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Single Crystal Growth and Properties of Incongruently Melting TbB_6, DyB_6, HoB_6, and YB_6

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Details of the single crystal growth of incongruently melting TbB_6, DyB_6, HoB_6, and YB_6 using a crucible-free vertical floating zone method are reported. Magnetic susceptibility is reported and discussed. It is suggested that antiferro-quadrupolar ordering occurs in DyB_6 between 30 and 25.6 K.

INTRODUCTION

Rare-earth hexaborides with a simple cubic CaB_6-type structure have been attracting much attention because of their variety of electronic and magnetic properties. Recent development of the study is due to a single crystal growth technique that overcomes the very high melting temperature ($\sim 2500^\circ$C). Heavy rare-earth hexaborides melt incongruently in a condition which makes it difficult to grow big single crystals. We have, however, succeeded in growing big single crystals of them by a crucible-free vertical floating zone method. The details of sample preparation are similar to those described in Ref. (1) except for the starting composition of materials and the growing speed. The purpose of the present paper is to show (a) the details of the single crystal growth procedure and (b) the results of magnetic susceptibility measurements.

SAMPLE PREPARATION AND CRYSTAL GROWTH

Incongruently melting rare-earth hexaborides were first obtained in powder form by the following reactions. $Tb_4O_7 + 31B \rightarrow 4TbB_6 + 7BO$ and $RE_2O_3 + 15B \rightarrow 2REB_6 + 3BO$ (RE = Dy, Ho, and Y). Rare-earth oxide powders (99.99%) were purchased from Japan Yttrium Company. For the borothermal reduction, we used an amorphous submicron boron powder of 99.999% purity, purchased from Aldrich Chemical Company (USA). In the case of 11-boron-enriched samples for neutron measurements, 99.5 at.% enriched ^{11}B was purchased from Isotec (USA). Mixed powders of oxide and boron were pressed into a square rod ($10 \times 10 \times 200\ mm^3$) at 2.5 kg/mm^2. The reactions were performed at about 1650°C for 2 h, removing the vaporized BO in vacuum. An induction furnace was used with a graphite susceptor surrounded outside by a carbon felt for temperature insulation. To avoid graphite contamination we used a boron-nitride pipe surrounding the powder rod. By the above procedure, however, we always got a mixture of three compounds, REB_4, REB_6, and REB_{12}, due to the incongruently melting property. Based on diffusion and reaction kinetics, the intensity ratio among the three types of diffraction lines is changeable depending on the reaction temperature. Therefore we can arrange the overall composition of the mixed compounds at P on the liquidus curve of Fig. 1. The powder of the mixed compounds was pressed hydrostatically into a rod of 10 mm ∅ (diameter) × 100 mm at 2.5 kg/mm^2 using a special rubber scak and then sintered at 1700°C for 2 h in the same surface. Using the sintered rod obtained above, the incongruently melting rare-earth hexaborides have been grown by a crucible-free vertical floating zone method under 1 MPa pressurized high-purity (99.9995%) argon. The single crystal growing speed was 4 mm/h. Figure 2 shows the cross section of the growing crystal; the total length of it is about 10 cm. There is a surface skin (~ 1 mm thick) indicated in Fig. 2 that is always formed when growing REB_6 crystals. Only inside is the single crystal of REB_6. REB_4 and REB_{12} completely disappeared and only REB_6 remains. In Fig. 1, REB_6 is not a line compound; that is, REB_6 has some width of composition. However, Fig. 1 represents the situation under normal pressure (1 atm), whereas the rare-earth element is always defective (see $B/REB_6 = 85.7\%$ ($= 6/7$) $\sim 89\%$ in the DyB_6 case). In our floating zone procedure, we use 1 MPa of pressurized argon, preventing rare-earth defects. This is confirmed by lattice parameter (a_0) measurements in which (a_0) is consistent with stoichiometric REB_6 (3).

RESULTS AND DISCUSSIONS

To know the magnetic ground state, magnetic susceptibility and specific heat measurements have been carried out.

