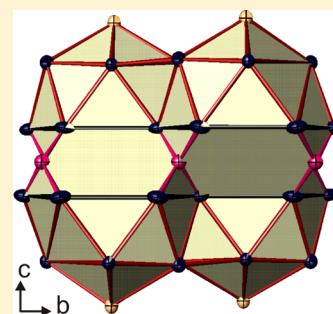


Structural and Physical Properties Diversity of New CaCu_5 -Type Related Europium Platinum BoridesLeonid Salamakha,^{†,‡} Ernst Bauer,^{*,†} Gerfried Hilscher,[†] Herwig Michor,[†] Oksana Sologub,[§] Peter Rogl,^{*,§} and Gerald Giester^{||}[†]Institute of Solid State Physics, Vienna University of Technology, A-1040 Wien, Austria[§]Institute of Physical Chemistry and ^{||}Institute of Mineralogy and Crystallography, University of Vienna, A-1090 Wien, Austria[‡]Department of Physics of Metals, Lviv National University, 79005 Lviv, Ukraine

S Supporting Information

ABSTRACT: Three novel europium platinum borides have been synthesized by arc melting of constituent elements and subsequent annealing. They were characterized by X-ray powder and single-crystal diffraction: EuPt_4B , CeCo_4B type, $P6/mmm$, $a = 0.56167(2)$ nm, $c = 0.74399(3)$ nm; $\text{Eu}_3\text{Pt}_7\text{B}_2$, $\text{Ca}_3\text{Al}_7\text{Cu}_2$ type as an ordered variant of PuNi_3 , $R\bar{3}m$, $a = 0.55477(2)$ nm, $c = 2.2896(1)$ nm; and $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$, a new unique structure type, $Fmmm$, $a = 0.55813(3)$ nm, $b = 0.95476(5)$ nm, $c = 3.51578(2)$ nm. These compounds belong to the CaCu_5 family of structures, revealing a stacking sequence of CaCu_5 -type slabs with different structural units: CaCu_5 and CeCo_3B_2 type in EuPt_4B ; CeCo_3B_2 and Laves MgCu_2 type in $\text{Eu}_3\text{Pt}_7\text{B}_2$; and CaCu_5 , CeCo_3B_2 , and site-exchange ThCr_2Si_2 -type slabs in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$. The striking motif in the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ structure is the boron-centered Pt tetrahedron $[\text{BPt}_4]$, which build chains running along the a axis and plays a decisive role in the structure arrangement by linking the terminal fragments of repeating blocks of fused Eu polyhedra. Physical properties of two compounds, EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$, were studied. Both compounds were found to order magnetically at 36 and 57 K, respectively. For EuPt_4B a mixed-valence state of the Eu atom was confirmed via magnetic and specific heat measurements. Moreover, the Sommerfeld value of the specific heat of $\text{Eu}_3\text{Pt}_7\text{B}_2$ was found to be extraordinarily large, on the order of 0.2 J/mol K^2 .



INTRODUCTION

Phases with CaCu_5 -type related structures are frequently found in binary RE–T and ternary RE–T–X (RE = rare-earth metal, T = transition metal, X = B, Si, Al, Ga, Ge, Sn) systems.^{1,2} These compounds are extremely diverse in their structural and physical properties. Among them are the following: (i) phases that form by stacking of binary CaCu_5 -type fragments and slabs of Laves phases with MgZn_2 and MgCu_2 type (and/or their ternary ordered derivatives)³ and play an important role for improvement of technological characteristics of RE–Ni-based negative electrode material in Ni–metal hydride batteries;⁴ (ii) compounds that can yield magnets appropriate for high-temperature application, namely, RECo_7 of TbCu_7 type, where part of the atoms in the Ca site of the CaCu_5 structure are substituted by the dumbbells of the transition metal and the third element like Ti, Zr, Hf, Cu, Ga, Si, and Ag is required to stabilize the structure and increase the magnetoanisotropy;^{5,6} (iii) magnetic materials $\text{RE}_2\text{Co}_{17}$ revealing the intergrown CaCu_5 - and Zr_4Al_3 -type slabs structures where the interstitial sites can be occupied by elements of IIIA, IVA, or VIA groups, thus leading to the increase in Curie temperature, uniaxial anisotropy, and spontaneous magnetization.⁷ The small atomic radius of boron imposes replacement of the Cu atom at the Wyckoff position 2c in the CaCu_5 structure (space group $P6/mmm$; Ca in 1a (0,0,0), Cu1 in 2c (1/3,2/3,0), Cu2 in 3g (1/2,0,1/2)) and formation of the ordered ternary substitution

