Each of these arrangements is fixed by the primitive cell translations of the pyrite cell and by the inversion centers at the Fe atoms and the midpoints of the dimers. Hence every element of the normal subgroup $P\bar{1}$ of $Fm3m$ corresponds to the identity permutation on S. The distinct permutations of S engendered by $Fm3m$ are therefore represented by the elements of the quotient group $Fm3m/P\bar{1}$ of order 96. The elements of this group are the cosets represented by the 24 elements of the point group $\bar{4}3m = T_d$ of the point $^1/_4$, $^1/_4$, $^1/_4$ of the NaCl cell and the 72 operations obtained by following these 24 by a reflection in one of the mirrors at $x, y, 0$; $x, 0, z$, or $0, y, z$.

The set S can also be simplified a bit. The centers of the four translationally inequivalent dimers are at the vertices of a tetrahedron centered at $^1/_4$, $^1/_4$, $^1/_4$ (Figure 18). Hence S can be regarded as the set of all 256 ways to place at each vertex of this tetrahedron a dimer parallel to one of the four 3-fold axes of the tetrahedron (not necessarily the 3-fold axis passing through that vertex). The elements of $\bar{4}3m$ permute these objects in the obvious way, and the mirror planes act on them as shown in Figure 19.

To determine $\Phi(g)$ for every $g \in Fm3m/P\bar{1}$ is not as difficult as might at first appear. In particular, it is not necessary to consider all 256 elements of S. Consider, for example, how to evaluate $\Phi(3)$, the number of elements of S fixed by a 3-fold rotor in $\bar{4}3m$. Plainly the dimer on the apical vertex—that through which the rotor passes—of such an element of S must point along that 3-fold axis. The basal dimers need not have this orientation, but once one basal dimer has been specified, the 3-fold symmetry determines the orientations of the others. Thus $\Phi(3) = 4$. This type of consideration makes determination of $\Phi(g)$ for any g fairly easy. It is also extremely helpful that $\Phi(g)$ is a class function.

Table IV lists the value of $\Phi(g)$ for every $g \in Fm3m/P\bar{1}$. Summation of these and division by 96, the order of $Fm3m/P\bar{1}$, produce the answer that there are nine orbits, i.e., nine structures with the same size unit cell as pyrite and with dimers pointing along ±1±1±1.

Registry No. Pyrite, 1309-36-0; marcasite, 1317-66-4; $NaHF_2$, 1333-83-1; CaC_2, 75-20-7; CaF_2, 7789-75-5; XeF_2, 13709-36-9; $IrSe_2$, 12030-55-6; TiO_2, 13463-67-7; $PbCl_2$, 7758-95-4; CdI_2, 7790-80-9; löllingite, 12255-65-1; $FeAs_2$, 12006-21-2; FeS_2, 12068-85-8.

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Structural Chemistry and Magnetic Properties of the Compounds $EuOs_4B_4$ and $EuIr_4B_4$ and of the Solid Solutions $(RE)Os_4B_4$–$(RE)Ir_4B_4$ (RE = Ce, Pr, Sm)

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New ternary metal borides, $EuOs_4B_4$ and $EuIr_4B_4$, have been synthesized from the elements. The compounds were found to crystallize with the structure type of $NdCo_4B_4$. Effective paramagnetic moments derived from χ^{-1} vs. T plots over the range 1.8–800 K are in good agreement with theoretical values according to a Hund's rule ground-state $^8S_{1/2}$ for a free Eu^{2+} ion. Complete solid solution was found for mixed crystals of $CeOs_4B_4$–$CeIr_4B_4$ (arc melted, quenched, $NdCo_4B_4$-type structure) revealing a positive deviation from Vegard's law. Magnetic susceptibilities were determined for the temperature range 1.8–1000 K. At high temperature the magnetic properties are characterized by Van Vleck paramagnetism of closely spaced multiplets due to admixture of the excited term $J = {}^7/_2$ of the Ce^{3+} $F_{5/2}$ ground state. At lower temperatures the paramagnetic behavior of cerium changes from that of a practically pure Ce^{4+} state in $CeOs_4B_4$ ($\mu_{eff} = 0.49\ \mu_B$) to that of a pronounced Ce^{3+} state in $CeIr_4B_4$ ($\mu_{eff} = 2.21\ \mu_B$) presumably due to the larger iridium metal framework and/or the higher electron-to-atom ratio. At very low temperatures, ≤3.5 K, ferromagnetic ordering was observed for $CeIr_4B_4$ and $CeIr_3Os_1B_4$. For comparison, the magnetic behavior was studied over the range 1.5–300 K of the pseudobinary sections $PrOs_{4-x}Ir_xB_4$ and $SmOs_{4-x}Ir_xB_4$. Although a slight negative deviation from Vegard's law was observed, there was practically no change from a valence state of Sm^{3+} for samarium. On the basis of Miedema's model, a thermodynamic calculation for the valence change ($Ce^{III} \rightarrow Ce^{IV}$, $Eu^{II} \rightarrow Eu^{III}$) has been found to be in good accord with the magnetic behavior observed.

Introduction

Recently published papers[1-3] have shown that 1:4:4 combinations of large rare-earth (RE) metals (La to Gd) with noble metals of highest density (Os and Ir) and boron commonly adopt the $NdCo_4B_4$ type of structure. No data, however, were provided for the corresponding europium compounds due to the extremely high vapor pressure of europium metal at elevated temperatures, which demands more special reaction techniques. So far as crystal chemistry is concerned, following the general behavior of the RE[Os,Ir]$_4$B$_4$ series of compounds for large RE members, europium was expected to form $NdCo_4B_4$-type analogues in both cases: $EuOs_4B_4$ and $EuIr_4B_4$. Thus, a careful investigation with respect to compound formation and crystal structure, as well as magnetic and superconducting properties, became the subject of the present work.

