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MULTIPLE PHASE TRANSITIONS IN RARE EARTH TETRABORIDES
AT LOW TEMPERATURE

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We report the temperature dependence of the magnetic susceptibility
of single crystals of PrB₄, GdB₄, TbB₄, HoB₄ and TmB₄, both parallel
and perpendicular to the tetragonal c-axis. We also present low
temperature resistance measurements on crystals of GdB₄ through
TmB₄. Two magnetic phase transitions are found for TbB₄, DyB₄,
HoB₄ and TmB₄. For the latter two compounds, the lower transitions
appear to be first order. For HoB₄, we have measured the low tem-
perature specific heat. The lower transition in TbB₄ and HoB₄ is
rapidly depressed upon dilution with YB₄.

Introduction

All the rare earth elements, except Eu,
form isostructural, metallic tetraborides (RB₄)
crystallizing in the tetragonal space group P4/
mbm. There are four equivalent rare earth
sites per unit cell with site symmetry mm.

Buschow¹ has reviewed the magnetic data
on the tetraborides. Almost all of these data
are for polycrystalline material. For the heavy
rare earth tetraborides, the Curie-Weiss tem-
peratures (θ) approximately follow the deGennes
factor, but the ordering temperatures do not.
The RB₄ compounds, NdB₄ through TbB₄, order
antiferromagnetically. PrB₄ is anomalous
in that it orders ferromagnetically.²

Schäfer et al.³ have studied the low tem-
perature magnetic structure of ErB₄ and DyB₄.
They find simple commensurate antiferro-
magnetic ordering for both compounds with the R
moments aligned along the c-axis.

Small single crystals of RB₄ suitable for
magnetic and electrical measurements can be
easily grown.⁴ It is the purpose of this com-
unication to report on the anisotropic magnetic susceptibilities and/or resistivities of PrB₄ and
GdB₄ through TbB₄, and on the presence of a
second low temperature phase transition in
TbB₄, DyB₄, HoB₄ and TmB₄. This second
transition in DyB₄ and HoB₄ was seen previous-
ly by E. Bücher⁵ in crystals grown by Fisk and
Schmidt. This work was not published.

Experimental Details

RB₄ crystals were grown from molten Al,
except for PrB₄. The flux used in this case was
Pr₃Co, the Pr₃Co plus PrB₄ being cooled slow-
ly from 1200°C in a sealed 3/8" diameter Ta
tube. Pr₃Co dissolves rapidly in HCl, and the
much slower attack on PrB₄ allowed crystals
with sizes up to 4 mm × 4 mm × 1 mm to be iso-
lated. Some of the crystals were grown with B-
enriched ¹¹B; these are so indicated.

Resistivity measurements were made be-
tween 1.6 K and 300 K using a 4-probe ac tech-
nique at 220 Hz. A Faraday magnetometer was
used for the magnetic measurements between
1.4 K and 300 K. The c-axis of the crystals was
determined by Laue photographs, and magnetic
measurements were made parallel and perpen-
dicular to this direction. The specific heat
measurements were made with a pulse method
in a semi-adiabatic ³He calorimeter.⁶ A large
number of small crystals were packed tightly in
copper cups, and the heat capacity of the assem-
bly was measured. The data presented are, of
course, corrected for the contribution of the
addenda.
Results and Discussion

Our susceptibility ($\chi$) results for the PrB$_4$, GdB$_4$, TbB$_4$, HoB$_4$, and TmB$_4$ are shown in Figs. 1 and 3. Figure 2 displays low temperature resistance data on the heavy rare earth RB$_4$ compounds. All resistance measurements presented are $\parallel c$-axis, except for GdB$_4$, where we give the results for a plane $\perp c$-axis: other measurements show no qualitative differences for the resistivity measured perpendicular to the direction shown. The small size of the crystals only allowed an approximate determination of the absolute value of the electrical resistivity, so that we have plotted the data on an arbitrary resistance scale which varies from sample to sample. For GdB$_4$, the spin disorder contribution to the resistivity $\rho_m$ is $\sim 15 \, \mu\Omega \cdot \text{cm}$, while for HoB$_4$, the total $\rho_m$ (from both transitions) is $\sim 0.75 \, \mu\Omega \cdot \text{cm}$. The data are summarized in Table I. The compounds GdB$_4$ and ErB$_4$ appear to have only a single, second order phase transition, while TbB$_4$ and DyB$_4$ appear to have two second order phase transitions. The compounds HoB$_4$ and TmB$_4$ both appear to have a second order phase transition followed by a first order transition at lower temperature.

Some features which stand out are (i) the susceptibility of GdB$_4$ is not anisotropic above the Néel temperature ($T_N$); (ii) the susceptibilities of PrB$_4$, TbB$_4$, and TmB$_4$ are markedly anisotropic; and (iii) the R magnetic moments appear to align along the $c$-axis, except in the case of GdB$_4$ and TmB$_4$, as judged by the behavior of $\chi$ below $T_N$.