derivative CeCo_3B_2 (Ce in 1a, Co in 3g, and B in 2c).⁸ As relevant to the study presented herein, the CeCo_3B_2 structural unit intergrown with fragments of different structures reveals a variety of borides exhibiting different degrees of structural complexity. For example, the family of structures where the slabs of CeCo_3B_2 are stacked with slabs of the binary CaCu_5 type or Laves phases are frequently encountered among ternary rare-earth borides with Co and Ni.^{1,2,9–12} Formation of these structures in unexplored yet multinary systems may result in unpredicted changes of expected properties, and their investigation is necessary to understand and control the behavior of alloys.

The diversity of CaCu_5 -derivative structures is enhanced if the ternary rare-earth boride phases with noble metals are considered. For example, (i) the series of compounds formed by stacking blocks of CeCo_3B_2 and CaRh_2B_2 (ThCr_2Si_2) type were observed in Eu–Rh–B,¹³ Y–Os–B, and La–Ru–B systems;¹⁴ (ii) $\text{PrRh}_{4.8}\text{B}_2$ revealed CeCo_3B_2 -type slabs and hexagon-mesh rhodium nets.¹⁵ In this respect, systems containing Pt and RE metals were not investigated; the only information available on CaCu_5 -type derivatives concerns the crystal structure and physical properties studies for the REPt_4B series (CeCo_4B type, $P6/mmm$, RE = La, Ce, Pr, Sm).^{16,17} In this article we present the results of our exploratory study of the Eu–Pt–B system

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focused on the Pt-rich concentration range where we observed a series of new CaCu_5 -related structures. Our interest in this investigation was driven not only by the structural flexibility and diversity of CaCu_5 -type derivative phases but also by the interesting physical properties which europium compounds may exhibit, such as, for example, mixed-valence states or magnetic ordering at comparatively high ordering temperatures, observed in Eu-based binary Laves phases.¹⁸ Results presented herein expand knowledge on a family of CaCu_5 derivative structures to (i) the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ phase showing a new structural arrangement formed by stacking of inverse ThCr_2Si_2 -type slabs with CaCu_5 - and CeCo_3B_2 -type fragments along the c -axis direction, (ii) a new member of rather simple structural series exhibiting the combination of CaCu_5 - and CeCo_3B_2 -type slabs, namely, EuPt_4B where a mixed-valence state of Eu has been observed, and (iii) a new compound $\text{Eu}_3\text{Pt}_7\text{B}_2$, composed of CeCo_3B_2 - and Laves phase- (MgCu_2 -) type fragments showing interesting transport properties accompanied by a relatively large Sommerfeld coefficient. Structural relationships between the structures are discussed.

EXPERIMENTAL SECTION

Synthesis. All samples, each of a total amount of ca. 0.5–2 g, were prepared by argon arc-melting elemental pieces of europium (99.99%, Metal Rare Earth Ltd., China), platinum foil (99.9%, Ögussa, A), and crystalline boron (98%, Alfa Aesar, D). Due to the low boiling point and high vaporization of europium, Eu weight losses were compensated by adding carefully assigned extra amounts of Eu before melting. For homogeneity, samples were remelted several times. Part of each alloy was wrapped in Mo foil, sealed in an evacuated silica tube, and heat treated for 10 days at 1020 K prior to quench by submerging the capsules in cold water.

X-ray Diffraction Studies. Single crystals suitable for X-ray diffraction studies were isolated from a fragmented annealed alloy of $\text{Eu}_3\text{Pt}_7\text{B}_2$; however, for EuPt_4B and $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ crystals of good quality were obtained from as cast samples. Crystal quality, unit cell dimensions, and Laue symmetry of the specimens were inspected on an AXS-GADDS texture goniometer prior to X-ray intensity data collections at room temperature on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071069$ nm). Orientation matrices and unit cell parameters were derived using the program DENZO.¹⁹ No absorption corrections were performed because of the rather regular crystal shapes and small dimensions of the investigated specimens. Space groups were determined from analysis of systematic absences performed with the help of the ABSEN program.²⁰ Structures were solved and refined with the aid of the WinGX-1.70.00 software package²¹ applying SHELXS-97²² and SHELXL-97²³ programs. Reduced cell calculations and noncrystallographic symmetry tests were performed applying the program PLATON2003²⁴ in order to check for higher lattice symmetry. Data collection and refinement parameters for the three structures are listed in Tables 1 and 2.

