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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 PrB_4, GdB_4, TbB_4, HoB_4 and TmB_4, both parallel and perpendicular to the tetragonal c-axis. We also present low temperature resistance measurements on crystals of GdB_4 through TmB_4. Two magnetic phase transitions are found for TbB_4, DyB_4, HoB_4 and TmB_4. For the latter two compounds, the lower transitions appear to be first order. For HoB_4, we have measured the low temperature specific heat. The lower transition in TbB_4 and HoB_4 is rapidly depressed upon dilution with YB_4.

Introduction

All the rare earth elements, except Eu, form isostructural, metallic tetraborides (RB_4) crystallizing in the tetragonal space group P4/mbm. There are four equivalent rare earth sites per unit cell with site symmetry mm.

Buschow[1] 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 temperatures (θ) approximately follow the deGennes factor, but the ordering temperatures do not. The RB_4 compounds, NdB_4 through TmB_4, order antiferromagnetically. PrB_4 is anomalous in that it orders ferromagnetically.[2]

Schäfer et al.[3] have studied the low temperature magnetic structure of ErB_4 and DyB_4. They find simple commensurate antiferromagnetic ordering for both compounds with the R moments aligned along the c-axis.

Small single crystals of RB_4 suitable for magnetic and electrical measurements can be easily grown.[4] It is the purpose of this communication to report on the anisotropic magnetic susceptibilities and/or resistivities of PrB_4 and GdB_4 through TmB_4, and on the presence of a second low temperature phase transition in TbB_4, DyB_4, HoB_4 and TmB_4. This second transition in DyB_4 and HoB_4 was seen previously by E. Bücher[5] in crystals grown by Fisk and Schmidt. This work was not published.

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Experimental Details

RB_4 crystals were grown from molten Al, except for PrB_4. The flux used in this case was Pr_3Co, the Pr_3Co plus PrB_4 being cooled slowly from 1200°C in a sealed 3/8" diameter Ta tube. Pr_3Co dissolves rapidly in HCl, and the much slower attack on PrB_4 allowed crystals with sizes up to 4 mm × 4 mm × 1 mm to be isolated. Some of the crystals were grown with B-enriched ^{11}B: these are so indicated.

Resistivity measurements were made between 1.6 K and 300 K using a 4-probe ac technique 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 perpendicular 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 a copper cup and the heat capacity of the assembly was measured. The data presented are, of course, corrected for the contribution of the addenda.

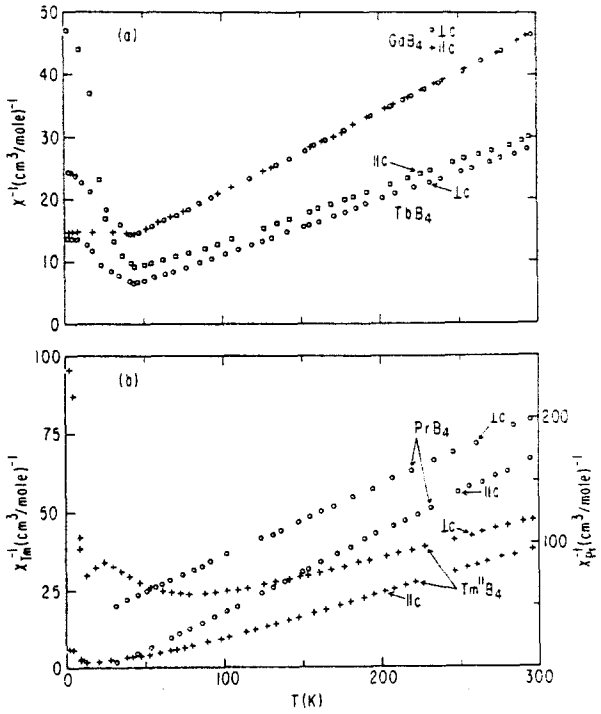

Fig. 1. Inverse molar magnetic susceptibility χ^{-1} vs temperature T of RB_4 compounds measured both ∥c-axis and ⊥c-axis.

Results and Discussion

Our susceptibility (χ) 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 ∥c-axis, except for GdB_4, where we give the results for a plane ⊥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 ρ_m is $\sim 15\ \mu\Omega$-cm, while for HoB_4, the total ρ_m (from both transitions) is $\sim 0.75\ \mu\Omega$-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 χ 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

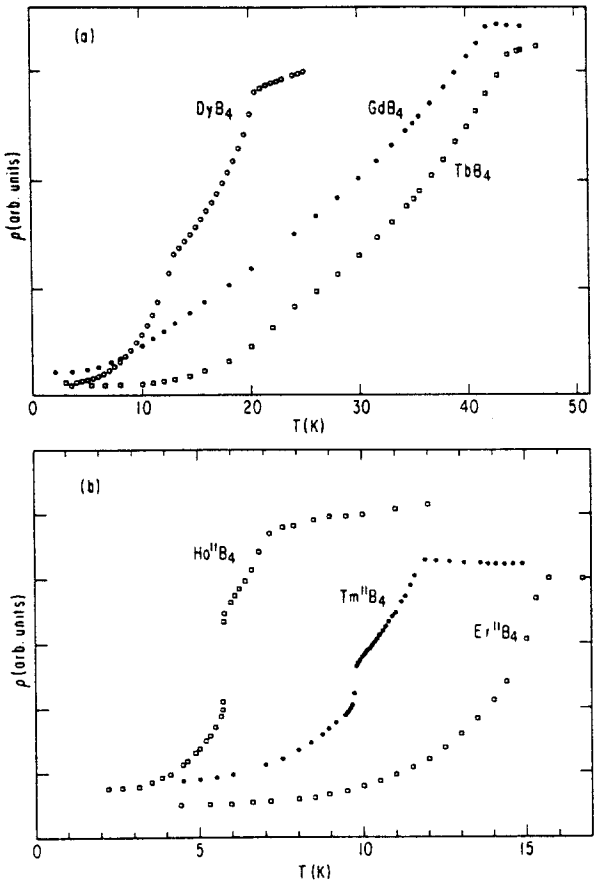

Fig. 2. Relative low temperature electrical resistivity ρ vs temperature T of heavy rare earth RB_4 compounds ∥c-axis, except for GdB_4 for which the data is ⊥c-axis.

