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Magnetism and Structural Chemistry of Ternary Borides RE_2MB_6 (RE = rare earth, M = Ru, Os)*

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The magnetic behavior of the ternary borides RE_2RuB_6 and RE_2OsB_6 (RE = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was studied in the temperature range 1.5 K < T < 1100 K. All compounds crystallize with the Y_2ReB_6-type structure and are characterized by direct RE–RE contacts and the formation of planar infinite two-dimensional rigid boron nets. The magnetic properties reveal a typical Van Vleck paramagnetism of free RE^{3+}-ions at temperatures higher than 200 K with ferromagnetic interaction in the low-temperature range T < 55 K. The ferromagnetic ordering temperatures vary with the De Gennes factor. There is no indication for a magnetic contribution from the Ru(Os)-sublattice. Above 1.8 K none of the samples were found to be superconducting. © 1984 Academic Press, Inc.

Introduction

From a comprehensive review (*1*) on the phase equilibria and compound formation in ternary and higher-order phase diagrams containing rare earth elements and boron, a pronounced tendency toward the formation of higher borides (ratio B : T ≃ 2) was observed particularly for those transition metal constituents (Ru, Os) with a higher stability (*2*) of their d^5-electron states as compared to a d^{10}-configuration. Four structure types are encountered among ternary diborides: $YCrB_4$, $ThMoB_4$, Y_2ReB_6, and $CeCr_2B_6$ (*1, 3*), which all are characterized by the formation of a rigid, covalently bonded boron net. But whereas a detailed magnetic characterization of binary transition metal diborides generally is available (see, i.e., Ref. (*6*)), very little is known about the magnetism of ternary combinations.

A systematic investigation of the thermodynamic phase equilibria and crystal chemistry in ternary systems RE–(Ru, Os)–B revealed the existence of $YCrB_4$-type borides $RERuB_4$, $REOsB_4$ (RE = Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu); and we recently discussed their crystallographic, magnetic, and superconducting properties (*4, 5*).

In a later paper we have reported about the formation and crystal chemistry of the ternary borides RE_2RuB_6 and RE_2OsB_6 (*7*); therefore a detailed investigation of their

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magnetic behavior became the intention of the present work.

Experimental

All ternary compounds were prepared from commercially available high-purity elements: rare earths metals (filings from ingots, 99.9%, Ventron GmbH., Karlsruhe, BRD); ruthenium (powder, 99.9%, Degussa, Hanau, BRD); osmium (powder, 99.9%, Degussa, Hanau, BRD); and boron (powder, crystalline, 99%, Koch Light Lbs., England). Specimens with a total weight of 0.5–1 g and a nominal composition *RE* (22 at.%)Ru(Os) (11 at.%)B(67 at.%) were compacted in steel dies without the use of binder materials. Except for the Yb_2(Ru, Os)B_6-alloys (see below) the samples were reacted in an arc-melting furnace on a water-cooled copper hearth using a nonconsumable tungsten electrode in a Ti/Zr-gettered argon atmosphere. Weight losses due to the arc-melting process generally were less than 1 wt%. A part of each alloy button was heat-treated on a tungsten substrate for 24 hr at 1400°C under a high vacuum of 10^{-4} Pa.

To minimize ytterbium-vapor losses, the ytterbium-containing specimens were synthesized from powder compacts, wrapped in tantalum foil, and sealed in evacuated quartz capsules. After a first reaction for 24 hr at 1000°C the obtained sinteralloys were crushed, reground, recompacted, and subjected to a final heat treatment at 1000°C for 120 hr.

No significant differences could be detected from X-ray powder diffraction analysis of the as-cast and the annealed specimens. Except for the Yb-samples which contained secondary phases, the X-ray inspection proved the alloys to be practically homogeneous.

Lattice parameters and standard deviations were evaluated by a least-square extrapolation method (*8*) from Guinier powder photographs (obtained at room temperature) using monochromatized $CuK\alpha_1$-radiation with an internal standard of 99.9999% pure Ge. X-Ray powder intensities were recorded by means of a KD-530 microdensitometer.

For the susceptibility measurements in the temperature range $80 < T < 1100$ K a pendulum susceptibility meter was employed (*9*), using a Faraday compensation method under He for $T < 300$ K and under high-purity argon at $T > 300$ K.

For low-temperature susceptibility data ($1.5 < T < 80$ K) a Faraday balance with Spectrosil quartz buckets and Cahn-electrobalance recording was used under helium (*10*). The determination of the superconducting critical temperatures was performed by use of an ac-induction equipment (*11*).