X-ray powder diffraction patterns collected from the EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$ alloys annealed at 1020 K for 10 days employing a Guinier–Huber image plate system with monochromatic Cu $K\alpha_1$ radiation ($8^\circ < 2\theta < 100^\circ$) revealed single-phase materials; however, for $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ several samples synthesized with identical conditions but varying boron concentration were multiphase and contained mixtures with EuPt_4B and/or unknown neighboring phases, suggesting a different temperature range of existence (Figure 1, Supporting Information). Structural parameters obtained from Rietveld powder data refinement²⁶ of all three compounds validate those from the single crystal.

Physical Properties Studies. Physical properties have been studied for two compounds, EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$. The third phase, $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$, is an interesting material with respect to magnetism according to structural and bonding features described below, and currently, special efforts are aimed at optimization of synthesis conditions for this

new compound. A superconducting quantum interference device (SQUID) served for determination of the magnetization from 2 to 300 K and in fields up to 7 T where bar-shaped polycrystalline specimens of about 20 mg were used. Specific heat measurements on samples of about 1 g were performed at temperatures ranging from 1.5 to 120 K by means of a quasi-adiabatic step heating technique. Electrical resistivity and magnetoresistivity of bar-shaped samples (about $1 \times 1 \times 5$ mm³) were measured using a four-probe ac-bridge method in the temperature range from 0.4 K to room temperature and fields up to 12 T.²⁷

DETERMINATION AND ANALYSIS OF CRYSTAL STRUCTURES

$\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ ($x = 1$). Systematic extinctions in the single-crystal X-ray data were consistent with three possible space group types: $Fmmm$, $Fmm2$, and $F222$. The structure was solved in the centrosymmetric space group, and direct methods provided 9 atom positions, 3 of which in further refinement were assigned to europium. Refinement of the structure with all sites fully occupied resulted in rather large anisotropic displacement parameters for two Pt sites (Pt1 in 16*m* and Pt5 in 8*i*) with high residual electron densities (29 000 and 20 000 e/nm³) near these atoms. Accordingly, the platinum atom sites were split in two near-neighboring positions (Pt1–Pt11 0.037 nm, Pt5–Pt55 0.029 nm) with occupancy parameters refined to 0.8/0.2 for Pt1/Pt11 and Pt5/Pt55. In the next step, all atoms were refined with anisotropic displacement parameters except for the atoms on split sites. Subsequent difference Fourier synthesis revealed two significant residual peaks (about 11 400 and 7000 e/Å³) at a distance of about 0.2 nm from the nearest platinum atoms, which were attributed to boron atoms (16*m* and 8*f*). Refinement with both boron positions fully occupied led to a low reliability factor ($R_F = 0.0353$); however, it showed a large isotropic thermal parameter for B2 in 8*f*. Refinement of the B2 occupancy parameter did not improve the value of U_{iso} but reduced the occupancy factor to about 0.5. At this point collected data were also processed in space group $F222$, which provides the possibility to split the B 8*f* site into two crystallographically distinct sites 4*c* (1/4,1/4,1/4) and 4*d* (1/4,1/4,3/4). Despite almost identical agreement factors, refinement did not improve the isotropic displacement parameters of boron atoms which were found to partially occupy both 4-fold sites (occupancy ratio 33%:67%), suggesting a disordered distribution of boron atoms. The small difference between these solutions concerned also the positions of B1 and the Pt1–Pt11 split sites which all were slightly shifted along the a axis due to the free x parameter of the 16*k* (x,y,z) site (Pt1 $x = 0.5010(13)$, $y = 0.1745(2)$, $z = 0.28417(5)$ /Pt11 $x = 0.008(5)$, $y = 0.1455(9)$, $z = 0.2098(2)$; B1 $x = 0.011(12)$, $y = 0.167(2)$, $z = 0.1071(6)$). Except these slender deviations, refinement in $F222$ revealed Eu and Pt atoms in the Wyckoff positions corresponding to those in space group $Fmmm$. Accordingly, the test for higher symmetry applying PLATON²⁴ indicated space group $Fmmm$. Reconsidering the refinement in $Fmmm$, it was found out that the isotropic thermal parameter of B2 can be improved by fixing the occupancy to a predetermined value: in agreement with the results obtained for space group $F222$, the most satisfactory value for the thermal displacement parameter was observed for an occupation factor fixed at 0.5 for B2 in 8*f*. Final refinement in $Fmmm$ resulted in a reliability factor as low as 0.0331 and residual electron densities smaller than 3710 e[−]/nm³. Refinement results are given in Table 1.

