indicating the possibility of the existence of an additional transition at high fields. Magnetization measurements of REB_{50} (RE = Tb, Dy, Ho, Er) up to 55 kG showed that the compounds saturated universally at around only half the saturation magnetization value of free rare-earth ions, which also indicated the likelihood of a further transition. The structure of the REB_{50}-type compounds has a one-dimensional character with the rare-earth atoms forming an alternating bond length chain along the *c*-axis. These results are quite interesting in the context with the recent high activity in Haldane gap related compounds in which fundamental quantum phenomena are observed.

Key Words: **borides; rare earth; boron rich; B_{12} icosahedra; antiferromagnetic-like transition; specific heat; alternating bond.**

1. INTRODUCTION

Magnetic rare-earth borides have attracted much interest over the years as systems exhibiting intriguing properties of f-electron magnetism. In the case of the comparatively metal rich rare-earth borides, such as REB_2, REB_4, REB_6, and REB_{12}, the magnetic behavior has been investigated extensively (1). Various interesting properties such as ferromagnetic and antiferromagnetic transitions, strong magnetic anisotropy, and multiple transitions have been observed for these comparatively metal-rich compounds.

However, up to recently, no interesting magnetic behavior had yet been found for the boron-rich higher borides. Quite recently, we discovered that an antiferromagnetic-like transition occurs in the REB_{50} compounds and isostructural $REB_{41}Si_{1.2}$ compounds (2–4). This was an interesting result, because REB_{66} compounds synthesized at the metal-rich end of the homogeneity region, which have comparable magnetic atom concentration, and REB_{25} compounds, which have a denser concentration, showed no transition down to 2 K. The transition observed in TbB_{50}, for example, had the relatively high transition temperature of 17 K. These are the first magnetic transitions observed in the higher borides.

We successfully grew a $TbB_{41}Si_{1.2}$ crystal and used it for measurements. $TbB_{41}Si_{1.2}$ has an orthorhombic crystal structure with lattice constants of $a = 16.651$ Å, $b = 17.661$ Å, $c = 9.500$ Å, and 346 atoms in a unit cell. The structure of $TbB_{41}Si_{1.2}$ is displayed in Figs. 1a and 1b, using previously determined crystallographic parameters (5). As can be seen in Fig. 1a, B_{12} linear icosahedral chains run along the *c*-axis and the terbium atoms are also aligned along this axis and form a one-dimensional alternating bond chain in the nearest neighbor direction. Interesting features of the structure are the one-dimensional character of the structure and the fact that it has the shortest lattice constant along the B_{12} icosahedral axis ever observed for the B_{12} chain compounds. From the previous investigations it was indicated that this short B_{12} icosahedral lattice constant was a significant factor for the magnetic transition to appear (2–4).

In this study we report the results of specific heat measurements together with magnetization measurements which were made on floating zone (FZ)-grown $TbB_{41}Si_{1.2}$ crystals in order to investigate the newly discovered antiferromagnetic-like transition. The magnetization of REB_{50} compounds is also presented. An interesting magnetic field

[1] To whom correspondence should be addressed. Fax: 81-298-52-7449. E-mail: moritk@nirim.go.jp.