Results and Discussion

A. Structural Chemistry

The crystallographic data and the crystal chemistry of the new ternary borides RE_2RuB_6 and RE_2OsB_6 have been discussed in an earlier paper (*7*): The powder patterns of the new phases RE_2RuB_6 and RE_2OsB_6 were indexed completely on the basis of a primitive orthorhombic unit cell; lattice parameters, composition and X-ray powder intensities (extinctions ($h0l$), $h \neq 2n$ and ($0kl$), $k \neq 2n$) were all consistent with the structure type of Y_2ReB_6 (space group *Pbam*) and minor variations of the lattice parameters in multiphase alloys indicated rather narrow homogeneity regions (*7*). Powder X-ray intensities were calculated for all RE_2(Ru, Os)B_6 representatives on the basis of the atom parameters as derived from a single-crystal study of Y_2ReB_6 (*12*) and confirmed the structural analogy.

A linear dependence of lattice parameters and volumes was found from a graph against the corresponding values of the

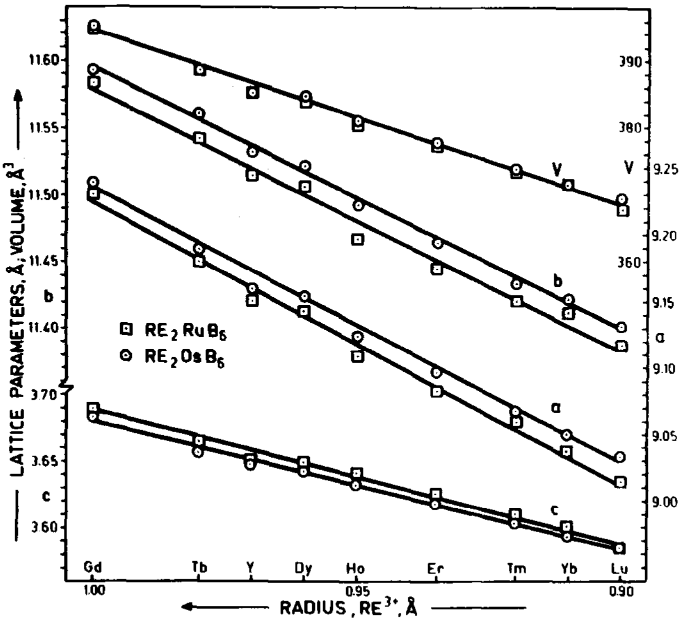

FIG. 1. Lattice parameters and volumes of RE_2RuB_6- and RE_2OsB_6-borides versus the radius $R_{RE^{3+}}$; the radii were taken from Dickinson (*13*); values for Y from Spear (*14*).

RE^{3+} ionic radii (see Fig. 1 and also the following section for magnetic properties). With regard to the observed lattice parameters both Yb-members Yb_2RuB_6 and Yb_2OsB_6 suggest a paramagnetic behavior corresponding to a magnetic Yb^{3+}-state.

Binary and ternary transition metal borides have been classified (*15, 3*) as typical boron-net-type compounds with a rigid boron net of almost uniform covalent B–B bonds (1.76–1.82 Å).

In case of the structure type of Y_2ReB_6 planar boron nets consist of irregular five-, six-, and seven-membered boron rings of which the five-membered boron rings are centered above and below by the smaller transition metal atoms and the six- and seven-membered rings by the rare earth at-

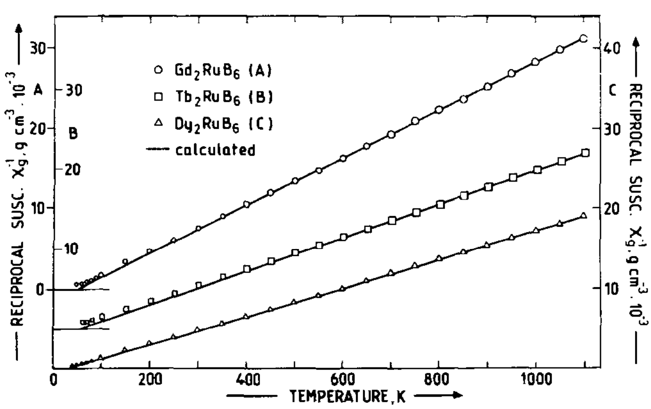

FIG. 2. Reciprocal gram susceptibility for (Gd, Tb, Dy)$_2$RuB$_6$ and calculated least-square fit.