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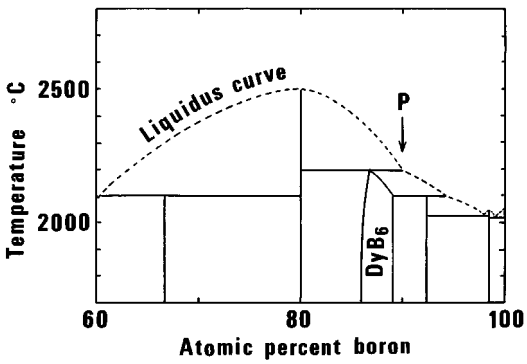

FIG. 1. The phase diagram of the Dy–B system after (2).

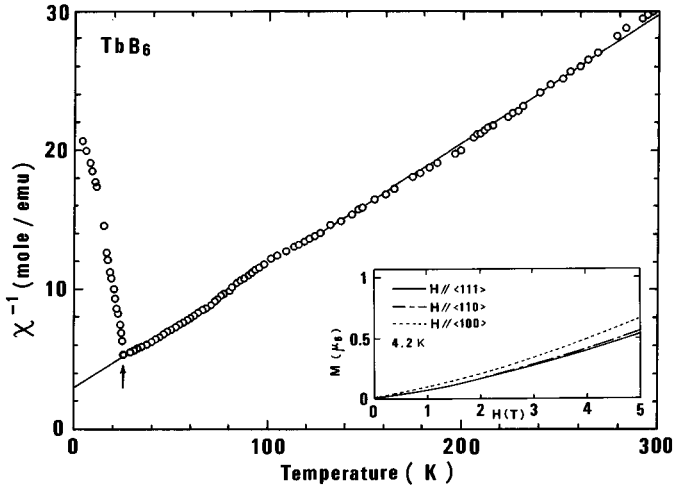

FIG. 3. Temperature dependence of the inverse susceptibility of TbB_6. (Inset) Magnetization M (in units of μ_B/Tb) versus field H (tesla) at 4.2 K.

We have already reported on the electrical resistivity of REB_6 (RE = Tb, Dy, and Ho) (4) and YB_6 (5) and on the specific heat (4, 6). Some investigations (7–9) of the magnetic properties of heavy rare-earth hexaborides have been carried out earlier except for HoB_6 and at rather high temperatrue. Our susceptibility measurements were performed using both a magnetic balance and a magnetic pendulum. Figures 3–5 show the temperature dependence of the inverse susceptibility for TbB_6, DyB_6, and HoB_6, respectively. Curie–Weiss behavior is obeyed at higher temperature, and the effective Bohr magnetons are near the free-ion values (Table 1). This means the electric crystal field splitting of the ground state is within the energy of the corresponding linear-deviation temperature indicated by arrows in Figs. 3–5, which is consistent with the entropy analysis of the specific heat measurements (10). A detailed specific heat analysis will be published in a forthcoming paper.

For DyB_6 there are two anomalies indicated by the arrows in Fig. 4. From recent X ray and neutron diffraction measurements at various temperatures (11), the anomaly at the higher temperature (30 K) was found to correspond to a cubic → rhombohedral structure transition. The other anomaly at 25.6 K corresponds to the antiferromagnetic transition temperature revealed by our recent neutron diffraction measurement (11). At the higher transition temperature (30 K), a Jahn–Teller distortion is induced and the degeneracy of the magnetic ground state is removed. At this

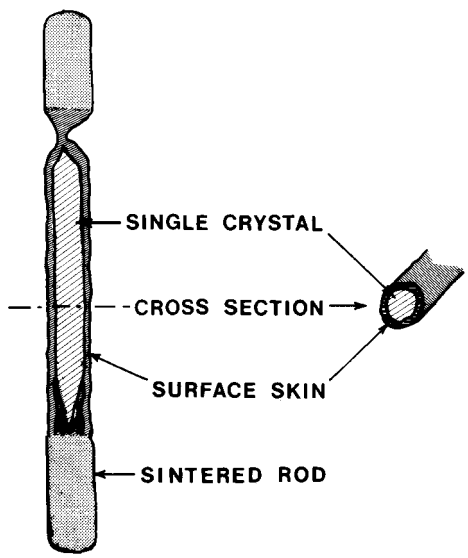

FIG. 2. The schematic growing crystal.