Second, we have undertaken a detailed study of the crystal chemistry and magnetic properties within the series of solid solutions of mixed crystals $CeOs_{4-x}Ir_xB_4$, $PrOs_{4-x}Ir_xB_4$, and $SmOs_{4-x}Ir_xB_4$, especially in relation to possible intermediate valence behavior of the rare-earth atoms.

Experimental Section

All the compounds were made from commercially available high-purity materials: crystalline boron, 99.7%, from Ventron GmbH, Karlsruhe, Federal Republic of Germany; Os, Ir powders, 99.9%, Degussa, Hanau, Federal Republic of Germany; RE metal ingots, m3N, Ventron GmbH; EuB_6 powder (≤100 ppm, a = 4.1852 Å), Electroschmelzwerk Kempten, Federal Republic of Germany. Powders of the elements and filings of the RE metals wre compacted in steel dies without the use of binders or lubricants. Sample preparation was different for europium and [Ce, Pr, Sm]-containing specimens. (a) The [Ce, Pr, Sm]-containing pellets (~1 g) were arc melted on a water-cooled copper hearth, with use of a nonconsumable tungsten

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(1) Rogl, P. *Monatsh. Chem.* **1979**, *110*, 235.
(2) Rogl, P. *Monatsh. Chem.* **1980**, *111*, 517.
(3) Rogl, P.; Nowotny, H. In "The Rare Earths in Modern Science and Technology"; McCarthy, G. J., Rhyne, J. J., Silber, H. B., Eds.; Plenum Press: New York, 1980; Vol. 2, p 173.

Table I. Crystallographic and Magnetic Data of Ternary Borides $RE[Os,Ir]_4B_4$ (RE = Eu, Sm, Pr)

phase	a, Å	c, Å	c/a	V, Å^3	Θ_p, K	μ_{eff}, μ_B	
						exptl	theor
$EuOs_4B_4$	7.5262 (9)	4.0159 (6)	0.534	227.5	0.0	7.20	7.94
$EuIr_4B_4$	7.6219 (9)	3.9771 (5)	0.522	231.0	2.5	7.84	7.94
$SmOs_4B_4$	7.526 (3)	4.009 (2)	0.533	227.1		1.69[a]	1.60[a]
$SmOs_3IrB_4$	7.5406 (8)	3.9949 (6)	0.530	227.1		1.87[a]	1.60[a]
$SmOs_2Ir_2B_4$	7.5538 (6)	3.9860 (4)	0.528	227.4		1.71[a]	1.60[a]
$SmOsIr_3B_4$	7.5742 (7)	3.9822 (4)	0.526	228.4		1.62[a]	1.60[a]
$SmIr_4B_4$	7.590 (3)	3.976 (2)	0.524	229.0		1.55[a]	1.60[a]
$PrOs_2Ir_2B_4$	7.5991 (12)	3.9835 (5)	0.524	230.0	22	3.55	3.58

[a] Values at 295 K.

electrode in a Ti/Zr-gettered argon atmosphere. (b) The high vapor pressure of europium metal prohibits the arc melting procedure so a sintering technique was adopted with use of a vapor-tight assembly of a covered internal crucible made from boronitride, placed within a nicely fitted and tightly screwed tantalum container. Also, most of the europium was introduced in the form of europium hexaboride. The compacted pellets, contained in the boronitride crucible, were allowed to react at a temperature of 1400 °C for 2 h under high-purity argon. After being crushed and recompacted, the samples in BN/Ta containers were subjected to a final heat treatment for 24 h at 1400 °C and then radiation cooled.

Except for the europium-containing samples, in which small amounts of impurity boride phases were present (i.e., $IrB_{1.1}$, $IrB_{0.9}$, and $OsB_{1.1}$, respectively), metallographic as well as X-ray powder diffraction analysis indicated that the described preparation techniques were adequate for obtaining practically single-phase products. Precise lattice parameters and standard deviations were evaluated by a least-squares refinement procedure[4] on X-ray diffraction data obtained from Debye–Scherrer or Guinier photographs as well as from a Siemens powder diffractometer, using filtered Cr Kα and Cu Kα_1 radiation.

Susceptibility measurements in the range 80–1000 K were performed with a pendulum susceptibility meter (Faraday compensation method[5]) under nitrogen (<300 K) as well as high-purity argon (300–1000 K). In the range 1.8–80 K, a Faraday balance under helium with Spectrosil quartz buckets and Cahn electrobalance recording was used.[6] An ac induction method as describedd elsewhere[7] was employed for determination of superconducting critical temperatures.

Results and Discussion

Crystal Structures of $EuOs_4B_4$ and $EuIr_4B_4$. Powder patterns of samples with a nominal composition Eu:[Os,Ir]:B = 1:4:4 revealed a close resemblance to the powder patterns of the larger rare-earth compounds $RE[Os,Ir]_4B_4$. After subtraction of the IrB or $OsB_{1.1}$ reflections, Guinier photographs could be indexed completely on the basis of a tetragonal unit cell (Table I). Composition, lattice parameters, as well as powder intensities of $Eu[Os,Ir]_4B_4$ prove structural analogy with the structure type of $NdCo_4B_4$.[8] The slightly different c/a ratio observed was already found earlier[1,2] to be characteristic for the two series of $NdCo_4B_4$ compounds, $(RE)Os_4B_4$ and $(RE)Ir_4B_4$, and is reflected in small but significant intensity differences due to small variations of the noble atom parameters. By use of the atom parameters of $NdOs_4B_4$[9] and $LaIr_4B_4$,[2] calculated[10] and observed powder intensities were found to be in excellent agreement for both $EuOs_4B_4$ and $EuIr_4B_4$. The details of the powder diagram of $EuIr_4B_4$ are presented in Table II. Interatomic distances are consistent with the general characteristics of the crystal chemistry of $NdCo_4B_4$-type borides as discussed earlier.[1,2,9]