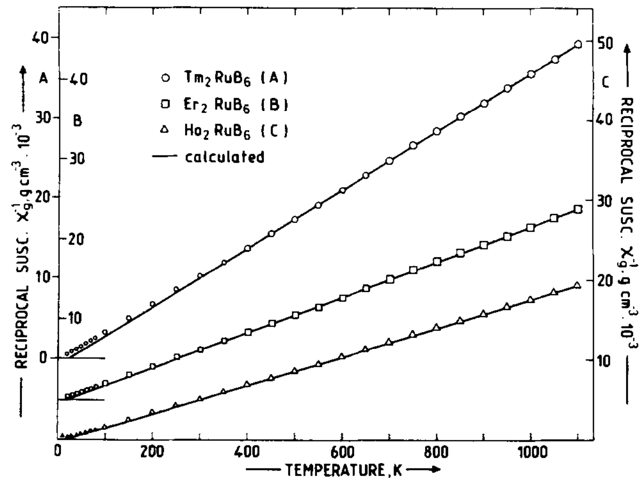

FIG. 3. Reciprocal gram susceptibility for (Ho, Er, Tm)$_2$RuB$_6$ and calculated least-square fit.

oms occupying two distinct crystallographic sites.

Despite bonding in net type borides is dominated by the covalent boron–boron bonds, some general features in the bonding of ternary rare earth-transition metal-borides (*16*) are seen from the interatomic distances: weak *RE*(T) metal-boron bonding is compensated by a strong *RE*-transition metal bonding within the metal layers where *RE*–T bonds are generally shorter by 5–10% as compared to the sum of the metal radii. With the exception of the $CeCr_2B_6$ type of structure (starting boron net formation of open B_6-net fragments at a distance of ~2.00 Å) all diborides including the RE_2(Ru, Os)B_6 compounds are obviously controlled by the formation of rigid boron nets and by a resulting limiting size factor which restricts the known representatives to those rare earth members which are smaller in size than Eu.

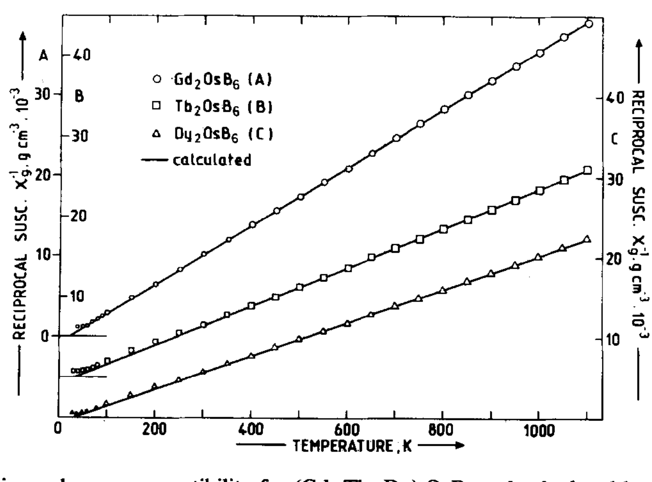

FIG. 4. Reciprocal gram susceptibility for (Gd, Tb, Dy)$_2$OsB$_6$ and calculated least-square fit.

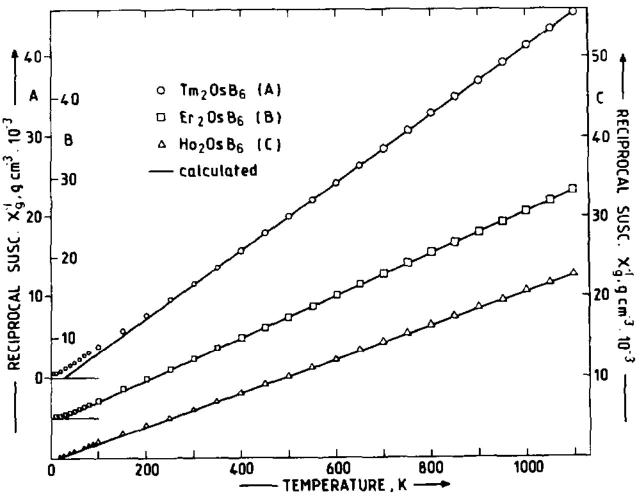

FIG. 5. Reciprocal gram susceptibility for (Ho, Er, $Tm)_2OsB_6$ and calculated least-square fit.