The structure of $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ shown in Figure 1a, can be considered as built up of two kinds of blocks alternating along

Table 1. X-ray Single-Crystal Structure Data^a for Eu₅Pt₁₈B_{6-x}

nominal composition	Eu ₁₈ Pt ₆₄ B ₁₈
space group	<i>Fmmm</i> ; No. 69
structure type	Eu ₅ Pt ₁₈ B _{6-x}
formula from refinement	Eu ₅ Pt ₁₈ B _{6-x} (<i>x</i> = 1)
range for data collection	3.48° < θ < 29.95°
cryst size	35 × 35 × 15 μm^3
<i>a</i> [nm]	0.55813(3)
<i>b</i> [nm]	0.95476(5)
<i>c</i> [nm]	3.51578(2)
<i>Z</i>	4
reflins in refinement	619 <i>F</i> _o > 4 σ (<i>F</i> _o) of 796
mosaicity	<0.4
no. of variables	52
$R_F^2 = \Sigma F_o ^2 - F_c^2 / \Sigma F_o^2$	0.0331
GOF	1.073
extinction (Zachariasen)	0.000004(3)
M1 ; occ.; <i>U</i> ₁₁ , ^{<i>b,c</i>} <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, <i>U</i> ₁₂	Eu1 in 8i (0,0, <i>z</i>) <i>z</i> = 0.29362(5); 1.00; 0.0216(9), 0.0137(8), 0.0135(7), 0.0000(0)
M2 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = <i>U</i> ₁₂ = 0	Eu2 in 8i (0,0, <i>z</i>) <i>z</i> = 0.39475(4); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0096(7), 0.0141(7)
M3 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = <i>U</i> ₁₂ = 0	Eu3 in 4b (0,0,1/2); 1.00; 0.036(2), 0.027(1), 0.017(1)
M4 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂ ^{<i>d</i>}	Pt1 in 16m (0, <i>y</i> , <i>z</i>) <i>y</i> = 0.1742(2); <i>z</i> = 0.21582(5); 0.797(4)
	Pt11 in 16m (0, <i>y</i> , <i>z</i>) <i>y</i> = 0.1437(10); <i>z</i> = 0.2094(3); 0.203(4); 0.0305(6), 0.0216(10), 0.0087(8), -0.0023(6), <i>U</i> ₁₃ = <i>U</i> ₁₂ = 0
M5 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, <i>U</i> ₁₂	Pt2 in 16j (1/4, 1/4, <i>z</i>) <i>z</i> = 0.06367(2); 1.00; 0.0082(4), 0.0097(4), 0.0120(4), -0.0009(3)
M7 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, <i>U</i> ₁₂	Pt3 in 16j (1/4, 1/4, <i>z</i>) <i>z</i> = 0.14811(2); 1.00; 0.0079(4), 0.0102(4), 0.0119(4), -0.0006(3)
M9 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, <i>U</i> ₁₂	Pt4 in 8i (0, 0, <i>z</i>) <i>z</i> = 0.06519(3); 1.000; 0.0092(5), 0.0078(5), 0.0135(5), <i>U</i> ₁₂ = 0
M10 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, <i>U</i> ₁₂ ^{<i>d</i>}	Pt5 in 8i (0, 0, <i>z</i>) <i>z</i> = 0.15178(5); 0.802(4)
	Pt55 in 8i (0, 0, <i>z</i>) <i>z</i> = 0.1433(4); 0.198(4); 0.0101(6), 0.0081(5), 0.0099(12), <i>U</i> ₁₂ = 0
M11 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ = <i>U</i> ₁₂ = 0, <i>U</i> ₁₃	Pt6 in 8h (0, <i>y</i> , 0) <i>y</i> = 0.1622(2); 1.00; 0.0322(8), 0.0228(7), 0.0089(5), <i>U</i> ₁₃ = 0
M12 ; occ.; <i>U</i> _{iso} ^{<i>b,c</i>}	B1 in 16m (0, <i>y</i> , <i>z</i>) <i>y</i> = 0.169(3); <i>z</i> = 0.1070(7); 1.00; 0.012(4)
M13 ; occ.; <i>U</i> _{iso}	B2 in 8f (1/4, 1/4, 1/4); 0.5; 0.011(12)
residual density; max; min [electrons/nm ³] × 1000	3.71; -3.79

interatomic distances (nm)