0022-4596/00 $35.00

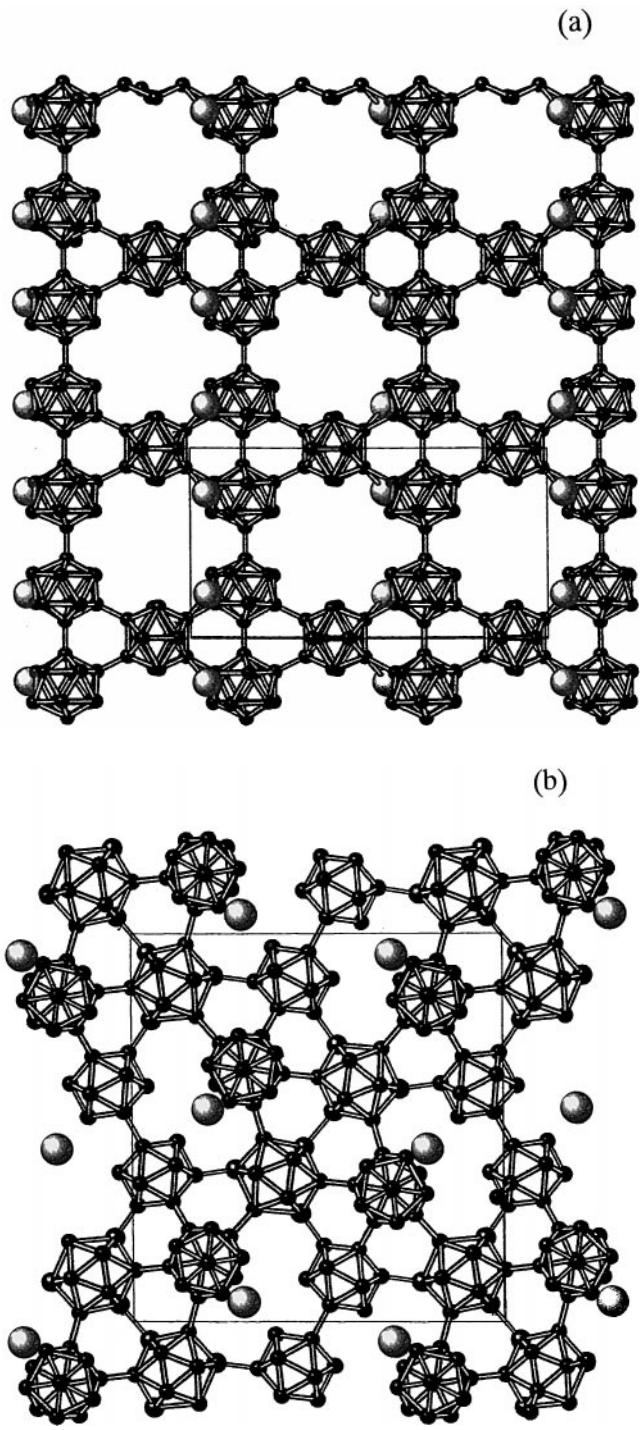

FIG. 1. Crystal structure of $TbB_{41}Si_{1.2}$. (a) B_{12}-4 and B_{12}-5 icosahedra, $B_{12}Si_3$ polyhedra, and terbium atom arrangement as seen along the c-axis, within the range of $z = 0.30$–0.92. (b) Arrangement of B_{12}-2 and B_{12}-4 icosahedra and terbium atoms as seen along the a-axis, within the range of $x = 0.09$–0.41. The numbers denote crystallographically different B_{12} icosahedra, of which there are five. Two of the icosahedra B_{12}-1 and B_{12}-3 are out of the range of a and are not seen. The small circles indicate boron atoms, the medium sized circles indicate silicon atoms, while the large circles indicate terbium atoms. Parameters determined in Ref. 5 were used to make the figures.

dependence was observed for both magnetization and specific heat measurements.

2. EXPERIMENTAL

The $TbB_{41}Si_{1.2}$ crystals were prepared in the following way (6). Feed rods were prepared by two-step sintering. First, TbB_{50} was synthesized by using a borothermal reduction method at 1740°C. Then the desired amount of silicon was added and sintered again at 1840°C in vacuum. These feed rods were used in the floating zone (FZ) method to obtain crystals. Our crystals were identified by X ray powder diffraction and chemical analyses to be of the $TbB_{41}Si_{1.2}$-type phase. Polished surfaces of the highest quality grown samples showed the existence of multigrains and we have not yet been able to assign any particular alignment by Laue measurements. REB_{50} (RE = Tb, Dy, Ho, Er) compounds were also synthesized by the borothermal reduction method with sintering at 1700–1800°C.

The specific heat was measured by a transient heat pulse method with a small temperature increase of 2% relative to the system temperature. A polished face of a flat sample was attached to an alumina plate holder using Apiezon N grease. Results from a blank run of the holder and grease were subtracted from the data to obtain the specific heat of the sample. The measured temperature region was from 300 to 2 K.

