

conformations required for tetradentate binding in square-planar, tetrahedral, and pentacoordinate geometries in addition to PNP and PNN binding modes. Clearly the tetrahedral complexes (Cu(I) and Ag(I)) are very labile even with this relatively rigid tetradentate chelating agent (only 4 of the 44 nonhydrogen chelate atoms are sp^3). It is likely that this rapid inversion process can be stopped by locking the conformation of the en backbone, and experiments along these lines are in progress and promise to provide unusual examples of optically stable tetrahedral metal complexes.

The substitution of one imine in the $Cu(en=P_2)$ cation by *t*-BuNC affords a very unusual example of an *in situ* preparation of a large chelate ring; there is little precedence for metal complexes of this structure. This substitution pattern is a nice illustration of the domination of geometric effects, i.e., preference for tetrahedral geometry, over electronic effects, i.e., N vs. P donors. This view is reinforced by observed lability of the $[Cu(tn=P_2)(t-BuNC)]ClO_4$ complex relative to the en analogue. The pentacoordinate complexes undergo ligand exchange at rates which are extremely fast and which limit mechanistic insight. Lastly, the electrochemical results are

very satisfying, particularly with nickel wherein it is seen that three different oxidation states are accessible; future work along these lines will define the salient geometric and electronic features of the reduced species.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also thank The Australian National University Computer Services Centre for the use of their facilities. Acknowledgment is also due to Ms. Janet Hope and Dr. G. A. Lawrence for electrochemical measurements and Dr. G. B. Robertson for use of X-ray equipment.

Registry No. 1, 74684-87-0; 2, CH_2Cl_2 , 74709-78-7; 3, 74709-80-1; 4, 74709-82-3; 5, 74724-74-6; 6, 74709-84-5; 7, 74709-86-7; 8, 74709-88-9; 9, 74709-89-0; PCHO, 50777-76-9; en, 107-15-3; tn, 109-76-2.

Supplementary Material Available: Listings of microanalytical results, structure factor tables, and bond lengths and angles in phenyl groups, anions, and solvents of crystallization (46 pages). Ordering information is given on any current masthead page.

Contribution from the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853, and the Institut für Physikalische Chemie, Universität Wien, Wien A-1090, Austria

Magnetic Behavior and Structural Chemistry of $RERu_3B_2$ Borides¹

K. HIEBL,^{2a} P. ROGL,^{2b} E. UHL,^{2b} and M. J. SIENKO*^{2a}

Received April 7, 1979

New ternary metal borides $[RE,Y]Ru_3B_2$ have been prepared and found to crystallize with the $CeCo_3B_2$ type of structure. Magnetic susceptibilities were determined over a temperature range extending from 1.8 to 1100 K. At higher temperatures (>300 K) typical RE^{3+} paramagnetic Curie-Weiss behavior was found for most of the compounds. With the exception of $[Ce,Sm]Ru_3B_2$ the experimentally obtained effective paramagnetic moments are in good agreement with Hund's rule values for free RE^{3+} ions. The magnetic properties of the ceric rare-earth compounds $[Pr,Nd,Sm]Ru_3B_2$ are characterized by a Van Vleck paramagnetism of closely spaced multiplets. The susceptibility of $CeRu_3B_2$ is described by the analytical expression $\chi_M = (0.025/T) + 0.6 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ ($T = 1.8-300 \text{ K}$); $\mu_{\text{eff}} = 0.45 \mu_B$ corresponds to a high percentage of Ce^{4+} (82%). Ferromagnetic ordering was found for $[Pr,Nd,Gd,Tb,Dy,Ho,Er,Tm]Ru_3B_2$ at low temperatures; ordering temperatures were in the range 5-83 K. No superconductivity was found on heat-treated samples for temperatures as low as 1.8 K.

Introduction

Compounds of the rare-earth elements with noble metals and boron of the type REM_4B_4 have recently become of major scientific interest, especially in order to study the interaction between superconductivity and long-range magnetic order.³⁻⁸ A close inspection of ternary phase equilibria within $RE-[Ru,Rh,Os,Ir]-B$ systems revealed the existence of several new structure types at lower boron concentration and stimulated our interest in the structural chemistry as well as the magnetic

behavior of these new compounds. The subject of the present work is a description of structural and magnetic properties of the new $RERu_3B_2$ series of compounds.

