

Magnetic Behavior of New Ternary Metal Borides with YCrB₄-type Structure

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New ternary metal borides YbRuB₄, YbOsB₄ and GdFeB₄ have been prepared. The compounds were found to crystallize with the structure type of YCrB₄. Magnetic measurements (80–300°K) were performed on compounds of the isostructural series MM'B₄ (YCrB₄-type; M = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb; M' = Ru, Os and M = U, Gd; M' = Cr, Mn, Fe, Co). Paramagnetic Curie-Weiss behavior is shown in all cases; Y and the R.E. (Rare Earth) metals are trivalent in these compounds.

Introduction

A group of either superconducting or ferromagnetic ternary metal borides MM'B₄ (M = Y, Th, R.E., M' = Ru, Rh) were recently reported (1, 2). Whereas a new unique structure type: LuRu₄B₄ was derived (1) for the isostructural series MRu₄B₄, MRh₄B₄ borides crystallize with the structure type of CeCo₄B₄ (2).

Boron rich compounds MM'B₄ (M = Y, Gd, Tb, Dy, Ho, Er, Tm; M' = Ru, Os) recently were proved (3) to be isotypic with the crystal structure of YCrB₄. A large number of representatives of this structure type is already known from the investigations by Kuz'ma and coworkers (4–7). Uranium-containing compounds UMB₄ (M = Cr, Mn, Fe, Co) were reported with the same crystal structure (8) and later on confirmed by Kuz'ma *et al.* (9).

The subject of the present work is a study of the magnetic behavior of MM'B₄ borides (M = R.E., Y, U; M' = Ru, Os, Cr, Mn, Fe, Co). Attempts are made to synthesize the compounds YbRuB₄, YbOsB₄ and GdFeB₄,

which up to now are not known from literature.

Experimental

High purity powders¹ of the elements and filings of the R.E. metals were compacted in steel dies without the use of binders or lubricants. Except for Mn- and Yb-containing samples (Preparation Technique, see below) the pellets (~1 g) were arc-melted on a water-cooled copper hearth with a nonconsumable tungsten electrode under a purified argon atmosphere. Weight losses during arc melting were negligible. The obtained buttons were heat treated in vacuum (5 · 10⁻⁶ Torr, 12 hr at 1600°C) on a tungsten substrate and radiation cooled.

¹ B: cryst., Koch Light Lbs., England 99% B; Y, R.E.: metal ingots, Ventron GmbH., Karlsruhe BRD, m3N; U: turnings, E. Merck, Darmstadt BRD, nuclear grade, surface cleaned in HNO₃; Cr: electrolyt., pieces, Schmelztechnik, München, 99, 5% Cr; Mn: electrolyt., pieces, Fluka, Buchs, Schweiz, "puriss.," surface cleaned in HNO₃; Fe: Carbonyl powder, Fluka, 99, 5% Fe; Co: powder, Koch Light, 99, 5% Co.

Due to the high vapor pressure of Yb and Mn, arc melting was not recommended for Yb- as well as Mn-containing samples. Yb filings, Mn and GdB₄ powders were used as constituents (GdB₄ was prepared by arc melting and subsequent crushing; 30 μ, $a = 7.147(8)$, $c = 4.049(3)$ Å). In all these cases pellets were wrapped in molybdenum foil, sealed in evacuated ($\sim 10^{-3}$ Torr), fused silica tubes and sintered for 48 hr at 900°C, followed by 12 hr at 1200°C. After crushing and renewed pressing the samples were subjected to a final heat treatment at 1400°C (5 hr, BN substrate, argon atmosphere). X-ray diffraction data (Debye-Scherrer) were obtained on powder specimens using vanadium filtered Cr-K α radiation. Except for the Yb-containing samples, in which small amounts of impurity boride phases (mainly YbB₄) were present, all samples were found to be single phase or nearly so. A least-squares analysis was employed to obtain values for the lattice parameters and standard deviations.

Susceptibility measurements (80–300°K) were performed with a pendulum susceptibility meter (compensation Faraday method²), originally developed in our laboratory (10). The temperature range available was 80–525°K.