Magnetic susceptibility was measured by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer from 300 to 2 K.

3. RESULTS AND DISCUSSION

3.1. Magnetic Susceptibility of $TbB_{41}Si_{1.2}$

The static magnetic susceptibility of $TbB_{41}Si_{1.2}$ is given in Fig. 2a, while the magnetization is given in Fig. 2b. The magnetic susceptibility increases as temperature is lowered, but shows a significant decrease below around 18 K, indicating the antiferromagnetic-like transition. At further lower temperatures an upturn is observed.

The high temperature susceptibility can be well described as the sum of a temperature-independent term χ_0 and Curie–Weiss term,

$$\chi = \chi_0 + N\mu_{\text{eff}}/3k_{\text{B}}(T - \theta),$$

with $\chi_0 = -8.9 \times 10^{-3}$ emu/mol, an effective number of Bohr magnetons μ_{eff} of 10.7 μ_{B}/Tb atom, and a Curie–Weiss temperature θ of -18.1 K.

The transition temperature T_{N}, which is taken to be the peak in the susceptibility, is 18 K. The low temperature upturn of the susceptibility is attributed to paramagnetic impurities such as defects or Tb_{66} impurities. To obtain an

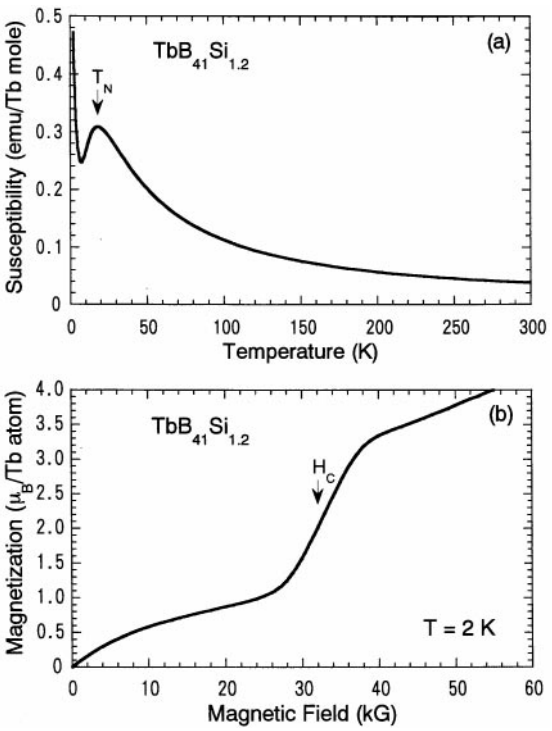

FIG. 2. Temperature dependence of the static magnetic susceptibility of $TbB_{41}Si_{1.2}$. Data include contributions from paramagnetic impurities. The transition temperatures T_N are indicated by arrows. T_N is defined as the temperature where the susceptibility takes a maximum before decreasing.

upper limit of the magnitude of the impurity component we fit the entire region below 5 K as a single Curie–Weiss curve. We obtain a Curie constant which is 9% of the total. We note that this value is significantly smaller than the values of 17 and 18% determined for polycrystalline TbB_{50} and arc melted $TbB_{41}Si_{1.2}$, respectively (2, 3). This is probably due to the fact that our crystals were grown by the FZ method and have fewer defects than the previous samples.

We stress that the actual magnitude of the impurity component is expected to be much smaller than the upper limit values given, since the entire low-temperature region was fitted by assuming the susceptibility of intrinsic TbB_{50} and $TbB_{41}Si_{1.2}$ to be zero in this region for the fit.

Magnetization was measured by varying the magnetic field up to 55 kG. The curve for the magnetization at 2 K is shown in Fig. 2b. A metamagnetic transition is observed. The arrow in the figure indicates the critical magnetic field $H_C = 31$ kG, which is defined as the field where the derivative of magnetization has a peak.