B. Magnetism

The magnetic properties of the RE_2MB_6 (M = Ru, Os) compounds are shown in Figs. 2–8 and Table I. The magnetic susceptibility of Y_2RuB_6 and Lu_2RuB_6 is essentially temperature independent (2–300 K). In the latter case the $4f$ shell is filled, suggesting that there is no itinerant magnetism arising from the noble metal atoms. Thus $(Y,Lu)_2RuB_6$ can be regarded as Pauli paramagnets.

The magnetic rare earth compounds in general exhibit a Curie–Weiss-like behavior

TABLE I

CRYSTALLOGRAPHIC AND MAGNETIC DATA FOR THE TERNARY BORIDES RE_2MB_6 (RE IS ONE OF THE RARE EARTH ELEMENTS, M = Ru, Os) STRUCTURE TYPE: Y_2ReB_6, SPACE GROUP: D_{2h}^9-$Pbam$, No. 55, Z = 4

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)	μ (eff.) (BM) Exp.	Theor.	Asymp. Curie temp. θ_p(K)	Ferromagn. ordering temp. T_M(K)
Y_2RuB_6	9.1498(16)	11.5139(32)	3.6501(2)	384.53(13)	χ_m(300 K) = 0.00071 cm^3 mole^{-1}			—
Y_2OsB_6	9.1592(10)	11.5311(25)	3.6473(2)	385.21(9)	—	—	—	—
Gd_2RuB_6	9.2384(30)	11.5843(36)	3.6902(3)	394.92(18)	8.0	7.94	55	46
Tb_2RuB_6	9.1796(20)	11.5407(19)	3.6650(2)	388.37(11)	9.6	9.72	50	38
Dy_2RuB_6	9.1433(23)	11.5067(18)	3.6489(2)	383.90(12)	10.5	10.63	28	29
Ho_2RuB_6	9.1083(54)	11.4666(51)	3.6407(3)	380.24(38)	10.5	10.58	14	14
Er_2RuB_6	9.0822(31)	11.4439(56)	3.6266(4)	376.92(22)	9.5	9.59	22	7.5
Tm_2RuB_6	9.0605(28)	11.4203(31)	3.6091(3)	373.45(16)	7.4	7.55	26	1
Yb_2RuB_6	9.0371(67)	11.4129(58)	3.6011(8)	371.41(52)	—	4.55	—	—
Lu_2RuB_6	9.0138(39)	11.3880(17)	3.5826(8)	367.75(39)	χ_m(300 K) = 0.000036 cm^3 mole^{-1}			
Gd_2OsB_6	9.2475(36)	11.5912(41)	3.6814(3)	394.61(23)	7.9	7.94	22	34
Tb_2OsB_6	9.1889(19)	11.5612(43)	3.6567(2)	388.47(17)	9.7	9.72	36	27
Dy_2OsB_6	9.1542(26)	11.5211(51)	3.6435(2)	384.26(22)	10.6	10.63	30	16
Ho_2OsB_6	9.1229(15)	11.4909(35)	3.6320(2)	380.74(13)	10.6	10.58	12	13
Er_2OsB_6	9.0973(21)	11.4644(21)	3.6169(3)	377.22(11)	9.5	9.59	21	4.5
Tm_2OsB_6	9.0677(29)	11.4336(36)	3.6037(3)	373.62(17)	7.5	7.55	29	2
Yb_2OsB_6	9.0504(53)	11.4224(48)	3.5939(6)	371.53(54)	—	4.55	—	—
Lu_2OsB_6	9.0331(35)	11.4113(49)	3.5842(9)	369.46(32)	—	—	—	—

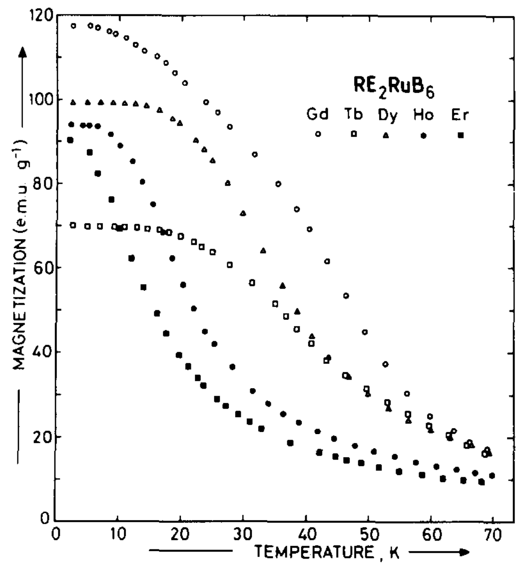

FIG. 6. Magnetization vs temperature for RE_2RuB_6 at a field $H = 1.13$ Tesla.