Results and Discussion

A. Structure Determination

X-ray diffraction inspection of alloy samples within the systems Gd-Fe-B, Yb-Ru-B as well as Yb-Os-B and with a boron concentration of 65–70 at% boron showed in all three cases the existence of a new compound with an approximate formula R.E.MB₄. Homogeneous and well-crystallized samples GdFeB₄ were prepared with a nominal composition (in at%)

Gd(17)Fe(16)B(67). Yb-containing samples (nominal composition Yb(17)Ru(Os)(15)B(67)) were not found completely single phase from Debye-Scherrer photographs due to small amounts of YbB₄ impurities. However in all cases, the powder patterns of the new phases could be indexed completely³ with an orthorhombic unit cell (see Table I). Formula, lattice parameters as well as powder intensities indicate structural analogy with the crystal structure of YCrB₄ (4). By use of the atom parameters of YCrB₄ (4), calculated (Program Pulver (11)) and observed powder intensities are in excellent agreement for GdFeB₄ (see Table II). Excellent agreement for observed and calculated powder intensities was also found for YbRu(Os)B₄ borides using atomic parameters, as earlier derived for YMoB₄ (5). Intensity calculations can be obtained on request. Linear dependency is obvious from the graphs of the lattice parameters or the unit cell volumes of the MM'B₄ borides ($M = Y, R.E.$; $M' = Ru, Os$) vs the corresponding values of the trivalent ionic radii $R_{R.E.3+}$; values for the Y compounds are found between those for the Gd and Tb members, thus Y and the R.E. elements (including Yb) can be considered to be trivalent in these compounds (see also section: Magnetic Measurements). Small homogeneity regions however are likely to exist for most compounds, as is indicated by a slight scattering of lattice parameter values in Fig. 1.

No problems were encountered in preparing single-phase samples of UMB₄ ($M = Cr, Mn, Fe, Co$) and GdMB₄ ($M = Cr, Mn, Co$) (Lattice Parameters, see Table I). However it is interesting to note, that in all samples prepared in our laboratory, no deviations from the lattice geometry $b/a = \sqrt{\frac{15}{4}} = 1.937$ could be detected, compared to different values reported by Kuz'ma *et al.* for GdMB₄ (4, 6, 7) and UMB₄ (9).

² Susceptibility measuring device SUS 10, A. Paar KG., Graz, Austria.

³ Subtracting the YbB₄-reflections.

TABLE I
CRYSTALLOGRAPHIC AND MAGNETIC DATA FOR $MM'B_4$ BORIDES ($M = R.E., U; M' = Cr, Mn, Fe, Co$)

Phase	(a) $\pm 0.003 \text{ \AA}$	(b) $\pm 0.006 \text{ \AA}$	(c) $\pm 0.002 \text{ \AA}$	$\mu (\mu_B)/\text{Form. unit}$		
				Exp.	Theor.	θ_p (K)
YRuB ₄	5.954	11.524	3.559	Pauli paramagnetism		—
GdRuB ₄	5.973	11.568	3.570	7.92	7.94	20
TbRuB ₄	5.958	11.532	3.551	9.45	9.70	30
DyRuB ₄	5.948	11.513	3.541	10.60	10.60	22
HoRuB ₄	5.933	11.480	3.533	10.60	10.60	6
ErRuB ₄	5.930	11.481	3.536	9.60	9.60	14
TmRuB ₄	5.913	11.440	3.511	7.92	7.60	14
YbRuB ₄	5.907	11.429	3.520	~4.4	4.5	-18
YOsB ₄	5.955	11.527	3.556	Pauli paramagnetism		—
GdOsB ₄	5.988	11.587	3.572	7.85	7.94	17
TbOsB ₄	5.966	11.553	3.561	9.95	9.70	20
DyOsB ₄	5.954	11.527	3.553	10.60	10.60	10
HoOsB ₄	5.943	11.495	3.548	10.60	10.60	8
ErOsB ₄	5.928	11.482	3.539	9.60	9.60	18
TmOsB ₄	5.919	11.461	3.532	7.88	7.60	17
YbOsB ₄	5.911	11.449	3.535	~4.4	4.5	-26
GdCrB ₄	5.953	11.527	3.494	7.70	7.94/Gd	20
GdMnB ₄	5.922	11.466	3.451	7.5		90
GdFeB ₄	5.918	11.456	3.457	10.00		-46
GdCoB ₄	5.924	11.472	3.453	8.06		-12
UCrB ₄	5.891	11.413	3.497	$5.4 \cdot 10^{-6}$	weak temperature dependency practically temperature independent	-400
UMnB ₄	5.875	11.387	3.454	$5.26 \cdot 10^{-6}$		—
UFeB ₄	5.877	11.389	3.438	$3.6 \cdot 10^{-6}$		—
UCoB ₄	5.883	11.402	3.430	$3.2 \cdot 10^{-6}$		—