A particular feature of the magnetization curve is that the sample appears to saturate at a value around only half the value of the saturation moment for trivalent free ions $9\mu_B$/Tb atom.

3.2. *Magnetization of REB_{50}*

As noted above, the magnetization of $TbB_{41}Si_{1.2}$ appeared to saturate at about half the value of the trivalent free ion case. We investigated the magnetization of the other rare-earth REB_{50} to find out whether this is a universal phenomena.

The magnetization of REB_{50}, including that of polycrystalline TbB_{50}, is shown in Figs. 3a and 3b. As in Fig. 2b, the arrows in the figures indicate the critical magnetic fields H_C which are defined as the fields where the derivatives of magnetization have a peak.

It is found that indeed all of the samples appear to saturate at a value around only half the value of the saturation moment for trivalent free ions.

Compared to Fig. 3a, the magnetization curve of the grown crystal $TbB_{41}Si_{1.2}$ in Fig. 2b shows a bend at around 39 kG and a plateau-like feature is more pronounced. We think that this is due to the smaller amount of paramagnetic impurities in the crystal sample and thus, the plateau-like behavior is thought to better describe the intrinsic behavior of $TbB_{41}Si_{1.2}$. In any case, universal behavior of the REB_{50} compounds is observed, with magnetization saturating at values roughly half that expected for free ions. The significance of this result will be discussed later.

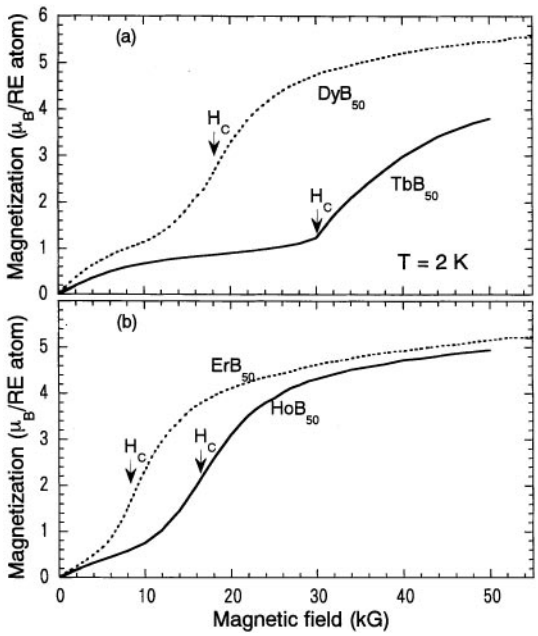

FIG. 3. Magnetic field dependence of the magnetization at 2 K of (a) TbB_{50} (bold lines) and DyB_{50} (dotted lines) and (b) HoB_{50} (bold lines) and ErB_{50} (dotted lines). Data include contributions from paramagnetic impurities. The critical magnetic fields H_C are indicated by arrows. The critical magnetic field is defined as the field where the derivative of magnetization has a peak.

3.3. Zero Field Specific Heat of $TbB_{41}Si_{1.2}$

The temperature T dependence of the specific heat C of $TbB_{41}Si_{1.2}$ is plotted in Fig. 4 for low temperatures and over the whole measurement region in the inset. Smooth behavior is observed throughout the higher temperature range. A hump in the specific heat is observed below 20 K. This supports the conclusion that a magnetic transition is occurring in this system.

The low temperature data are plotted in the conventional C/T versus T^2 plot in Fig. 5. Fairly linear behavior is observed as temperature is lowered with an anomalous hump below $\sim$20 K. A further sharp upturn is observed below 4 K. The origins of this upturn are not known at present. Two small jumps in the data can be observed around 18 K, but we judge them to be of spurious nature, since they were not observed for more detailed low-temperature measurements which will be given in the next section.

Since a linear curve is obtained above the hump we first attempt to interpret this specific heat as the sum of a linear electronic specific heat term and phonon T^3 term:

$$C = \gamma T + C_2 T^3.$$

The parameters $\gamma = 225$ mJ/mol/K^2 and $C_2 = 109$ mJ/mol/K^4 are determined, which correspond to a density of states at the Fermi energy $D(E_F)$ of 2.0×10^{23} states/eV cm^3 and an unrealistic value of the Debye temperature θ_D of 94 K.