Table II. Powder Diffraction Data for $EuIr_4B_4$ ($NdCo_4B_4$ Type)[a]

(hkl)	$10^4.\sin^2\theta$ obs.	$10^4.\sin^2\theta$ calc.	Intensity obs.	Intensity calc.
(110)	204	204	17	23.9
(200)	*	409	*	0.5
(101)	477	477	2	2.5
(111)	579	579	18	20.5
(201)	784	784	4	5.2
(220)	817	817	1	1.1
(211) (121)	885	886	100	100.0 4.5
(310) (130)	1021	1021	63	9.5 50.9
(221)	1192	1192	29	25.7
(301)	*	1294	*	0.0
(311) (131)	1396	1396	13	11.7 0.9
(002)	1500	1501	3	2.6
(102)	1603	1603	25	23.4
(400)	1634	1634	12	10.7
(321) (231) (112)	1702	1703 1705	17	6.9 9.1 0.3
(330)	1839	1836	2.0	2.1
(202)	*	1909	*	1.0
(401) (212) (122)	2010	2011	2	0.3 0.0 1.6
(420) (240)	2043	2043	15	12.2 0.8
(411) (141)	2112	2111	3	0.7 1.9
(331)	*	2213	*	0.4
(222)	*	2318	*	0.8
(421) (241) (302)	2420	2418 2420	20	2.0 0.1 15.4
(312) (132)	2523	2522	7	1.4 3.7
(510) (150)	2655	2655	7	0.3 3.9
(322) (232)	2828	2828	4	2.0 1.5
(431) (341) (501)	2929	2928	19	0.8 8.4 8.5
(511) (151)	3030	3031	6	4.6 0.1
(402)	*	3135	*	0.0
(412) (142)	3237	3237	15	0.4 13.5
(440)	3268	3268	7	5.8
(521) (251) (332)	3337	3337 3339	10	5.0 3.4 0.1
(530) (350) (103)	3475	3472 3478	4	2.9 0.2 0.8
(422) (242)	3545	3543	3	1.7 0.1
(113)	3580	3580	3	3.2
(441)	*	3643	*	0.4
(600)	*	3677	*	1.1
(203)	*	3785	*	1.0
(531) (350)	3850	3848	6	0.0 5.2
(213) (123)	3887	3887	3	0.5 1.6
(601) (432) (342) (502)	4055	4054	18	2.3 10.7 1.0 1.5
(620) (260)	4086	4085	2	0.2 1.8
(611) (161) (512) (152)	4154	4154	7	4.1 0.3 0.4 0.9
(223)	4192	4193	9	8.0
(303)	*	4295	*	0.9
(313) (133)	4397	4398	6	4.2 0.3
(621) (261) (522) (252)	4462	4460 4462	8	1.5 1.4 3.1 0.3
(541) (451)	*	4563	*	0.1 0.5
(323) (233)	*	4704	*	2.3 0.0
(442)	*	4769	*	1.1
(631) (361) (532) (352)	4970	4971 4973	7	1.1 5.4 0.0 0.3

* not observed

[a] Material: Eu (11.2), Ir (44.4), and B (44.4), reacted for 6 h at 1400 °C, from Eu, Ir, EuB_6 in BN crucible contained in Ta capsules. Method: powder X-ray diffraction in a Siemens diffractometer with Ni-filtered Cu Kα radiation (99.9999% Ge standard). Lattice parameters: a = 7.6219 (9), c = 3.9771 (5) Å. $I[= mF^2(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta]$ is normalized to the strongest reflection with the intensity 100. The space group is $P4_2/n$ (C^4_{4h}; No. 86). Two Eu in (2b) $^1/_4$, $^1/_4$, $^3/_4$; eight Ir in (8g) 0.5937, 0.1397, 0.1441; eight B in (8g) 0.531, 0.409, 0.136.

Recent magnetic measurements[9] on $RE[Os,Ir]_4B_4$ borides of the $NdCo_4B_4$ type showed a general $(RE)^{3+}$-type paramagnetic behavior with rather linear dependence of lattice parameters or unit cell volumes on the $(RE)^{3+}$ radii.[3] From comparison of the lattice parameters of the new compounds $Eu[Os,Ir]_4B_4$ with those extrapolated from the general $(RE)^{3+}$ dependency, a typical Eu^{2+} ground state can be inferred to be responsible for the large positive volume differences, which, however, are found to be slightly larger for the Ir compound than for the Os compound. (See also section on magnetic properties.)

Solid Solutions $(RE)Os_{4-x}Ir_xB_4$ (RE = Ce, Pr, Sm). Metallography of arc-melted samples over the range $(RE)Os_{4-x}Ir_xB_4$ proved in all cases (Re = Ce, Pr, Sm) general congruent melting behavior as well as complete solid solubility,

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[4] Holocher-Ertl, M. Program GITTER, adapted version by H. Boller, University of Vienna, 1976.

[5] SUS-10: susceptibility measuring device, A. Paar KG, Graz, Austria.

[6] Young, J. E., Jr. Ph.D. Thesis, Cornell University, 1971.

[7] Fisher, W. G. Ph.D. Thesis, Cornell University, 1978.