Experimental Section

Starting materials were 99.7% crystalline boron from Ventron GmbH, Karlsruhe, BRD, 99.9% rare-earth-metal ingots from Ventron GmbH, and 99.9% Ru powder from Degussa, Hanau, BRD. Powders of the elements and filings of the RE metals were compacted in steel dies without the use of binders or lubricants. The pellets (~1 g) were arc melted on a water-cooled copper hearth by using a nonconsumable tungsten electrode in a Ti/Zr-gettered argon atmosphere. The melted buttons were subsequently heat treated in a high-vacuum furnace (24 h at 1400 °C, $\sim 5 \times 10^{-4}$ Pa) on a boron nitride substrate and finally quenched in high-purity argon.

Ytterbium-containing samples were reacted in evacuated silica tubes ($2 \times 24 \text{ h}$ at 1200 °C, $\sim 10^{-1}$ Pa). For protection against the silica walls the pellets were wrapped in molybdenum foil. Precise lattice parameters and standard deviations were evaluated by a least-squares refinement procedure⁹ on X-ray diffraction data obtained from De-

(1) Dedicated to Professor H. Bittner on the occasion of his 60th birthday.

(2) (a) Baker Laboratory. (b) Institut für Physikalische Chemie.

(3) Matthias, B. T.; Corenzwitt, E.; Vandenberg, J. M.; Barz, H. E. *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 1334, 1336.

(4) Fertig, W. A.; Johnston, D. C.; DeLong, L. E.; McCallum, R. W.; Maple, M. B.; Matthias, B. T. *Phys. Rev. Lett.* **1977**, *38*, 987.

(5) Chu, C. W. *J. Less-Common Met.* **1978**, *62*, 245.

(6) Hamaker, H. C.; Wolf, L. D.; MacKay, H. B.; Fisk, Z.; Maple, M. B. *Solid State Commun.* **1979**, *31*, 139.

(7) Maple, M. B.; Hamaker, H. C.; Johnston, D. C.; MacKay, H. B.; Wolf, L. D. *J. Less-Common Met.* **1978**, *62*, 251.

(8) Wang, R. H.; Laskowski, R. J.; Huang, C. Y.; Smith, J. L.; Chu, C. W. *J. Appl. Phys.* **1978**, *49*(3), 1392.

(9) Holocher-Ertl, M. Program GITTER (adapted version by H. Boller, of University of Vienna, 1976).

Table I. Crystallographic and Magnetic Data of Ternary Borides MRu₃B₂ (M = Y, RE, Th, U)

compd	<i>a</i> (±0.004), Å	<i>c</i> (±0.002), Å	<i>V</i> , Å ³	<i>c/a</i>	ordering temp, K	asym Curie temp, K	$\mu_{\text{eff}}^{\text{exptl}}$, μ_{B}	$\mu_{\text{eff}}^{\text{theor}}$ (RE ³⁺), μ_{B}
CeRu ₃ B ₂	5.523	2.991	79.0	0.542			1.24 ^a	2.54
PrRu ₃ B ₂	5.532	3.015	79.9	0.545	5	51	3.70	3.58
NdRu ₃ B ₂	5.538	3.010	79.9	0.543	39	61	3.63	3.62
SmRu ₃ B ₂	5.514	3.010	79.3	0.546			1.70 ^a	1.65 ^a
GdRu ₃ B ₂	5.493–5.505	3.024–3.015	79.0–79.1	0.551–0.548	10	65	8.04	7.94
TbRu ₃ B ₂	5.485	3.014	78.5	0.550	83	145	9.81	9.72
DyRu ₃ B ₂	5.474	3.016	78.3	0.551	50	105	10.78	10.63
HoRu ₃ B ₂	5.466	3.017	78.1	0.552	25	50	10.47	10.60
ErRu ₃ B ₂	5.461	3.016	77.9	0.552	32	130	9.54	9.60
TmRu ₃ B ₂	5.454	3.010	77.5	0.552	27	185	7.69	7.68
YbRu ₃ B ₂	5.454	3.003	77.4	0.551		0	4.49	4.54

compd	<i>a</i> (±0.004), Å	<i>c</i> (±0.002), Å	<i>V</i> , Å ³	<i>c/a</i>	χ_{g} (300 K), cm ³ /g
LuRu ₃ B ₂	5.439	3.016	77.2	0.554	7.2×10^{-7b}
YRu ₃ B ₂	5.471	3.027	78.4	0.553	7.8×10^{-7b}
ThRu ₃ B ₂	5.528	3.070	81.2	0.555	5.8×10^{-7b}
URu ₃ B ₂	10.950	5.934	616.1	0.542	2.0×10^{-6b}
single cryst	10.9531	5.9353	616.7	0.542	
UO ₃ B ₂	11.048	5.948	627.8	0.539	1.3×10^{-6b}

^a Values at 293 K. ^b Practically temperature independent.

bye-Scherrer films as well as from diffractometer readings, by using filtered Cr K α and Cu K α radiation.