Another unsatisfactory point of the above interpretation is that the line corresponding to the fitted curve crosses through the data at low temperatures, as can be seen in the graph. Furthermore, on integrating the difference between the total C/T and the nonmagnetic contribution determined from the fit to obtain the entropy associated with the magnetic specific heat, we obtain a very small value of 1.0 J/mol K, which corresponds to Rln1.1, much smaller than the Rln13 expected for this system. (Even taking into account the fact that a secondary transition is indicated in the next section to further occur at high fields.)

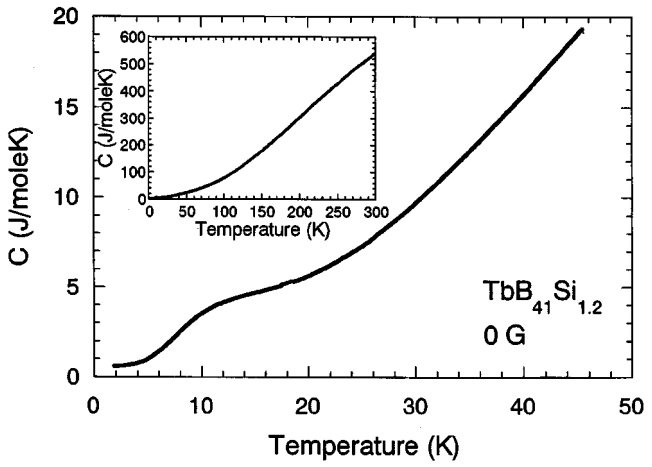

FIG. 4. Temperature dependence of the specific heat of $TbB_{41}Si_{1.2}$. (Inset) Specific heat over the whole temperature region of 300 to 2 K.

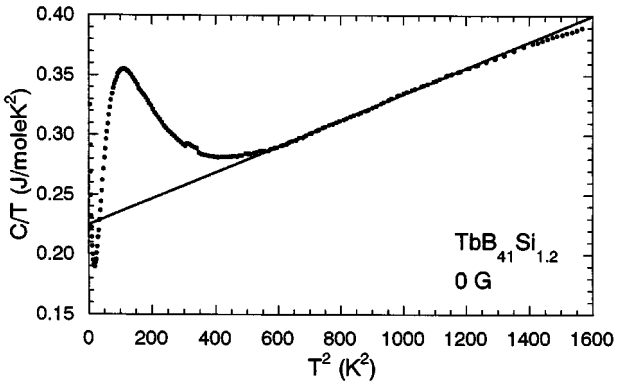

FIG. 5. Specific heat of $TbB_{41}Si_{1.2}$ shown in the form of the conventional C/T plots as a function of T^2 in the temperature range between 2 and 40 K. The line indicates the fitted curve to Eq. (1), with the parameters $\gamma = 225$ mJ/mol/K^2 and $C_2 = 109$ mJ/mol/K^4.

These results lead us to believe that we are not correctly evaluating the nonmagnetic contribution to the specific heat. At present we are attempting to grow crystals of suitable nonmagnetic analogs such as $LuB_{41}Si_{1.2}$ crystals and perform subsequent measurements to estimate the nonmagnetic specific heat.

On determining the derivative of the specific heat (Fig. 6), we find that it goes through a minimum at around 15 K, which we label as T_N^* (the two largely deviating points are due to the spurious small jumps noted above). This means that the peak of the total specific heat occurs at around 15 K. T_N^* is close to the transition temperature $T_N = 18$ K determined from the magnetic susceptibility measurements and we judge that it gives us a value representative of the transition temperature.