[8] Kuz'ma, Yu. B.; Bilonishko, N. S. *Dopov. Akad. Nauk Ukr. RSR, Ser. A: Fiz.-Mat. Tekh. Nauki* **1978**, *3*, 275.

[9] Hiebl, K.; Rogl, P.; Sienko, M. J. *J. Less-Common Met.* **1981**, *82*, 21.

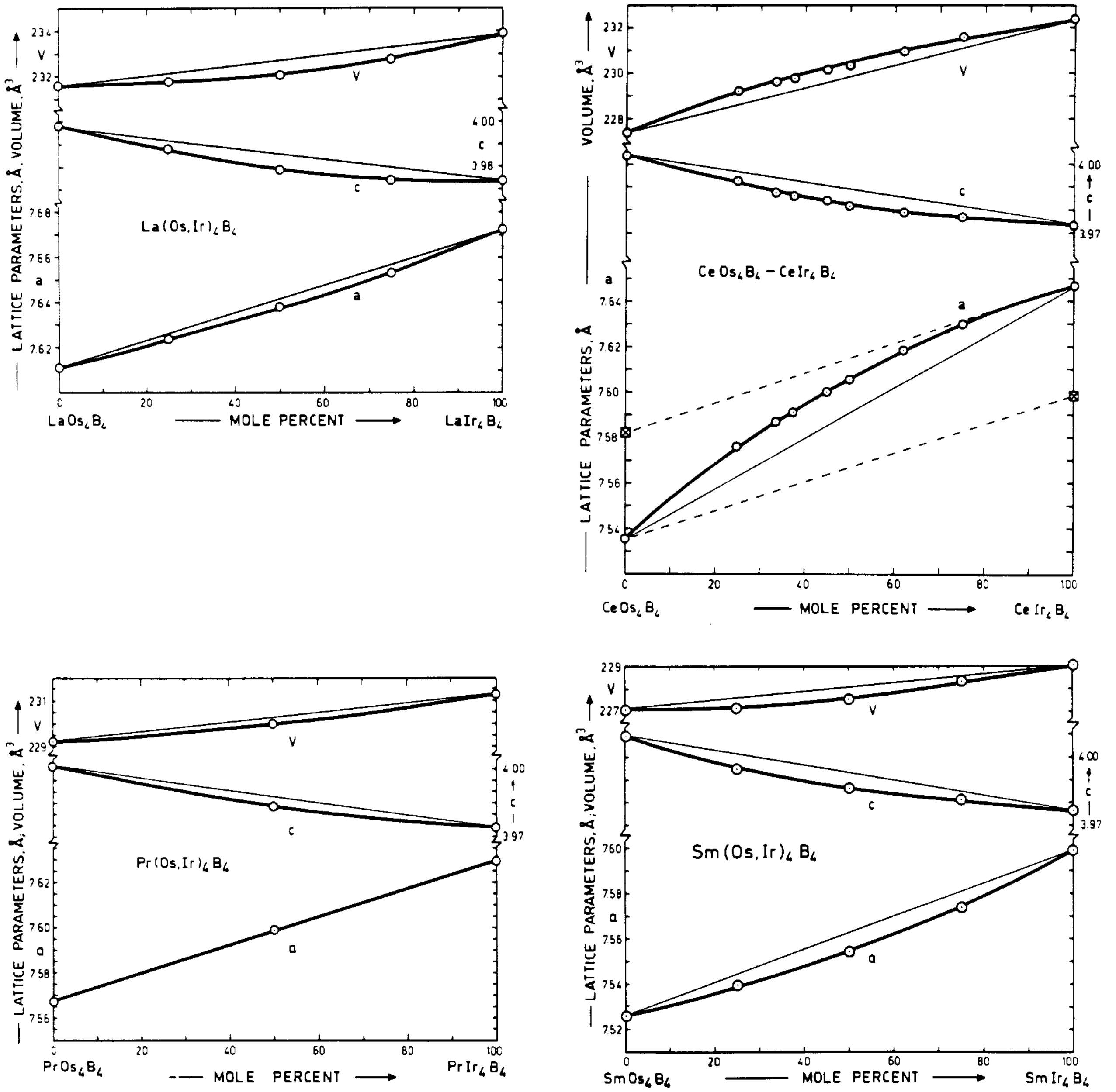

Figure 1. Lattice parameters and unit cell volumes in the pseudobinary systems (RE)$Os_{4-x}Ir_xB_4$ (RE = La, Ce, Pr, Sm). The crossed squares denote values extrapolated for hypothetical $Ce^{3+}Os_4B_4$ and $Ce^{4+}Ir_4B_4$.

which was also found from lower temperature heat treatments (1200 °C). Guinier powder patterns were completely indexed on the basis of a primitive tetragonal cell (Tables I and III), confirming the extinctions ($hk0$) for $h + k = 2n + 1$ and ($00l$) for $l = 2n + 1$. Thus, crystal symmetry ($P4_2/n$) as well as observed intensities reveal structural identity with the crystal structure of $NdCo_4B_4$.[8] Using noble metal atom parameters from linear interpolation of the values derived for $NdOs_4B_4$[9] as well as for $LaIr_4B_4$[2] and assuming statistical distribution of the noble metal atoms on their lattice sites, we find in all cases excellent agreement between observed and calculated[10] powder intensities.