Susceptibility measurements in the range 80–1100 K were performed with a pendulum susceptibility meter by using a compensation Faraday method¹⁰ under N₂ below 300 K and under high-purity argon in the range 300–1100 K. At low temperatures 1.8 K < *T* < 80 K a Faraday balance¹¹ under helium with Spectrosil silica buckets and Cahn Electrobalance recording was used. An ac induction method as described elsewhere¹² was employed for determination of superconducting critical temperatures.

No Eu or Pm samples were prepared.

Results and Discussion

I. Structure Determination. Powder patterns of alloy samples with a boron content of ~30 atom % indicated compound formation with the approximate formula MRu₃B₂ (M = Y, Th, RE). Except for lanthanum, for which no compound formation was observed at or above 1000 K, the samples of all the rare-earth members, Y, and Th were found to be well crystallized and single phase (or nearly so) for the following nominal composition (in atom %): M, 17; Ru, 50; B, 33. The Debye-Scherrer photographs were characterized by pronounced similarity and could be indexed completely with a hexagonal unit cell (see Table I). The formula and the lattice parameters, as well as the powder intensities, indicate structural analogy of the MRu₃B₂ borides with the structure type of CeCo₃B₂ (ordered CaCu₅ type¹³).

Recently the crystal structure of URu₃B₂ was solved from single-crystal four-circle diffractometer data and found to have a low-symmetry, fourfold superstructure (*a* = 2*a**, *c* = 2*c**) of the CeCo₃B₂ cell.¹⁴ Superstructure reflections, however, were very faint and were not discernible from ordinary powder photographs; i.e., deviation from higher symmetry (CeCo₃B₂) was rather small. Similar behavior seemed to be conceivable for the isotypic [Y,Th,RE]Ru₃B₂ series of compounds, despite the fact that no deviations from CeCo₃B₂ symmetry were found from the powder photographs. So far as the size factor is concerned, the similar alloying behavior of uranium in combination with noble metals and boron is comparable to that of the smallest RE members.^{15,16}

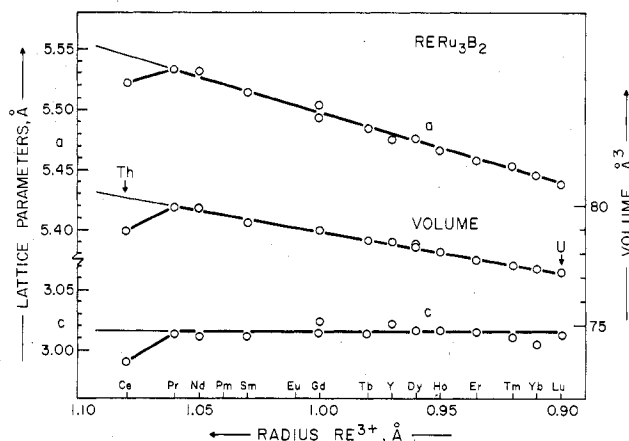


Figure 1. Lattice parameters and volumes of [RE,Y,Th,U]Ru₃B₂ borides vs. $R_{\text{RE}^{3+}}$ (CaCu₅-type subcell parameters).

In order to decide whether the URu₃B₂- or the CeCo₃B₂-type structure is adopted, we prepared Weissenberg photographs from an ErRu₃B₂ single crystal. High Laue symmetry 6/*mmm*, no observed extinctions, unit cell parameters, and reflection intensities obtained from single-crystal layer patterns (axis [001]) clearly indicate a CeCo₃B₂ structure type for ErRu₃B₂ (space group *P6/mmm*, No. 191). An evaluation of the powder diagram of ErRu₃B₂ is presented in Table II; it shows excellent agreement between observed and calculated intensities. From the smooth linear dependency of lattice parameters vs. RE size, the CeCo₃B₂-type structure seems likely to be adopted throughout the complete RERu₃B₂ series of compounds. Confirmation, however, would be desirable for each of the remaining RE members by detailed single-crystal studies.

For most of the compounds, only small changes in lattice parameters with composition were observed in multiphase alloys, indicating narrow homogeneity regions. GdRu₃B₂ was an exception (see Table I). Linear dependence of lattice parameters and unit cell volume was found from a graph against corresponding values of the RE³⁺ ionic radii (see Figure 1). The usefulness of this graph in revealing valency dif-

(10) SUS 10, susceptibility measuring device, A. Paar KG, Graz, Austria.