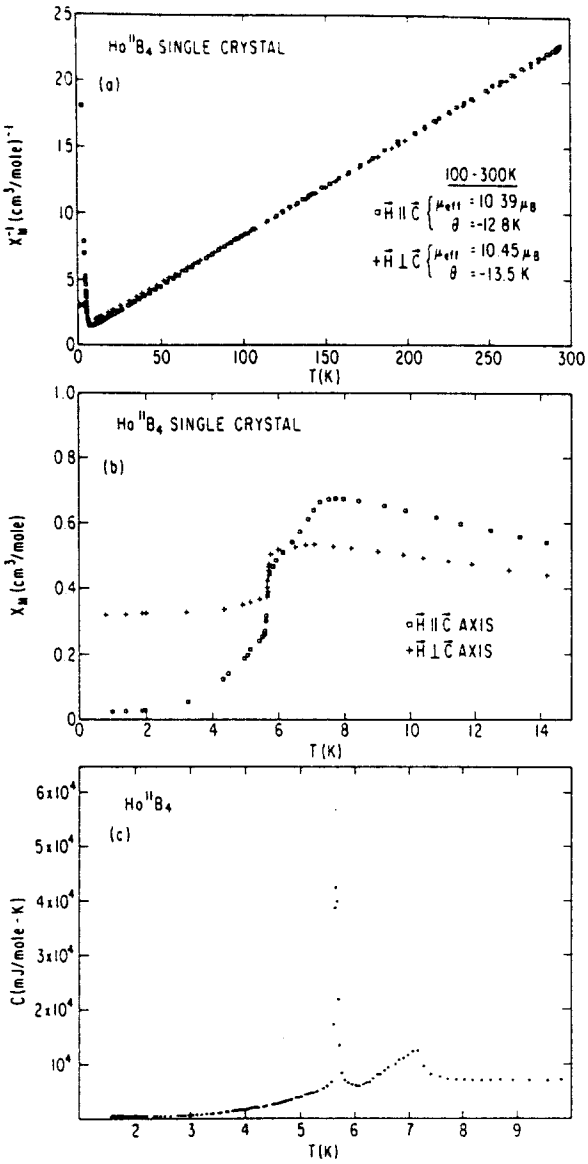

Fig. 3 (a) Inverse molar magnetic susceptibility χ_m^{-1} vs temperature T for HoB_4. (b) Detail of variation of χ_m with temperature T near the two low temperature phase transitions. (c) Low temperature specific heat C vs temperature T of HoB_4.

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 $R\,\ell n\ 1.77$, the contribution under the spike being only $R\,\ell n\ 1.11$.

The site symmetry of the rare earth here is mm. The crystal field can therefore lift all the degeneracy of the $^5I_8\ 4f^{10}$ Ho ground state. The fact that the entropy to the upper T_N is somewhat less than $R\,\ell n\ 2$ 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[7] 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.

Table I

	$\theta_{\parallel c}$(K)	$\mu_{eff_{\parallel c}}$(μ_B)	$\theta_{\perp c}$(K)	$\mu_{eff_{\perp c}}$(μ_B)	T_{mag}(K)[a]	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	$\parallel c$
$Tb_{0.29}Y_{0.21}B_4$[b]					37, < 1.7	
DyB_4[b]					20.4, 12.8	$\parallel c$ [3]
HoB_4	-12.8	10.39	-13.5	10.45	7.1, 5.7	$\parallel c$
$Ho_{0.85}Y_{0.15}B_4$[b]					6.3, 3.1	
$Ho_{0.69}Y_{0.31}B_4$[b]					5.0, <1.7	
$Ho_{0.51}Y_{0.59}B_4$[b]					3.5, < 1.7	
ErB_4					15.4	$\parallel c$ [3]
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 θ's of opposite sign for χ 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.[8] on crystals of PrB_4 made below the Curie temperature.

References

[1] K. H. J. Buschow, in Boron and Refractory Borides (V. I. Matkovich, ed.), Springer-Verlag: Berlin, 1977, p. 494.

[2] K. H. J. Buschow and J. H. N. Creighton, Journal of Chemical Physics 57, 3910 (1972).

[3] W. Schäfer, G. Will and K. H. J. Buschow, Journal of Chemical Physics 64, 1994 (1976).

[4] Z. Fisk, A. S. Cooper, P. H. Schmidt and R. N. Castellano, Materials Research Bulletin 7, 285 (1972).

[5] E. Bücher, private communication.

[6] C. A. Luengo, Ph. D. thesis, Universidad Nacional de Cuyo, Argentina (1972), unpublished.

[7] W. C. Koehler, private communication.

[8] A. Berrada, J. P. Mercurio, B. Chevalier, J. Etourneau, P. Hagenmuller, M. Lalanne, J. C. Gianduzzo and R. Georges, Materials Research Bulletin 11, 1519 (1976).