Table III. Crystallographic Data of Ternary Borides $CeOs_{4-x}Ir_xB_4$

phase	a, Å	c, Å	c/a	V, Å^3
$CeOs_4B_4$	7.5346 (23)	4.0037 (12)	0.531	227.3
$CeOs_3IrB_4$	7.5764 (8)	3.9930 (3)	0.527	229.2
$CeOs_{2.67}Ir_{1.33}B_4$	7.5865 (20)	3.9874 (13)	0.525	229.6
$CeOs_{2.5}Ir_{1.5}B_4$	7.5905 (14)	3.9860 (9)	0.525	229.7
$CeOs_{2.2}Ir_{1.8}B_4$	7.6001 (19)	3.9842 (7)	0.524	230.1
$CeOs_2Ir_2B_4$	7.6055 (5)	3.9815 (3)	0.524	230.3
$CeOs_{1.52}Ir_{2.48}B_4$	7.6190 (9)	3.9786 (4)	0.522	231.0
$CeOsIr_3B_4$	7.6304 (10)	3.9780 (7)	0.521	231.6
$CeIr_4B_4$	7.6473 (10)	3.9733 (3)	0.520	232.4

Figure 1 represents the variation of unit cell volume and lattice parameters for the pseudobinary sections (RE)$Os_{4-x}Ir_xB_4$ (RE = La,[9] Ce, Pr, Sm) as a function of the osmium/iridium exchange. La, Pr, and Sm seem to reflect the general mixing behavior within the solid solutions with slightly negative deviations from Vegard's rule. The significant positive deviation for the cerium series indicates a tendency of the solid solution toward phase separation at lower temperatures. The general, practically linear dependence of lattice parameters and volumes of $NdCo_4B_4$-type borides on $(RE)^{3+}$ radii[3] offers a method of estimating the corresponding parameters for hypothetical $Ce^{3+}Os_4B_4$ as well as for $Ce^{4+}Ir_4B_4$. Thus the dashed lines in Figure 1 represent the expected variation of the a parameter with respect to "ideal" Os/Ir exchange with no change in the Ce^{4+}:Ce^{3+} ratio. On the other hand, no valence instability or valence change is indicated by the lat-

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(10) Boller, H. Program PULVER for calculation of powder X-ray intensities, University of Vienna, 1976.

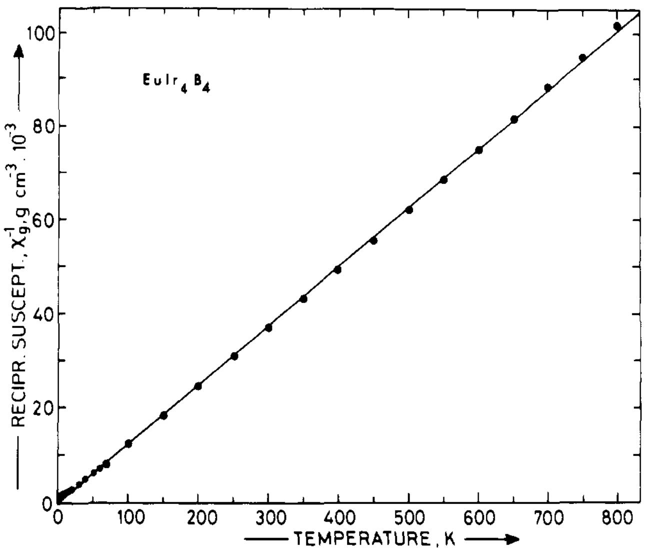

Figure 2. Reciprocal gram susceptibility vs. temperature for $EuIr_4B_4$.

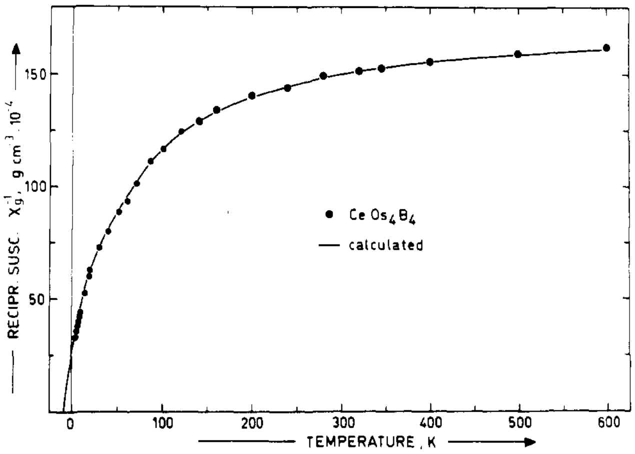

Figure 3. Reciprocal gram susceptibility vs. temperature for $CeOs_4B_4$. Solid line indicates calculated least-squares fit to eq 1.

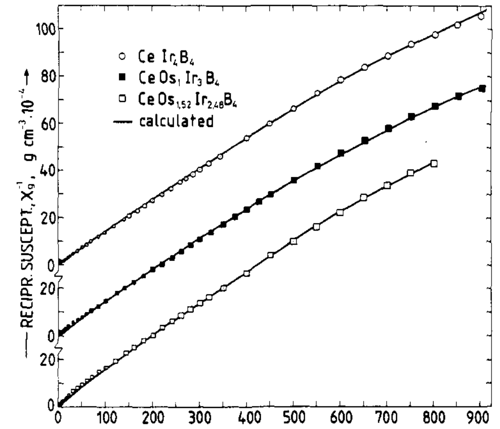

Figure 4. Reciprocal gram susceptibility vs. temperature for $CeIr_4B_4$, $CeOsIr_3B_4$, and $CeOs_{1.52}Ir_{2.48}B_4$. Solid lines indicate calculated least-squares fit to eq 1.

tice-parameter behavior of the Pr or of the Sm series of compounds. (See also the next section.)

Magnetic Properties. Results of the magnetic measurements are summarized in Figures 2–6, representing the reciprocal gram susceptibility χ_g^{-1} (cm^3 g^{-1}) as a function of temperature.