(11) Young, J. E., Jr. Ph.D. Thesis, Cornell University, 1971.

(12) Fisher, W. G. Ph.D. Thesis, Cornell University, 1978.

(13) Kuz'ma, Yu. B.; Kripyakevich, P. I.; Bilonishko, N. S. *Dopov. Akad. Nauk Ukr. RSR, Ser. A: Mat. Tekh. Nauki* 1969, 10, 939.

(14) Rogl, P., to be submitted for publication.

(15) Valyovka, I. N.; Kuz'ma, Yu. B. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1978, 14(3), 469.

(16) Rogl, P. *Monatsh. Chem.*, in press.

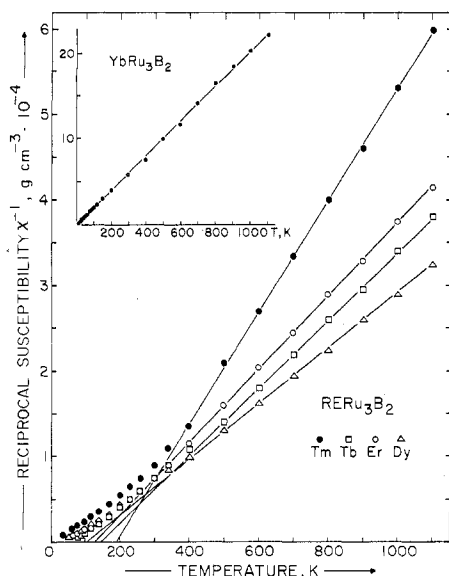


Figure 2. Reciprocal gram-susceptibility vs. temperature for $RERu_3B_2$ borides ($RE = Tb, Dy, Er, Tm, Yb$).

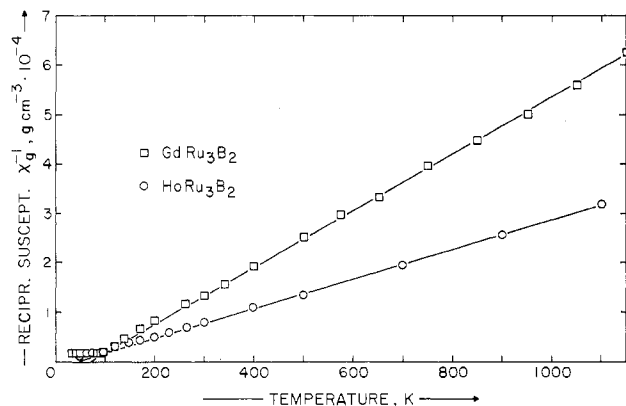


Figure 3. Reciprocal gram-susceptibility vs. temperature for $[Gd, Ho]Ru_3B_2$.

ferences is shown in the case of $YbRu_3B_2$, yielding trivalency of Yb, as well as in the case of $CeRu_3B_2$, where the small lattice parameters indicate the Ce^{4+} type of behavior. (See also section II, Magnetic Properties.)

According to the classification scheme of ternary transition-metal borides¹⁷ based upon boron-boron aggregation, the structural chemistry of $RERu_3B_2$ borides is characterized by isolated boron atoms in tetrakaidecahedral Ru_6RE_3 coordination. Ru-Ru distances ($a/2, R_{Ru} = 1.34 \text{ \AA}$) range from 2.72 ($LuRu_3B_2$) to as much as 2.76 \AA for $PrRu_3B_2$. Ru-Ru distances derived from extrapolated (Figure 1) lattice parameters for hypothetical " $LaRu_3B_2$ " ($a = 5.575, c = 3.02 \text{ \AA}$) greatly exceed the sum of metal radii. Hence, a decisive size factor may explain the upper stability limit of $RERu_3B_2$ -type borides as being located near $PrRu_3B_2$. Despite the larger volume of $ThRu_3B_2$ compared to that of the Pr compound, its Ru-Ru distances (2.76 \AA) are well within the above-mentioned range (due to a slightly larger c/a ratio). In this context, it is interesting to note that the $CeCo_3B_2$ -type related series $REIr_3B_2$ ¹⁴ exhibits a much larger c/a ratio compared to $RERu_3B_2$. The smaller a axis of $LaIr_3B_2$ yields Ir-Ir distances close to the sum of Ir-metal radii (Ir-Ir ($LaIr_3B_2$) = 2.76, $R_{Ir} = 1.36 \text{ \AA}$). On the other hand, no $LaRh_3B_2$ ¹⁴ has been found so far ($R_{Rh} = R_{Ru}$).