3.4. Magnetic Field Dependence of the Specific Heat

The magnetic field dependence of the specific heat was investigated next. Shown in the figures is the specific heat under a magnetic field of (Fig. 7a) 0 G, 12 kG, 15 kG, (Fig. 7b) 0 G, 30 kG, 40 kG, and (Fig. 7c) 0 G, 55 kG, 70 kG. In Fig. 7a, it can be seen that there is not much variation of behavior under 20 K on applying the magnetic field up to 15 kG. Below 7 K, a slight variation is observed, with the specific heat increasing with the application of field. Since the temperature is well below the transition temperature, the origin of this difference may be due to magnetic impurities which were briefly discussed above. On further

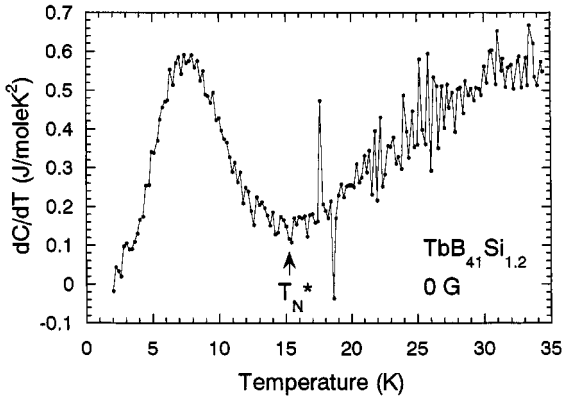

FIG. 6. Temperature dependence of the derivative of the specific heat of $TbB_{41}Si_{1.2}$. The arrow indicates the temperature T_N^*, where the derivative goes through a minimum.

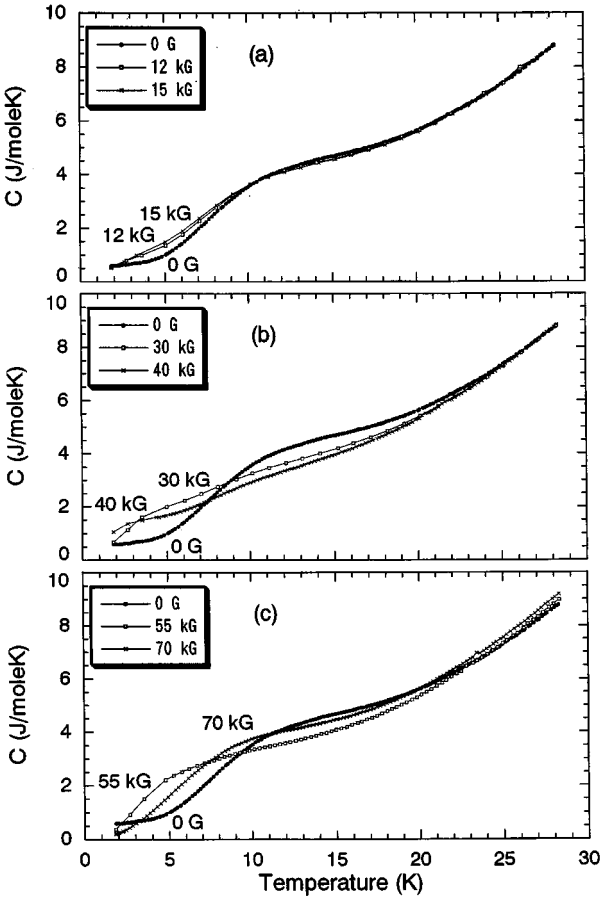

FIG. 7. Temperature dependence of the specific heat of $TbB_{41}Si_{1.2}$ under a magnetic field of (a) 0 G, 12 kG, 15 kG, (b) 0 G, 30 kG, 40 kG, and (c) 0 G, 55 kG, 70 kG.

increase of the magnetic field up to 30 and 40 kG, a large change in behavior is observed. At 30 kG, which is near the metamagnetic critical field of 31 kG, the hump appears to shift to lower temperatures approaching 0 K. At 40 kG the hump is depressed further and virtually no hump is apparent. However, on further increasing the magnetic field to 55 and 70 kG, a new hump in the specific heat appears, indicating the possibility of the existence of an additional transition at high fields. This hump appears to shift to higher temperatures with the increase of field from 55 to 70 kG.