In the case of $EuIr_4B_4$ (Figure 2) a linear dependence of χ_g^{-1} vs. temperature was found within the temperature range $1.8 < T < 800$ K. The paramagnetic moment derived from the slope corresponds to a Curie–Weiss behavior with $\mu_{eff} = 7.84$ μ_B and $\Theta_p = 2.5$ K. The moment is in excellent agreement with the theoretical value of 7.94 μ_B for a free Eu^{2+} ion in a $^8S_{7/2}$ Hund's rule ground state.[11] At temperatures less than 10 K, increasing field dependence of the magnetic susceptibility indicates onset of (ferro)magnetic ordering at rather low temperatures ($T < 1.8$ K).

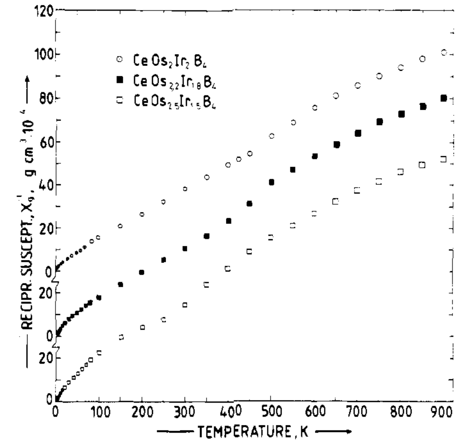

Figure 5. Reciprocal gram susceptibility vs. temperature for $CeOs_2Ir_2B_4$, $CeOs_{2.2}Ir_{1.8}B_4$, and $CeOs_{2.5}Ir_{1.5}B_4$.

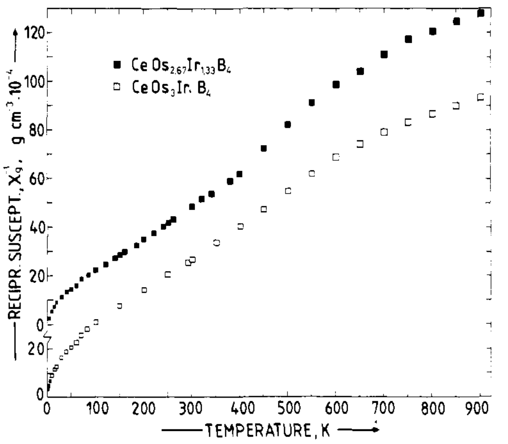

Figure 6. Reciprocal gram susceptibility vs. temperature for $CeOs_{2.67}Ir_{1.33}B_4$ and $CeOs_3IrB_4$.

The magnetic behavior of $EuOs_4B_4$ was found to be quite similar to that of $EuIr_4B_4$, yielding a Eu^{2+} ground state in agreement with observed much larger lattice parameters as well as volumes compared to extrapolated values for hypothetical $Eu^{3+}[Os,Ir]_4B_4$ compounds. However, the smaller magnetic moment of $EuOs_4B_4$ (Table I) in combination with unit cell parameters suggests a larger fraction of Eu^{3+}.

The ternary borides $CeOs_4B_4$ and $CeIr_4B_4$ show distinct magnetic properties, reflecting a different valence state of cerium, which was already indicated above from the lattice geometry. The strong variation of reciprocal susceptibility vs. temperature observed for $CeOs_4B_4$ (Figure 3) can be interpreted according to eq 1 as being mainly due to a small

$$\chi_M = \frac{N\mu_{eff}^2}{3k_B(T-\Theta)} + N\alpha - \frac{Ne^2}{6mc^2}\sum r_i^2 + \chi_{Pauli} \qquad (1)$$

paramagnetic moment in combination with a temperature-independent Van Vleck correction term $N\alpha$ (second-order Zeeman effect) due to multiplet splitting.[11] (The thermal energy for $T < 300$ K is considered to be small compared to

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

Table IV. Magnetic Data of the System $CeOs_4B_4$–$CeIr_4B_4$

phase	μ_{eff}, μ_B	Θ_p, K	$10^4\chi_0$, cm^3/mol^a
$CeOs_4B_4$	0.49	−8.9	5.4
$CeOs_{1.52}Ir_{2.48}B_4$	2.14	0	2.2
$CeOsIr_3B_4$	2.22	4.5	2.7
$CeIr_4B_4$	2.21	4.75	2.0

[a] χ_0 is the temperature-independent part of the molar magnetic susceptibility in the expression $\chi_M = C/(T - \Theta) + \chi_0$ and comprises the diamagnetic core correction, the Van Vleck term, and the Pauli susceptiblity.

the multiplet spacing $J = {}^5/_2, {}^7/_2$ of the Ce^{3+} ${}^2F_{5/2}$ ground state, for which the excitation energy is 2250 cm^{-1}.[12]) N is Avogadro's number and k_B is the Boltzmann constant. Diamagnetic core corrections for the third term in eq 1 were taken from Selwood's data.[13] Due to the metallic nature of these boride compounds, a paramagnetic contribution (χ_{Pauli}) arising from the conduction electrons was included. From a least-squares fit[14] of the data, a rather small paramagnetic moment $\mu_{eff} = 0.49\ \mu_B$ and a slightly negative asymptotic Curie temperature $\Theta_p = 8.9$ K were derived. This suggests a valency of 3.96 for the cerium, corresponding to 96% Ce^{4+}. The high ratio Ce^{4+}:Ce^{3+} = 24 is in good agreement with the cell parameters.