B. Magnetic Behavior

The results of the magnetic measurements on the ternary borides $R.E.MB_4$ ($M = Ru, Os$) and $GdMB_4$ ($M = Cr, Mn, Fe, Co$) are represented in three graphs showing the reciprocal gram susceptibility (emu/g) vs. temperature (K) (Figs. 2-4). Linear dependency indicated Curie-Weiss-type behavior in all cases. Small amounts of Pauli paramagnetism may be neglected, compared to the strong paramagnetism of the R.E. component.

No graph was prepared for the uranium-containing borides UMB_4 ($M = Cr, Mn, Fe, Co$) due to their essentially temperature-

independent paramagnetism (χ_g values at 300°K are listed in Table I).

Paramagnetic moments per formula unit were calculated from the Curie-Weiss constant ($\mu = 2.83\sqrt{C}\mu_B$) and are compared with the theoretical values for R.E. metals. In addition the extrapolated Curie-Weiss temperatures $\theta_p[\chi_{Mol} = (C/T - \theta_p)]$ are listed in Table I. Except for the Yb members (small amounts of YbB₄ impurities) comparison between experimental and theoretical moments is excellent for R.E. metals in trivalent state (see also Fig. 1). Despite the higher error figures for the Yb members no doubt exists about the trivalency of Yb in these compounds.

TABLE II

POWDER DIFFRACTION DATA FOR GdFeB₄; Cr-K_α RADIATION ($\lambda = 2.2909 \text{ \AA}$), INTENSITY $I = mF^2(1 + \cos^2 2\theta)/\sin^2 \theta \cdot \cos \theta$ IS NORMALIZED TO THE STRONGEST REFLECTION HAVING INTENSITY 100