Eu1–2Pt1 0.3128(2)	Eu2–4Pt2 0.3128(1)	Eu3–4Pt6 0.3191(1)	Pt1–2B2 0.1978(1)	Pt11–2B2 0.2239(8)
Eu1–2Pt11 0.3404(1)	Eu2–2Pt4 0.3126(1)	Eu3–2Pt6 0.3225(1)	Pt1–Pt5 0.2797(3)	Pt11–Pt5 0.2443(1)
Eu1–4B2 0.316 (1)	Eu2–4Pt3 0.3149(1)	Eu3–8Pt2 0.3557 (1)	Pt1–Pt55 0.3044(9)	Pt11–Pt55 0.269(1)
Eu1–2Pt1 0.3201(3)	Eu2–3B1 0.316(3)	Eu3–4Pt4 0.3611(1)	Pt1–Pt1 0.2806(3)	Pt11–Pt11 0.274(1)
Eu1–2Pt11 0.326 (1)	Eu2–3B1 0.322(1)	Eu3–2Eu2 0.3700(1)	Pt1–Pt11 0.315(1)	Pt11–2Pt3 0.2761(9)
Eu1–4Pt1 0.3266(1)	Eu2–2Pt5 0.3234(1)	Pt4–2B1 0.218(3)	Pt1–2Pt3 0.2853(2)	Pt11–Pt1 0.315(1)
Eu1–4Pt11 0.3112(4)	Eu2–2Pt55 0.3095(5)	Pt4–4Pt2 0.2765(1)	Pt1–Eu1 0.3128(2)	Pt11–Eu1 0.326(1)
Eu1–2Pt5 0.3387(1)	Eu2–Eu1 0.3556(2)	Pt4–2Pt6 0.2766(1)	Pt1–Eu1 0.3201(3)	Pt11–Eu1 0.3404(1)
Eu1–2Pt55 0.3565(7)	Eu2–Eu3 0.3700(1)	Pt4–Pt5 0.3044(2)	Pt1–2Eu1 0.3266(1)	Pt11–2Eu1 0.3112(4)
Eu1–4Pt3 0.3441(1)	Pt3–2B1 0.216(2)	Pt4–Pt55 0.2746(11)	Pt5–2B1 0.225(3)	Pt6–2Pt4 0.2766(1)
Eu1–Eu2 0.3556(2)	Pt3–2Pt5 0.27678(2)	Pt4–2Eu2 0.3126(1)	Pt5–4Pt3 0.27678(2)	Pt6–4Pt2 0.2768(1)
Pt2–2B1 0.221(2)	Pt3–2Pt55 0.2770(1)	Pt4–2Eu3 0.3611(1)	Pt5–2Pt1 0.2797(3)	Pt6–Pt6 0.3097(2)
Pt2–2Pt4 0.2765(1)	Pt3–2Pt3 0.2790(1)		Pt5–2Pt11 0.2443(1)	Pt6–2Eu3 0.3191(1)
Pt2–2Pt6 0.2768(1)	Pt3–2Pt1 0.2853(2)		Pt5–Pt4 0.3044(2)	Pt6–Eu3 0.3225(1)
Pt2–2Pt2 0.2791(1)	Pt3–2Pt11 0.2761(9)		Pt5–2Eu2 0.3234(1)	
Pt2–Pt3 0.2968(1)	Pt3–Pt2 0.2968(1)		Pt5–2Eu1 0.3387(1)	
Pt2–2Eu2 0.3128(1)	Pt3–2Eu2 0.3149(1)			
Pt2–2Eu3 0.3557(1)	Pt3–2Eu1 0.3441(1)			
Pt55–2B1 0.206(3)	B1–2Pt3 0.216(2)	B2–4Pt1 0.1978(1)		
Pt55–4Pt3 0.2770(1)	B1–Pt4 0.218(3)	B2–4Pt11 0.2239(8)		
Pt55–2Pt1 0.3044(9)	B1–2Pt2 0.221(2)	B2–4Eu1 0.3162(1)		
Pt55–2Pt11 0.269(1)	B1–Pt5 0.225(3)			
Pt55–Pt4 0.2746(11)	B1–Pt55 0.206(3)			
Pt55–2Eu2 0.3095(5)	B1–Eu2 0.316(3)			
Pt55–2Eu1 0.3565(7)	B1–2Eu2 0.322(1)			