These materials are all good metals, and the crystals typically have resistance ratios of 50 or better. Point (i) above indicates that the anisotropy present for a number of the heavy rare earth tetraborides is not due to anisotropy in the conduction bands being reflected in the RKKY interaction. The anisotropy is probably not purely a single ion anisotropy due to crystal field effects either since in this case a variation in the magnetic moment ordering direction (point (iii)) would be expected between rare earths to the left of and including Ho and to the right of and including Er: the 4f quadrupole moment has opposite sign for these two groups. It seems likely, however, that the cause of the multiple phase transitions is related to this anisotropy.

We have examined HoB$_4$ in further detail. Figure 3(c) shows our low temperature specific
heat results. The data indicate a second order transition at the upper $T_N$, followed by a first order spike which seems to be superimposed on the smoothly decreasing heat capacity arising from the second order transition. The total molar entropy under the curve to the upper Néel temperature is $R \ln 2.77$, the contribution under the spike being only $R \ln 1.11$.

The site symmetry of the rare earth here is mm. The crystal field can therefore lift all the degeneracy of the $5f^{10}$ Ho ground state. The fact that the entropy to the upper $T_N$ is somewhat less than $R \ln 2$ makes it possible that Ho here has two nearby singlets lying lowest.

A few mixed crystals of $Ho_{1-x}Y_xB_4$ were grown. We find that the upper $T_N$ is nearly linear in $x$, extrapolating to $T_N = 0$ for $x = 1$. The lower $T_N$ falls off much faster and is below 1.7 K at $x = 0.3$. This is the kind of behavior that might be expected if the lower transition is driven by the internal field associated with the upper $T_N$. We note that a measurement made on a crystal of $Tb_{0.74}Y_{0.21}B_4$ only revealed one low temperature transition. W. C. Koehler has made a detailed study of some of our $HoB_4$ crystals using neutron diffraction. He finds a very complicated incommensurate phase between the upper and lower $T_N$'s and there is possibly a ferromagnetic component to the lowest temperature magnetic phase. He will report these results separately.
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Table I

|       | $\theta_{lc}$(K) | $\mu_{eff_{lc}}$(µB) | $\theta_{lc}$(K) | $\mu_{eff_{lc}}$(µB) | $T_{mag}$(K) | Ordered spin direction |
|-------|------------------|----------------------|------------------|----------------------|--------------|-----------------------|
| PrB$_4$ | 28.9             | 3.55                 | -59.0            | 3.76                 | 24           | $\parallel c$         |
| GdB$_4$ | -66.8            | 7.93                 | -68.4            | 7.93                 | 42           | $\perp c$             |
| TbB$_4$ | -52.7            | 9.63                 | -26.6            | 9.55                 | 44.24        | $\parallel c$         |
| Tb$_{0.29}Y_{0.21}$B$_4$ |             |                      |                  |                      |              |                       |
| DyB$_4$ |                  |                      |                  |                      |              |                       |
| HoB$_4$ | -12.8            | 10.39                | -13.5            | 10.45                | 7.1, 5.7     | $\parallel c$         |
| Ho$_{0.85}Y_{0.15}$B$_4$ |             |                      |                  |                      |              |                       |
| Ho$_{0.69}Y_{0.31}$B$_4$ |             |                      |                  |                      |              |                       |
| Ho$_{0.51}Y_{0.49}$B$_4$ |             |                      |                  |                      |              |                       |
| ErB$_4$ |                  |                      |                  |                      |              |                       |
| TmB$_4$ | 38.1             | 7.35                 | (c)              |                      | 11.7, 9.7    | $\perp c$             |

(a) Determined resistively.

(b) Resistance measurement only.

(c) Not Curie-Weiss.

Our results suggest that in a number of RB$_4$ compounds, the anisotropy energy is comparable to the exchange energy. PrB$_4$ is an extreme case in that the anisotropy is sufficient to give large $\theta$'s of opposite sign for $\chi$ parallel and perpendicular to the c-axis. These results on the uniaxial character of PrB$_4$ are in agreement with those of Berrada et al. on crystals of PrB$_4$ made below the Curie temperature.

References

1K. H. J. Buschow, in Boron and Refractory Borides (V. I. Matkovich, ed.), Springer-Verlag: Berlin, 1977, p. 494.
2K. H. J. Buschow and J. H. N. Creighton, Journal of Chemical Physics 57, 3910 (1972).
3W. Schäfer, C. Will and K. H. J. Buschow, Journal of Chemical Physics 64, 1994 (1976).
4Z. Fisk, A. S. Cooper, P. H. Schmidt and R. N. Castellano, Materials Research Bulletin 7, 285 (1972).
5E. Bucher, private communication.
6C. A. Luengo, Ph. D. thesis, Universidad Nacional de Cuyo, Argentina (1972), unpublished.
7W. C. Koehler, private communication.
8A. Berrada, J. P. Mercurio, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Lalanne, J. C. Gianduzzo and R. Georges, Materials Research Bulletin 11, 1519 (1976).