In quantitative terms, the temperatures at which the derivative of the specific heat goes through a minimum, T_N^*, are determined to be 15 K at 0 G, 12 kG, and 15 kG, while no well defined minimum was observed for 30 and 40 kG, 11 K at 55 kG, and 12.5 K at 70 kG. In the case of 40 kG the form of the specific heat indicates no transition, while, for the 30 kG data, the low-temperature tail of the specific heat indicates that T_N^* takes a value near 0 K. From the similarities of form of specific heat for the 0 G case and 55 and 70 kG, we judge that it is reasonable to assume that this hump which appears at 55 and 70 kG is indicative of a similar magnetic transition.

Previously, we determined the phase diagram of TbB_{50} from measurements on the field dependence of the magnetization at different temperatures (2). We plot these points together with the T_N^* obtained from the specific heat measurements to obtain the magnetic phase diagram for terbium TbB_{50}-type structure compounds, TbB_{50} and $TbB_{41}Si_{1.2}$ (Fig. 8). It must be noted that this is a conglomerate of parameters determined for two different isostructural compounds, TbB_{50} and $TbB_{41}Si_{1.2}$. However, there is only a slight difference of values of T_N (low field) and H_C (2 K) determined for the two isostructural compounds, namely, $T_N = 17$ K versus 18 K and $H_C = 30$ kG versus 31 kG, for TbB_{50} and $TbB_{41}Si_{1.2}$, respectively. Therefore, we think that this phase diagram gives us a good overall view of the behavior (physics) of this compound.

The phase diagram has an interesting structure, showing two branches. As magnetic field is increased a metamagnetic transition occurs, from the antiferromagnetic-like state to an intermediate higher field state which has only half value of saturation magnetization as noted in Sections 3.1 and 3.2. We assign this with the letter I in the phase diagram. On further increasing the field, a second transition to a higher field state is indicated. We assign this as H in the diagram.

We expect that the transition to the high field H state will result in the magnetization gaining its full value. As to the exact nature of the high field states and also the intermediate states, it is not known at present.

What is made clear in this work is that the existence of a further transition at high fields above the metamagnetic transition is indicated and that the intermediate state only has a saturation magnetization of roughly half value, universally for the different rare-earth REB_{50} compounds.

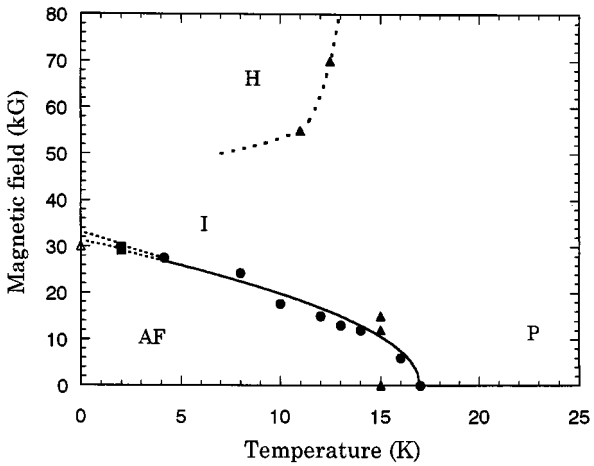

FIG. 8. Magnetic phase diagram of terbium TbB_{50}-type structure compounds, TbB_{50} and $TbB_{41}Si_{1.2}$. The closed round circles were determined from measurements of the field dependence of the magnetization of TbB_{50} at different temperatures (Ref. 2), while the open and closed triangles were determined from the specific heat of $TbB_{41}Si_{1.2}$ (this work). In detail, the closed round circles (H_C) are determined from the intersect of extrapolated curves from the lower field region and the higher field region of the magnetization of TbB_{50}. The closed triangles are determined from the temperature (T_N^*) where the derivative of the specific heat of $TbB_{41}Si_{1.2}$ goes through a minimum. The open triangle is estimated from the temperature dependence of the specific heat data at 30 kG. The lines are a guide to the eye. AF and P indicate the antiferromagnetic-like and paramagnetic regions, respectively. The *I* indicates the intermediate field state, while the *H* indicates the possible high field phase.