Similarly, a least-squares fit[14] of the susceptibility data for $CeIr_4B_4$ (Figure 4) according to eq 1 yielded a paramagnetic effective moment per formula unit $\mu_{eff} = 2.21\ \mu_B$ ($\Theta_p = 4.75$ K), compared to a theoretical moment of 2.54 μ_B for a ${}^2F_{5/2}$ ground-state free Ce^{3+} ion. The value 2.21 μ_B would correspond to 76% Ce^{3+} and 24% Ce^{4+}. Furthermore, from least-squares refinement of the lowest multiplet width according to eq 2, Van Vleck's general formula, an energy value

$$\chi = \frac{N \sum_J \{g_J^2\beta^2 J(J+1)(3kT) + \alpha_J\}(2J+1)\exp(-E_J/kT)}{\sum_J (2J+1)\exp(-E_J/kT)} \qquad (2)$$

of 2050 cm^{-1} was obtained for E_J, in good accord with the free Ce^{3+} ion value (2250 cm^{-1}). At very low temperatures (<50 K), deviations from paramagnetic behavior are observed, revealing ferromagnetic ordering at 3.1 K with an extrapolated saturation moment $\mu_S = 1.2\ \mu_B$.

The magnetic properties in the pseudobinary system $CeOs_4B_4$–$CeIr_4B_4$ show complicated behavior depending on the relative concentration of the noble metals Os and Ir. For low osmium contents (up to ~30%), the paramagnetic susceptibility closely obeys the Curie–Weiss law (Figure 4). The least-squares fit according to eq 1 gives the parameters shown in Table IV. Calculated paramagnetic moments per formula unit show decreasing values with increasing osmium concentration, indicating a change in the valence behavior of cerium. As can be seen from the plots of reciprocal susceptibility vs. temperature (Figures 5 and 6), for the solid solutions $CeOs_{4-x}Ir_xB_4$ ($1 < x < 2$) the deviation from linear dependence becomes more marked. From the high-temperature data, a decreasing magnetic moment as the Os:Ir ratio increases is obtained. However, least-squares refinement of the high-temperature susceptibility data according to eq 2 gave no significant change in the multiplet width with respect to Os/Ir exchange. Hence the magnetic behavior in the solid solutions $CeOs_4B_4$–$CeIr_4B_4$ seems to be characterized by a continuous change of the valence state of cerium from practically all Ce^{4+} in $CeOs_4B_4$ to Ce^{3+} in $CeIr_4B_4$. Furthermore, as is evident from Table IV, the temperature-independent part of the susceptibility χ_0 shows a significant decrease as the percentage of Ce^{4+} decreases. This is in contrast to the case of La[Os,Ir]$_4$B$_4$ where recent measurements[9] indicated a rather constant χ_0 over the whole range of Os/Ir exchange. The change in χ_0 in Ce[Os,Ir]$_4$B$_4$ is very likely dependent on enhancement of the paramagentic contribution of the conduction electrons (χ_{Pauli}) due to the valence change of the cerium ($Ce^{3+} \rightarrow Ce^{4+}$).

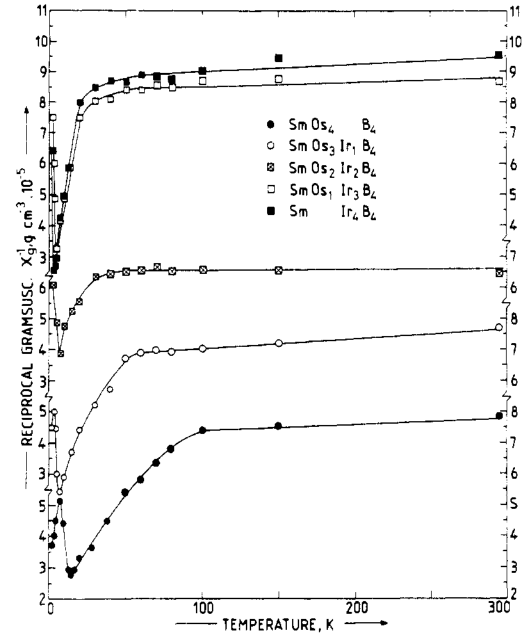

Figure 7. Reciprocal gram susceptibility vs. temperature for various compositions of $SmOs_{4-x}Ir_xB_4$.

The magnetic behavior of $CeOsIr_3B_4$ is characterized by the onset of ferromagnetic ordering at a temperature of 1.95 K, similar to $CeIr_4B_4$.

So far as the $PrOs_{4-x}Ir_xB_4$ solid solutions are concerned, the only composition analyzed, $x = 2$, revealed a magnetic moment close to the theoretical value for a free Pr^{3+} ion (Table I).

Magnetic behavior within the $SmOs_{4-x}Ir_xB_4$ system (Figure 7) is mainly characterized by a paramagnetism of closely spaced multiplets. Magnetic moments at room temperature (Table I) compare well with the theoretical value for the Sm^{3+} ion. However, at lower temperatures, Sm–Sm interactions seem to produce a similar deviation from ideal Van Vleck paramagnetism of noninteracting ions as is observed in samarium metal itself.[15]

Thermodynamic Estimation of Valence Changes. The energy differences (heat of formation) between trivalent cerium metal and hypothetical tetravalent cerium metal and between divalent and trivalent europium metal have been established to be about 209–240 kJ (mol Ce)$^{-1}$ and ~97 kJ (mol Eu)$^{-1}$, respectively.[16-18] Miedema[19,20] has derived an empirical equation for calculation of the heat of formation of intermetallic alloys and has furthermore shown its useful application with respect to the valence states of Ce, Eu, and Yb in their binary alloys.[21,22]