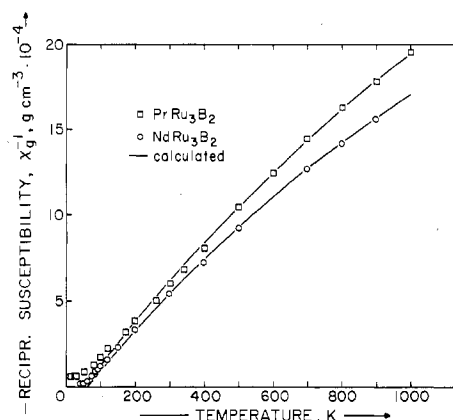


Figure 4. Reciprocal gram-susceptibility vs. temperature for $[Pr, Nd]Ru_3B_2$ and calculated least-squares fit to eq 2.

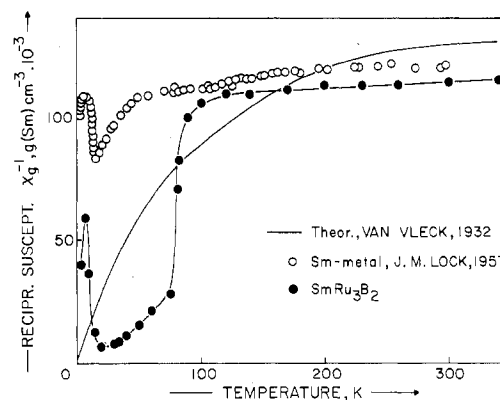


Figure 5. Reciprocal gram-susceptibility vs. temperature for $SmRu_3B_2$. For comparison with values obtained by Lock¹⁹ (Sm metal) as well as the theoretical values by Van Vleck¹⁸ (free Sm^{3+}) the $SmRu_3B_2$ values have been based on the Sm metal content.

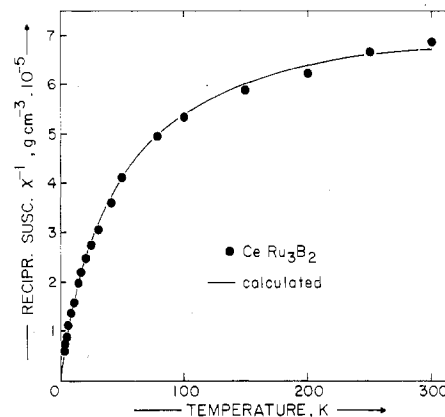


Figure 6. Reciprocal gram-susceptibility vs. temperature for $CeRu_3B_2$ and calculated least-squares fit to eq 2.

II. Magnetic Properties. The results of the magnetic measurements are summarized in Figures 2–7 and in Table I. The magnetic susceptibility of the Y, Lu, and Th as well as the U compounds was found to be practically independent of temperature, and thus $[Y, Lu, U, Th]Ru_3B_2$ and UOs_3B_2 can be regarded as Pauli paramagnets.

A. Paramagnetic Behavior. Most of the remaining $RERu_3B_2$ borides exhibited normal paramagnetic behavior and adhered closely to the Curie-Weiss law (Figures 2 and 3) over the major portion (300–1100 K) of the measured temperature region. For the heavier rare-earth alloys, $Gd \rightarrow Yb$, a linear dependence of the reciprocal gram-susceptibility χ_g ($cm^3 g^{-1}$)