We note that the magnetization plateau-like behavior observed at half value of saturation magnetization is also interesting in the following context.

Recently, much renewed interest is being focused on Haldane gap compounds (7, 8) and related compounds such as antiferromagnetic bond alternating chains (9), because of the macroscopic quantum phenomena which manifests in these system. For, example, magnetization plateaus in spin chains have been theoretically calculated (10).

Our compounds have the interesting structural feature that the rare-earth atoms form alternating linear chains fairly isolated from each other aligned along B_{12} icosahedral chains. It is possible that we have obtained a new family of one-dimensional AF chains. A particularly interesting feature of these compounds is that the value of spin can be varied through substitution of the rare-earth atoms. Further investigation of the physical properties of this compound should be of high interest.

Neutron scattering measurements should be useful in determining the spin structure of this compound. Magnetization measurements at high fields above 55 kG are also being planned. The growth of high-quality single crystals of $TbB_{41}Si_{1.2}$ is also underway.

4. CONCLUSION

A detailed measurement of the specific heat of FZ grown $TbB_{41}Si_{1.2}$ crystals was made. Magnetic susceptibility measurements indicated that an antiferromagnetic-like transition occurs at 18 K and a metamagnetic transition occurs at 31 kG in these crystals. TbB_{50} and isostructural $TbB_{41}Si_{1.2}$ are the first higher borides in which a magnetic transition was found to occur. A hump in the specific heat is observed below 20 K with a peak around 15 K, supporting the conclusion that a magnetic transition occurs in this system. An interesting magnetic field dependence was observed. Near the metamagnetic critical field of 31 kG, the hump shifts to lower temperatures approaching 0 K, and at 40 kG no hump is apparent. However, when the magnetic field is further increased to 55 and 70 kG, a new hump in the specific heat appears, indicating the possibility of the existence of a further transition at high fields. Magnetization measurements of REB_{50} (RE = Tb, Dy, Ho, Er) up to 55 kG showed that the compounds universally saturated at around only half the saturation magnetization value of free rare-earth ions, which also indicated the likelihood of a further transition.

The structure of the REB_{50} type compounds has a one-dimensional character with the rare-earth atoms forming an alternating bond length chain along the B_{12} icosahedral *c*-axis. These results are quite interesting in the context with the recent high activity in Haldane gap related compounds in which fundamental quantum phenomena are observed. Further investigations on the spin structure and high field magnetization of this compound are being planned.

ACKNOWLEDGMENTS

The authors thank to Dr. E. Takayama-Muromachi for helping us with all the measurements. This work is partially supported by a Science and Technology Agency (STA) fund project.

REFERENCES

1. J. Etourneau, *J. Less-Common Met.* **110,** 267 (1985).
2. T. Mori and T. Tanaka, *J. Phys. Soc. Jpn.* **68,** 2033 (1999).
3. T. Mori and T. Tanaka, *J. Alloys Comp.* **288,** 32 (1999).
4. T. Mori and T. Tanaka, *J. Phys. Soc. Jpn.* **69,** 579 (2000).
5. I. Higashi, T. Tanaka, K. Kobayashi, Y. Ishizawa, and M. Takami, *J. Solid State Chem.* **133,** 11 (1997).
6. T. Mori and T. Tanaka: Details of the growth of $TbB_{41}Si_{1.2}$ crystals will be reported elsewhere.
7. F. D. M. Haldane, *Phys. Lett.* **93A,** 464 (1983).
8. M. Hagiwara, Y. Narumi, K. Kindo, M. Kohno, H. Nakano, R. Sato, and M. Takahashi, *Phys. Rev. Lett.* **80,** 1312 (1997).
9. I. Affleck and F. D. M. Haldane, *Phys. Rev. B* **36,** 5291 (1987).
10. M. Oshikawa, M. Yamanaka, and I. Affleck, *Phys. Rev. Lett.* **78,** 1984 (1996).