^aCrystal structure data are standardized using the program Structure Tidy.²⁵ ^{*b,c*}Isotropic (*U*_{iso}) and anisotropic atomic displacement parameters (*U*_{ij}) are given in [10² nm²]. ^{*d*}Anisotropic thermal parameters were constrained for the atoms in split positions.

the *c* direction. One block is composed of two layers of edge-connected triangular prisms which share their faces to form

hexagonal channels linked via the 3⁶ net of platinum and europium atoms (Figure 1b), while the other one consists of

Table 2. X-ray Single-Crystal Structure Data^a for EuPt₄B and Eu₃Pt₇B₂

parameter/com-pound	EuPt ₄ B	Eu ₃ Pt ₇ B ₂	
nominal composition	Eu _{16.7} Pt _{66.7} B _{16.7}	Eu ₂₅ Pt _{58.3} B _{16.6}	
space group	<i>P6/mmm</i> ; No. 191	<i>R</i> $\bar{3}m$; No. 166	
structure type	CeCo ₄ B	Ca ₃ Al ₇ Cu ₂	
formula from refinement	EuPt ₄ B	Eu ₃ Pt ₇ B ₂	
range for data collection	2.09° < θ < 36.00°	2.16° < θ < 29.98°	
cryst size	40 × 40 × 25 μm^3	35 × 35 × 15 μm^3	
<i>a</i> [nm]	0.56167(2)	0.55477(2)	
<i>c</i> [nm]	0.74399(3)	2.28963(11)	
<i>Z</i>	2	3	
reflins in refinement	182 <i>F</i> _o > 4σ(<i>F</i> _o) of 1069	231 <i>F</i> _o > 4σ(<i>F</i> _o) of 777	
mosaicity	<0.4	<0.4	
no. of variables	14	17	
<i>R</i> _F ² = Σ <i>F</i> _o ² − <i>F</i> _c ² /Σ <i>F</i> _o ²	0.0259	0.027	
GOF	1.105	1.131	
extinction (Zachariasen)	0.0010(3)	0.00050(6)	
M1 ; occ.; <i>U</i> ₁₁ , ^{<i>b,c</i>} <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂	Eu1 in 1a (0,0,0); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.042(1), 0.035(2), <i>U</i> ₂₃ = <i>U</i> ₁₂ = 0, 0.0209(6)	Eu1 in 6c (0,0, <i>z</i>), <i>z</i> = 0.14405(5); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0100(4), 0.0092(7), <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, 0.0050(2)	
M2 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂	Eu2 in 1b (0, 0, 1/2); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0089(6), 0.0349(15), <i>U</i> ₂₃ = <i>U</i> ₁₂ = 0, 0.0044(3)	Eu2 in 3a (0,0,0); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0053(4), 0.0074(7), <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, 0.0026(2)	
M3 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂	Pt1 in 2d (1/3, 2/3, 1/2); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0494(7), 0.0036(5), <i>U</i> ₂₃ = <i>U</i> ₁₂ = 0, 0.0248(3)	Pt1 in 18h (<i>x</i> ₁ − <i>x</i> ₂ , <i>z</i>), <i>x</i> = 0.49858(3), <i>z</i> = 0.06542(2); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0044(3), 0.0055(1), −0.00005(7), 0.00005(19), 0.0029(3)	
M4 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂	Pt2 in 6i (1/2, 0, <i>z</i>) <i>z</i> = 0.19488(8); 1.00; 0.0102(3), 0.0070(3), 0.0068(4), <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, 0.0035(2)	Pt2 in 3b (0,0,1/2), 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.0078(4), 0.0031(4), <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, 0.0039(2)	
M5 ; occ.; <i>U</i> ₁₁ , <i>U</i> ₂₂ , <i>U</i> ₃₃ , <i>U</i> ₂₃ , <i>U</i> ₁₃ , <i>U</i> ₁₂ , <i>U</i> _{iso} ^{<i>b,c</i>}	B in 2c (1/3, 2/3, 0); 1.00; <i>U</i> ₁₁ = <i>U</i> ₂₂ = 0.014(8), 0.002(11), <i>U</i> ₂₃ = <i>U</i> ₁₃ = 0, 0.007(4)	B in 6c (0,0, <i>z</i>), <i>z</i> = 0.330(1); 1.00; <i>U</i> _{iso} = 0.011(4)	
residual density; max; min [electrons/nm ³] × 1000	4.94; −2.88	4.23; −4.66	
interatomic distances (nm)			
EuPt ₄ B		Eu ₃ Pt ₇ B ₂	
Eu1−12Pt2 0.31605(3)	Pt2−2B 0.21751(4)	Eu1−3Pt2 0.32445(2)	Pt1−B 0.216(2)
Eu1−2Eu2 0.37200(2)	Pt2−2Pt1 0.27896(4)	Eu1−3Pt1 0.32636(11)	Pt1−B 0.222(2)
Eu2−6Pt1 0.32428(1)	Pt2−5Pt2 0.2899(1)	Eu1−Eu2 0.32982(12)	Pt1−2Pt1 0.27502(3)
Eu2−12Pt2 0.36113(4)	Pt2−2Eu1 0.31605(3)	Eu1−6Pt1 0.33069(7)	Pt1−2Pt1 0.27975(3)
Eu2−2Eu1 0.37200(2)	Pt2−2Eu2 0.36113(4)	Eu1−3Eu1 0.33662(5)	Pt1−Pt2 0.28098(4)
Pt1−6Pt2 0.27896(4)	B−6Pt2 0.21751(4)	Eu2−12Pt1 0.31525(3)	Pt1−Pt1 0.29959(7)
Pt1−3Eu2 0.32428(1)		Eu2−2Eu1 0.32982(12)	Pt1−2Eu2 0.31525(3)
		Pt2−6Pt1 0.28098(4)	Pt1−Eu1 0.32636(11)
		Pt2−6Eu1 0.32445(2)	Pt1−2Eu1 0.33069(7)
			B−3Pt1 0.216(2)
			B−3Pt1 0.222(2)