Table II. Powder Diffraction Data for ErRu_3B_2 (CeCo_3B_2 -Type Structure)^a

<i>hkl</i>	$10^4(\sin^2 \theta)$		intens		<i>hkl</i>	$10^4(\sin^2 \theta)$		intens	
	obsd	calcd	obsd	calcd		obsd	calcd	obsd	calcd
100	267	266	vw	7	321	5701	5701	vw	10
001	654	653	vw	5	222	5805	5802	vw	17
110	800	797	vw	4	003	b	5880	b	0
101	918	919	st	77	312	b	6067	b	0
200	1064	1063	vst	100	103	6142	6146	vw	5
111	1445	1450	m	46	411	6234	6233	vw	11
201	1719	1716	vw	10	500	b	6642	b	0
210	b	1860	b	1	113	6679	6677	vw	6
300	b	2391	b	1	402	6860	6864	vw	15
211	2517	2513	w	33	203	b	6943	b	1
002	2616	2616	vw	9	330	b	7174	b	0
102	b	2879	b	1	501	7291	7296	vw	5
301	3043	3045	vw	14	420	7438	7439	vw	16
220	3189	3188	w	19	322	b	7661	b	1
112	b	3410	b	1	213	7738	7740	vw	11
310	b	3454	b	0	331	7826	7827	vw	6
202	3671	3676	w	28	421	8095	8093	vw	3
221	3846	3842	vw	2	412	b	8193	b	1
311	4107	4107	vw	15	510	b	8236	b	0
400	4259	4251	vw	11	303	8278	8271	vw	7
212	b	4473	b	1	511	8891	8890	vw	15
401	4897	4904	vw	2	223	b	9068	b	2
302	b	5004	b	0	502	b	9256	b	0
320	b	5048	b	0	313	9331	9334	w	20
410	b	5580	b	0	600	9558	9565	w	21

^a The material is the alloy $\text{Er}_{0.17}\text{Ru}_{0.50}\text{B}_{0.33}$ (arc melted). The method used was powder X-ray diffraction in a Debye-Scherrer camera with Ni-filtered $\text{Cu K}\alpha$ radiation. $I = mF^2(1 + \cos^2 2\theta)/(\sin^2 \theta \cos \theta)$ was normalized to the strongest reflection with the intensity 100. The space group is $P6/mmm-D_{6h}^2$, No. 191. Lattice parameters are $a = 5.461(3)$ and $c = 3.016(2)$ Å. One Er atom in (1a) 0, 0, 0, three Ru atoms in (3g) $1/2, 0, 1/2$, and two B atoms in (2c) $1/3, 2/3, 0$. ^b Not observed.

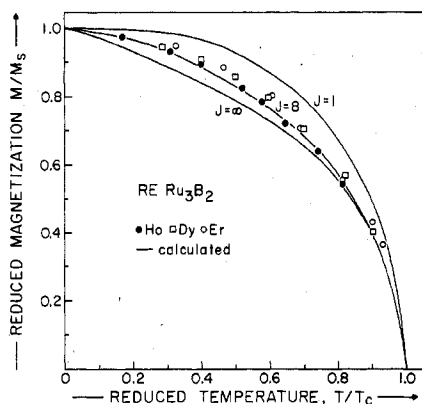


Figure 7. Reduced magnetization vs. reduced temperature for $[\text{Dy}, \text{Ho}, \text{Er}]\text{Ru}_3\text{B}_2$ borides.

vs. temperature was found above ferromagnetic ordering temperatures, T_{Curie} . Paramagnetic moments per formula unit, calculated from the Curie-Weiss constant $\mu_{\text{eff}} = 2.83C^{1/2} \mu_{\text{B}}$, and extrapolated Curie-Weiss temperatures Θ_p [$\chi_{\text{M}} = C/(T - \Theta_p)$] are listed in Table I. YbRu_3B_2 (Figure 2) exhibits ideal paramagnetic behavior, as its Θ_p is found to be zero. The paramagnetic moment derived for YbRu_3B_2 is very close to the theoretical value¹⁸ for Yb^{3+} in perfect agreement with lattice parameters and volume, as discussed in section I (Figure 1).

The susceptibility data for the ceric rare earths (Ce, Pr, Nd, Sm) cannot be described by a simple Curie-Weiss law. Nonetheless, in the case of $[\text{Pr}, \text{Nd}]\text{Ru}_3\text{B}_2$ the deviations of χ_{M}^{-1} vs. T from linear dependence at the highest temperatures ($T > 800$ K) seem to be typical examples of the temperature-independent Van Vleck type of paramagnetism, consistent with existence of relatively low-lying energy states above the

Table III. Comparison of Molar Susceptibilities $\chi_{\text{M}}(T)$ for Different Nd and Pr Compounds

compd	$\chi_{\text{M}}, \text{cm}^3 \text{mol}^{-1}$	$\mu_{\text{eff}}^{\text{exptl}}, \mu_{\text{B}}$	ref
Nd metal	$1.366/(T - 4.3) + 0.721 \times 10^{-3}$	3.3	19
Nd_2O_3	$1.684/(T + 68) + 0.60 \times 10^{-3}$	3.67	20
NdRu_3B_2	$1.65/(T - 61) + 0.66 \times 10^{-3}$	3.62	this work
PrRu_3B_2	$1.72/(T - 51) + 0.54 \times 10^{-3}$	3.58	this work