(hkl)	$10^4 \cdot \sin^2 \theta$ obs.	$10^4 \cdot \sin^2 \theta$ calc.	I obs.	I calc.	(hkl)	$10^4 \cdot \sin^2 \theta$ obs.	$10^4 \cdot \sin^2 \theta$ calc.	I obs.	I calc.
(020)	-	400	-	1	(350)	-	5871	-	1
(110)	477	475	vw	8	(207)	-	5990	-	0
(120)	785	775	w	38	(212)	-	5990	-	20
(001)	1106	1092	s	100	(042)	5995	5991	m	14
(130)	1203	1274	vs*	50	(400)	-	5994	-	15
(021)	-	1496	-	2	(341)	6073	6060	vw	12
(200)	-	1499	-	0	(410)	-	6094	-	0
(111)	1560	1572	vw	8	(261)	-	6195	-	0
(210)	-	1590	-	79	(222)	-	6290	-	0
(040)	1606	1600	vs	40	(142)	6378	6366	w*	12
(121)	1882	1872	w	32	(171)	-	6371	-	25
(220)	-	1898	-	0	(420)	-	6394	-	0
(140)	1961	1974	w	25	(270)	-	6307	-	0
(131)	2381	2372	-	52	(080)	-	6398	-	0
(230)	-2400	2392	m _d	19	(180)	6778	6773	-	12
(201)	-	2596	-	0	(232)	-6800	6790	w _d	12
(211)	-	2696	-	88	(430)	-	6894	-	0
(041)	2704	2697	vs	42	(351)	-	6969	-	1
(150)	-	2874	-	2	(360)	-	6971	-	2
(221)	-	2996	-	0	(401)	7095	7092	w	30
(141)	3076	3072	w	32	(411)	-	7192	-	0
(240)	-	3090	-	0	(152)	-	7265	-	1
(310)	-	3472	-	2	(242)	-	7490	-	0
(231)	3506	3496	w	30	(421)	-	7492	-	2
(060)	-	3599	-	3	(271)	7498	7495	vw	3
(320)	3775	3772	vw	6	(081)	-	7496	-	1
(151)	-	3972	-	3	(440)	7594	7594	vw	15
(160)	3975	3974	vw	5	(312)	-	7863	-	2
(250)	4001	3998	vw	17	(181)	7872	7871	w	30
(330)	4264	4271	vw	11	(280)	-	7897	-	0
(002)	4399	4392	vw*	24	(062)	-	7991	-	5
(311)	-	4570	-	1	(431)	-	7992	-	0
(061)	-	4697	-	3	(361)	-	8069	-	10
(022)	-	4791	-	0	(322)	8173	8163	vw	11
(112)	-	4866	-	1	(370)	8273	8270	vw	17
(321)	4873	4869	vw	6	(162)	-	8365	-	9
(340)	4975	4971	vw	8	(252)	8392	8389	w	32
(161)	5073	5072	vw	6	(190)	-	8473	-	3
(251)	-	5096	-	18	(450)	-	8495	-	0
(260)	5105	5098	vw	0	(332)	8670	8663	w	25
(122)	5176	5166	vw	6	(441)	8698	8692	m	48
(170)	5277	5273	vw	15	(281)	-	8995	-	0
(331)	5375	5369	vw	14	(342)	-	9363	-	29
(132)	5671	5666	vw	14	(371)	9367	9368	m	55

s = strong, w = weak, vw = very weak etc.; d = diffuse

There is obviously no influence of the ligand atoms of the R.E. atoms on the coupling of the spin and orbital momentum of the R.E.-4f electrons. The kind of coupling—characterized by the θ_p values—between the R.E. magnetic moments originates from the R.E. atoms as well. Among R.E.Ru(Os)B₄ phases a θ_p minimum value is encountered with HoRuB₄ and HoOsB₄ respectively. A similar behavior (12) is known from R.E.B₄ borides (T_N minimum for HoB₄ and θ_p minimum for neighboring ErB₄) as well as from R.E.B₂ borides (T_c minimum for HoB₂). Due to the contributions of the transition metals, the compounds GdMB₄ ($M = \text{Cr, Mn, Fe, Co}$) are expected to display a higher value for the paramagnetic moment/per formula unit than pure gadol-

inium, according to $\mu_{\text{total}} = \sqrt{P_{\text{Gd}}\mu_{\text{Gd}}^2 + P_{\text{T}}\mu_{\text{T}}^2}$ (P_{Gd} = percentage of Gd, P_{T} = percentage of transition metal). Surprisingly enough, this is the case in the GdFeB₄ compound only. Assuming $\mu_{\text{Gd}} = 7.94\mu_{\text{B}}$, a value of $\mu_{\text{T}} = 5.92\mu_{\text{B}}$ is calculated from μ_{total} . This is about exactly the value for 5 unpaired d electrons (Fe^{3+} , d^5 high-spin configuration).⁴ The contribution of the other transition metals (Cr, Mn, Co) is zero or $\leq 1.73\mu_{\text{B}}$ and may be covered by the overwhelming contribution of Gd itself

⁴ As one referee pointed out this moment can be due to the strongly polarizing Gd moments however. This would be the case if $N(E_{\text{F}})I_{\text{eff}}$ is smaller than one but close to it (Stoner criterion). Lacking a strong polarizing moment the UMB₄ compounds show no ($M = \text{Cr, Mn, Fe, Co}$) moment.