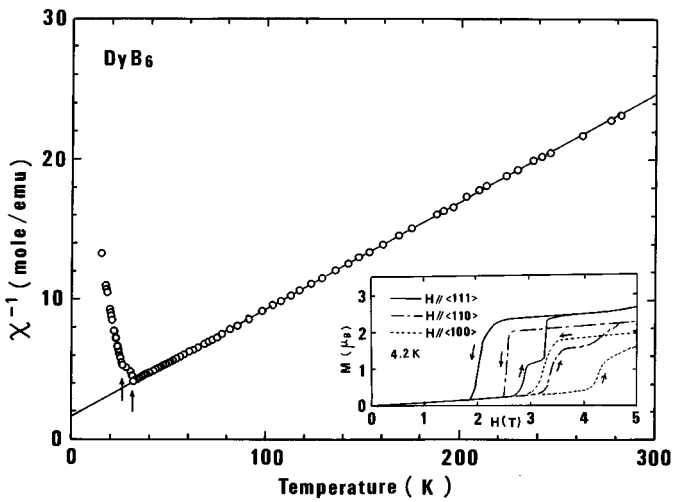

FIG. 4. Temperature dependence of the inverse susceptibility of DyB_6. (Inset) Magnetization M (in units of μ_B/Dy) versus field H (tesla) at 4.2 K.

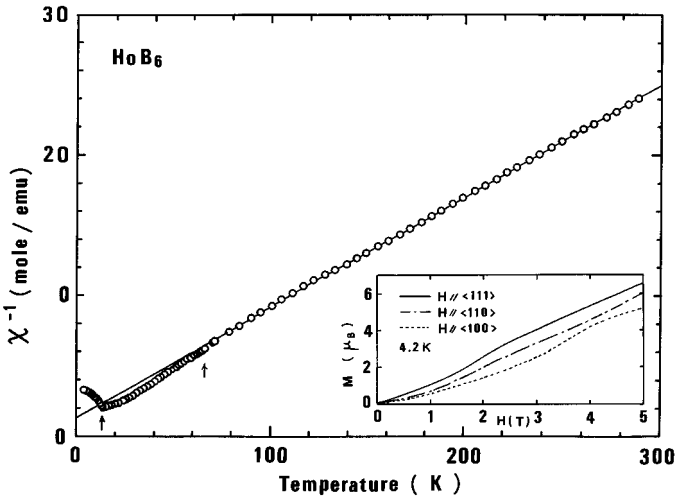

FIG. 5. Temperature dependence of the inverse susceptibility of HoB_6. (Inset) Magnetization M (in units of μ_B/Ho) versus field H (tesla) at 4.2 K.

temperature (30 K) the inverse magnetic susceptibility suddently increases with decreasing temperature in spite of no induced magnetic moment which is ascertained by the neutron diffraction measurement. Therefore susceptibility measurement suggests that the higher transition temperature corresponds to the antiferro-quadrupolar ordering temperature (12), in contrast to the ferro-quadrupolar moment of CeB_6 in which the magnetic susceptibility increases with decreasing temperature at the quadrupolar transition temperature of 3.2 K.

ACKNOWLEDGMENTS

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TABLE 1
Crystallographic and Magnetic Data on Rare-Earth Hexaborides

Boride	a_0 (Å)	f-shell	T_N (K)	μ_{eff} (calc.)	Exp. (μ_B)	Θ_P
TbB_6	4.105	f^8	19.5	9.721	9.3	− 22.9
DyB_6	4.097	f^9	25.6	10.646	10.2	− 21.7
HoB_6	4.095	f^{10}	5.6	10.607	10.1	− 16.3
YB_6	4.100	f^0	(7.5)[a]			

[a] For YB_6, 7.5 is the superconducting transition temperature. The magnetization curve of YB_6 shows a clear type II superconducting behavior, that is, perfect diamagnetism $M = -H/4\pi$ due to Meissnher effect was observed below H_{C1}.

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