Hund's rule ground state.¹⁸ Therefore, a least-squares fit of the data (>300 K) was made to function 1, where N is the

$$\chi_{\text{M}} = \frac{N(\mu_{\text{eff}}^2)}{3k_{\text{B}}(T + \Delta)} + N\alpha - \frac{N(e^2)}{6mc^2} \sum_i \overline{R_i^2} + \chi_{\text{Pauli}} \quad (1)$$

Avogadro number and k_{B} is the Boltzmann constant. The first (main) term represents a Curie-Weiss contribution from the ground state, and the second term is the temperature-independent Van Vleck correction (second-order Zeeman effect), while the third term represents the diamagnetic part. Finally, due to the generally metallic nature of the low-boron-content samples, a fourth term was included to account for the Pauli paramagnetism of the conduction electrons. With use of best-fit parameters μ_{eff} , Θ_p , etc. (see Table II), eq 1 in its analytically simpler form

$$\chi_{\text{M}} = \frac{C}{T + \Delta} + B \quad (2)$$

describes the experimental data fairly well in both cases $[\text{Pr}, \text{Nd}]\text{Ru}_3\text{B}_2$ at temperatures $T > 300$ K, Figure 4. Furthermore, the effective moments, μ_{eff} , so obtained are in excellent agreement with Hund's rule ground states for the free RE^{3+} ions (Table I). Table III gives a comparison of analytical

(18) Van Vleck, J. H., "The Theory of Electric and Magnetic Susceptibilities"; Clarendon: Oxford, 1932.

(19) Lock, J. M. *Proc. Phys. Soc., London, Sect. B* 1957, 70, 566.

expressions for χ_M of various Nd and Pr compounds, as derived by different authors.

For a theoretical calculation of the Van Vleck correction term, multiplet widths for Pr^{3+} and Nd^{3+} were used as compiled by Araj's;^{21,22} the diamagnetic core correction was based on Selwood's data.²³ Thus, a simple separation of the experimentally obtained B term $B = \chi_{\text{dia}} + \chi_{\text{Van Vleck}} + \chi_{\text{Pauli}}$ yielded a rough estimation for χ_{Pauli} . In both cases $[\text{Pr-Nd}]\text{Ru}_3\text{B}_2$ the derived values $\chi_{\text{Pauli}} \cong 1.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ are in fair agreement and are found to be of the same order of magnitude as those reported by Araj's²² for Pr metal ($1.15 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) as well as by Kittel for Ru metal ($0.5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$).

Considering the experimentally obtained paramagnetic effective moments for RERu_3B_2 phases (see Table I), excellent agreement is found with Hund's theoretically expected values for free RE^{3+} ions. Therefore, at least at higher temperatures ($>300 \text{ K}$), paramagnetic behavior of RERu_3B_2 borides is considered to be solely due to the rare-earth atom sublattice. The fact of a negligible paramagnetic contribution of the noble metal-boron sublattice is confirmed by the practically temperature-independent Pauli paramagnetic behavior of zero magnetic moment rare-earth combinations such as $[\text{Y,Lu}]\text{Ru}_3\text{B}_2$ (see Table I).

The Case of SmRu_3B_2 and CeRu_3B_2 . For both compounds a plot of the reciprocal susceptibility χ_g^{-1} vs. temperature shows remarkable deviations from a simple Curie-Weiss law (Figures 5 and 6). It is interesting to note from Figure 5 how closely the reciprocal gram-susceptibility χ_g^{-1} of SmRu_3B_2 follows the temperature dependence shown by pure Sm metal itself. The room-temperature paramagnetic moment μ_{eff} is in excellent agreement with the theoretically expected value for tripositive Sm according to the Van Vleck theory for closely spaced multiplets.¹⁸ Deviations from Van Vleck theory, however, become well pronounced at low temperatures and might be attributed to strong crystal field effects. Similar behavior was found for SmN ,²⁴ SmGa ,²⁵ and recently for $\text{Sm}[\text{Ir,Os}]_4\text{B}_4$.²⁶

On the other hand, the susceptibility function χ_g^{-1} vs. T for CeRu_3B_2 (Figure 6) reflects the generally ambivalent behavior of cerium as an alloying constituent. χ_g^{-1} vs. T for CeRu_3B_2 resembles most the theoretical χ_g^{-1} vs. T for ideally free Sm^{3+} Van Vleck paramagnetism.¹⁸ There is for Sm^{3+} a small Curie contribution $\mu_{\text{eff}}^{\text{Sm}^{3+}} = 0.84 \mu_B$, arising from the $J = 5/2$ Hund's

rule ground state and a second-order Zeeman effect, due to rather small multiplet splitting. Similarly, the CeRu_3B_2 susceptibility curve can be expressed by a least-squares-fitted analytical function $\chi_M = 0.025/T + 0.6 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$. From this, a small paramagnetic moment, $\mu_{\text{eff}} = 0.45 \mu_B$, is derived for CeRu_3B_2 , yielding a valency of 3.82, suggesting a rather high ratio $\text{Ce}^{4+}/\text{Ce}^{3+} = 4.55$, in fair agreement with lattice parameters and the volume of the CeRu_3B_2 unit cell.