at temperatures above ~200 K. The magnetic data, viz. paramagnetic moments μ_{eff} and Curie–Weiss temperatures θ_p, were calculated from a least-square fit according to the formula

$$\chi_m = \frac{C}{T - \theta_p} + \chi_0$$

where C is the Curie constant and χ_0 represents the temperature-independent contributions of the conduction electrons (Pauli paramagnetism), the temperature-independent Van Vleck paramagnetism, and the core diamagnetism. The observed effective moments are in good accord with the corresponding free trivalent rare earth ion moments $g_j \cdot \sqrt{J(J+1)}$ (*17*). At temperatures below 200 K a slight deviation of the Curie–Weiss law is observed due to a crystal field splitting of the Hund's rule ground state in orthorhombic symmetry and the onset of ferromagnetic ordering of the *RE*-sublattice. The temperature behavior of the magnetization for RE_2(Ru, Os)B_6 at a field of 1.13 Tesla is summarized in Figs. 6, 7. It is worthwhile to point out that the estimated saturation moments do not reach the theoretical values $\mu_s = g \cdot J$. The magnetic ordering temperatures T_M were obtained from Arrott plots (M^2 vs H/M). The values listed in Table I are generally higher for the RE_2RuB_6 compared with the homologous samples of the RE_2OsB_6 series, indicating a weaker magnetic coupling in the latter compounds. Similar to earlier observations on the $RERuB_4$–$REOsB_4$ series of compounds (*4*, *6*), a minimum value of the Curie–Weiss

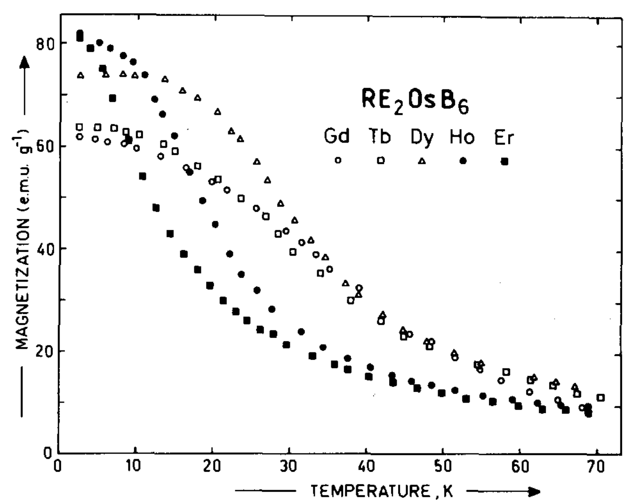

FIG. 7. Magnetization vs temperature for RE_2OsB_6 at a field $H = 1.13$ Tesla.

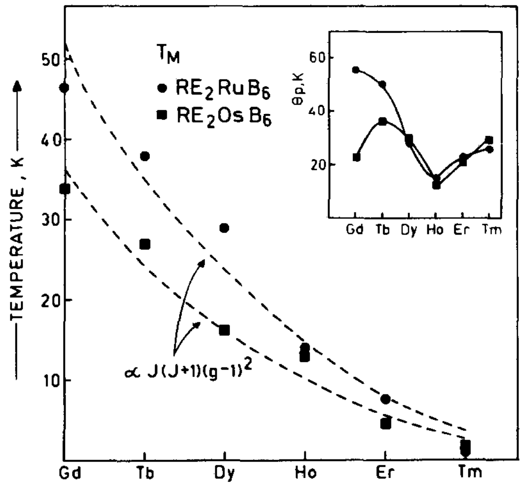

FIG. 8. Ferromagnetic ordering temperatures for RE_2RuB_6,RE_2OsB_6 versus the rare earth element, RE = Gd, Tb, Dy, Ho, Er, and Tm; the dashed lines are a least-square fit of T_M versus the De Gennes factor $T_M = K \cdot J(J + 1)(g - 1)^2$, K(Ru) ≃ 2.2. Curie–Weiss temperatures vs RE are given in the inset.

temperature θ_p is encountered with Ho_2RuB_6 and Ho_2OsB_6, respectively. For both series the Curie temperatures reveal typical De Gennes scaling $T_M = K(J + 1)J(g - 1)^2$ (see Fig. 8). Therefore it seems reasonable to explain the RE–RE interaction to be dominated by an indirect exchange interaction via the conduction electrons (RKKY-mechanism).

No superconductivity was observed in the temperature range investigated.

Acknowledgments

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