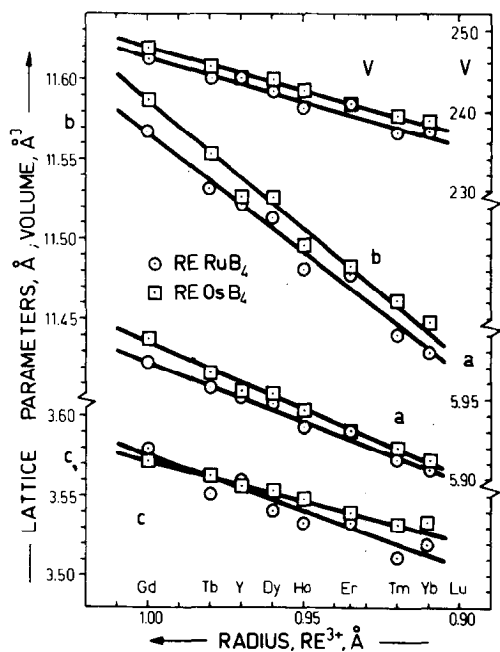


FIG. 1. Lattice parameters and volumes of the new ternary borides Y (R.E.) Ru(Os)B₄ vs. radius R_{RE³⁺}.

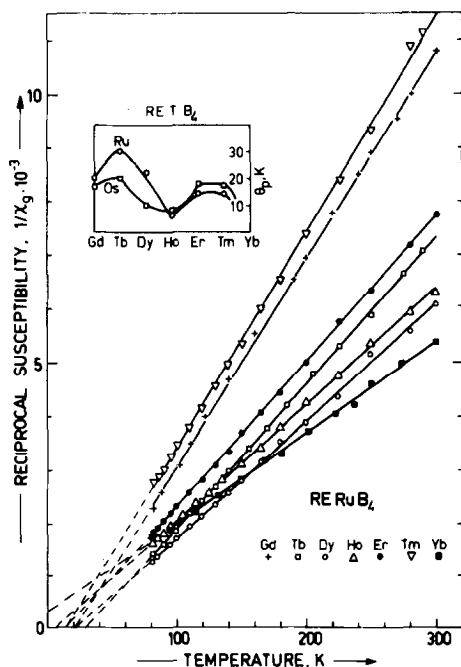


FIG. 2. Reciprocal gram-susceptibility versus temperature for R.E. RuB₄ borides.

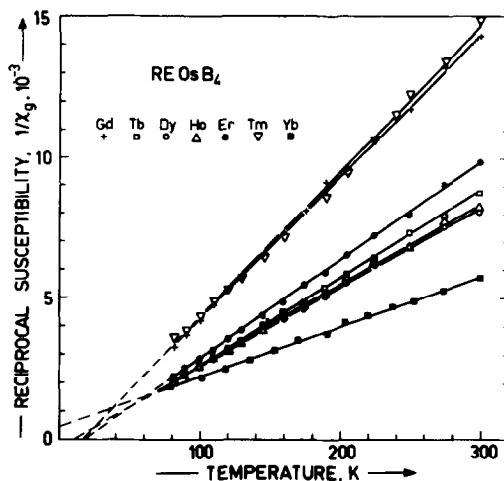


FIG. 3. Reciprocal gram-susceptibility versus temperature for R.E. OsB₄ borides.

(second-order dependency μ_{Gd}^2). Considering the interatomic distances in GdMB₄, no significant deviations from the sum of atomic radii are encountered; this is especially true for the trigonal prismatic boron coordination figure.

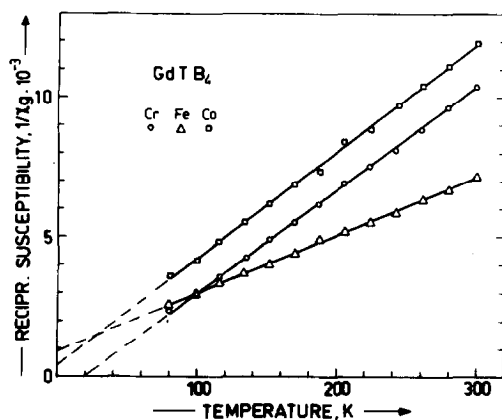


FIG. 4. Reciprocal gram susceptibility versus temperature for GdMB₄ borides, M = Cr, Fe, Co.

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