B. Ferromagnetic Behavior. The low-temperature ($T < 300 \text{ K}$) magnetic behavior of the RERu_3B_2 borides ($\text{RE} = \text{Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm}$) is characterized by onset of ferromagnetic ordering as indicated by large positive paramagnetic Curie-Weiss temperatures. Values for the ferromagnetic ordering temperature T_c were obtained from Arrott plots (M^2 vs. H/M) and are listed in Table I. The magnetization obtained in a field of 16 kG was in general smaller than the theoretical saturation moment gJ of the free RE^{3+} ion except for $[\text{Er,Dy,Ho}]\text{Ru}_3\text{B}_2$. Furthermore, except in the case of Ho we observed considerable differences between T_{Curie} and the asymptotic Curie temperatures Θ_p derived from extrapolations of the χ_g^{-1} vs. T plots. This suggests that in these cases magnetic ordering phenomena are more complicated than simple ferromagnetic ordering. Thus, only HoRu_3B_2 seems to obey rather closely the complete Brillouin expression for its magnetization ($J = 8$; see Figure 7), whereas remarkable discrepancies are obvious for Dy and Er ($J = 15/2$ in both cases; Figure 7). Due to the relatively high ordering temperatures, $T_{\text{Curie}} > 20 \text{ K}$ and strong magnetic interaction, superconducting behavior seems to be unlikely and was not found experimentally in measurements as low as 1.8 K, not even in the case of the zero-moment RE combinations. $[\text{Th,Lu}]\text{Ru}_3\text{B}_2$, however, was not investigated below 80 K.

Acknowledgment. This investigation was sponsored by the Air Force Office of Scientific Research under Grant No. 80-0009 and supported in part by the National Science Foundation and the Material Science Center at Cornell University. P.R. wants to express his gratitude to Dr. Endter, Degussa, Hanau, BRD, for kindly supplying us with the noble metals. His thanks are also due to the Austrian Science Foundation (Österr. Forschungsrat) for Grant No. 3620. H.K. is grateful to the Council for International Exchange of Scholars for award of a Fulbright travel grant. E.U. wants to thank the Austrian Science Foundation (Fonds zur Förderung der wiss. Forschung) for the use of the SUS 10 under Grant No. 2950.

Registry No. CeRu_3B_2 , 74744-14-2; PrRu_3B_2 , 74744-05-1; NdRu_3B_2 , 74744-07-3; SmRu_3B_2 , 74744-01-7; GdRu_3B_2 , 74744-11-9; TbRu_3B_2 , 74744-10-8; DyRu_3B_2 , 74744-15-3; HoRu_3B_2 , 74744-12-0; ErRu_3B_2 , 74744-13-1; TmRu_3B_2 , 74744-04-0; YbRu_3B_2 , 74744-00-6; LuRu_3B_2 , 74744-08-4; YRu_3B_2 , 74744-03-9; ThRu_3B_2 , 74744-02-8; URu_3B_2 , 74744-09-5; UOs_3B_2 , 74744-06-2.

(20) Smol'kov, N. A.; Dobrovol'skaya, N. V. *Neorg. Mater.* **1965**, *1*(9), 1564.

(21) Araj's, S.; Colvin, R. V. *J. Appl. Phys.* **1961**, *32*, 3365.

(22) Araj's, S.; Colvin, R. V.; Peck, J. M. *J. Chem. Phys.* **1961**, *34*, 1959.

(23) Selwood, P. W. "Magnetochemistry"; Interscience: New York, London, 1956.

(24) Schuhmacher, D. P.; Wallace, W. E. *Inorg. Chem.* **1966**, *5*, 1563.

(25) Fujii, H.; Shohata, N.; Okamoto, T. *J. Phys. Soc. Jpn.* **1971**, *31*, 1592.

(26) Rupp, B.; Rogl, P.; Sobczak, R. *Mater. Res. Bull.* **1979**, *14*, 1301.