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Extending Miedema's model to our ternary alloy systems RE[Os,Ir]$_4$B$_4$, we compare the following posssibilities:

$$\mathrm{Ce^{III}(metal) + 4IrB \rightarrow Ce^{III}Ir_4B_4\ (trivalent)}\quad \Delta H_f^{\mathrm{III}}$$

$$\mathrm{Ce^{IV}(metal) + 4IrB \rightarrow Ce^{IV}Ir_4B_4\ (tetravalent)}\quad \Delta H_f^{\mathrm{IV}}$$

and analogously for the europium-containing compound

$$\mathrm{Eu^{II}(metal) + 4IrB \rightarrow Eu^{II}Ir_4B_4\ (divalent)}\quad \Delta H_f^{\mathrm{II}}$$

$$\mathrm{Eu^{III}(metal) + 4IrB \rightarrow Eu^{III}Ir_4B_4\ (trivalent)}\quad \Delta H_f^{\mathrm{III}}$$

For the difference $\Delta(\Delta H_f)$ for each pair of reactions we calculate in the first case, $\mathrm{Ce^{III} \rightarrow Ce^{IV}}$, 206.7 kJ mol^{-1} and in the second case, $\mathrm{Eu^{II} \rightarrow Eu^{III}}$, 98.7 kJ mol^{-1}. Due to the very similar values for Os and Ir metal according to Miedema's model, it is impossible to differentiate between the heats of formation of, e.g., CeOs$_4$B$_4$ and CeIr$_4$B$_4$. However, the values $\Delta(\Delta H_f)$ obtained for a valence change in [Ce,Eu][Os,Ir]$_4$B$_4$ alloys are approximately enough to overcome the excitation $\mathrm{Ce^{III} \rightarrow Ce^{IV}}$ metal, in excellent accord with the experimental observations on the pseudobinary system CeOs$_{4-x}$Ir$_x$B$_4$.

Similarly, the thermodynamic values for Eu[Os,Ir]$_4$B$_4$ indicate this system again to be at the borderline for a $\mathrm{Eu^{II} \rightarrow Eu^{III}}$ valence change. This is reflected in the experimental observation of a slightly smaller magnetic moment of the EuOs$_4$B$_4$ compound (i.e., small fraction of Eu^{3+}).

Superconductivity. None of the compounds listed in Tables I and II showed any superconducting transition down to a temperature of 1.5 K.

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Registry No. EuOs$_4$B$_4$, 80447-57-0; EuIr$_4$B$_4$, 80447-59-1; CeOs$_4$B$_4$, 69865-87-8; CeIr$_4$B$_4$, 69865-86-7; SmOs$_4$B$_4$, 69866-01-9; SmIr$_4$B$_4$, 69865-95-8; PrOs$_4$B$_4$, 69866-00-8; PrIr$_4$B$_4$, 69865-94-7.

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Unusual Electronic Spectra of the Pseudotetrahedral Complex [Tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine]cobalt(II) Bis(tetraphenylborate)

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In the complex [tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine]cobalt(II) bis(tetraphenylborate), the metal ion is four-coordinate in a distorted tetrahedral geometry. The electronic spectra show d–d transitions at unusually high energies for tetrahedral complexes. Single-crystal polarized electronic spectra and polycrystalline powder EPR spectra were recorded in order to obtain a full understanding of the electronic structure of the complex. The experimental data were interpreted with the angular overlap model. The unusual electronic spectra have been attributed to a high ligand field strength of the pyrazole residues in the ligand.

Introduction

The characterization of the spectral properties of distorted tetrahedral cobalt(II) complexes is of large interest for the possible implications they may have in clarifying the structure of the active site of metalloproteins and metalloenzymes.[1-3]

Recently one of us reported the synthesis and the X-ray characterization of the structure of a four-coordinate cobalt(II) complex formed with the ligand tris((3,5-dimethyl-1-pyrazolyl)ethyl)amine (MeTPyEA), [Co(MeTPyEA)](BPh$_4$)$_2$.[4] The ligand is tetradentate, N–N$_3$, with three nitrogen atoms belonging to a pyrazole group; the fourth is an amine nitrogen. As such it is an interesting model for heterocyclic bases bonding to metal ions.

The cobalt(II) ion is four-coordinate by the MeTPyEA ligand. The coordination environment is a distorted tetrahedron, with an average N$_{\mathrm{ax}}$–Co–N$_{\mathrm{eq}}$ angle of 100°. The observed tetrahedral geometry is hardly reconciled with the electronic spectra since these show high-frequency bands that are not usually seen in tetrahedral cobalt(II) complexes and resemble more closely those of trigonal-bipyramidal cobalt(II) complexes.[5,6]

In order to obtain more information on the electronic structure of [Co(MeTPyEA)](BPh$_4$)$_2$, we decided to record the single-crystal polarized electronic spectra and the EPR spectra of the complex and wish to report here the results. Spectral data of the complex [Co(NCS)(MeTPyEA)]BPh$_4$ will be also reported for comparison purposes.

Experimental Section

The ligand was prepared starting from N(CH$_2$CH$_2$Cl)$_3$ and potassium 3,5-dimethylpyrazolate with a procedure already described.[7] The [Co(NCS)(MeTPyEA)]BPh$_4$ complex was prepared as follows: warm solutions (20 mL) of the ligand (10^{-3} mol) in absolute ethanol and NaBPh$_4$ (10^{-3} mol) in acetone were added in succession to a warm solution (30 mL) of a stoichiometric amount of cobalt(II) dithiocyanate in absolute ethanol. The resulting solution was concentrated and cooled to room temperature to induce crystallization. Anal. Calcd for C$_{46}$H$_{53}$N$_8$CoBS: C, 67.4; H, 6.51; N, 13.7; Co, 7.18. Found: C, 67.2; H, 6.94; N, 13.9; Co, 7.05.

The [Co(MeTPyEA)](BPh$_4$)$_2$ complex was prepared as above starting from a solution of any cobalt(II) halide. Anal. Calcd for

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