^aCrystal structure data are standardized using the program Structure Tidy.²⁵ ^{b,c}Isotropic (U_{iso}) and anisotropic atomic displacement parameters (U_{ij}) are given in [10^2 nm^2].

chains of edge-connected platinum tetrahedra interlinked via europium atoms (Figure 1c). Trigonal prisms are formed by platinum atoms are centered by boron. The 3636 kagomé nets of platinum atoms are slightly puckered, while 3⁶ nets are flat. One europium atom, namely, Eu3, is located in the center of a hexagon formed by Pt6 (at *z* = 0), while Eu2 is slightly shifted along *z* from the B1 atoms plane (Eu2 in 8i, *z* = 0.39475; B1 in 16m, *z* = 0.1070). Depending on which split position Pt1/Pt11 is locally occupied, the chains of tetrahedra are bridged via

(i) europium (for Pt1) or (ii) europium and platinum atoms (for Pt11, Pt11–Pt11 0.2740 nm) to form sheets extending perpendicular to *c*. Platinum tetrahedra are centered by borons; however considering that the B2 site within this block is fractionally (and randomly) occupied (occ. = 0.5), one-half of the tetrahedra is empty.

Eu1 is coordinated by 19 atoms revealing the combination of an elongated rhombic dodecahedron with the coordination polyhedron, which is typical for the rare-earth atom in the CaCu₅

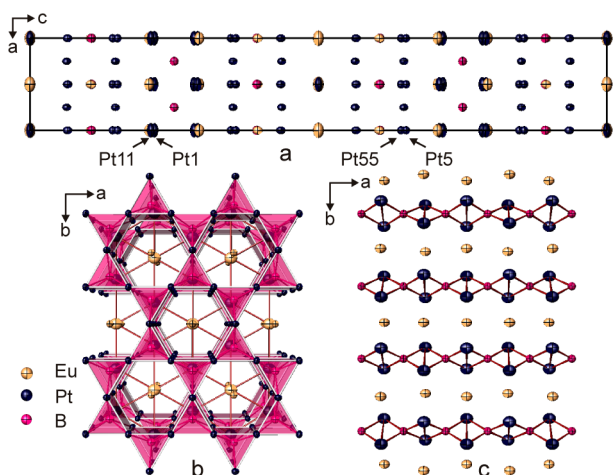


Figure 1. (a) Crystal structure of $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ with anisotropic displacement parameters for atoms from single-crystal refinement. Atoms in split sites are indicated. (b) Boron-centered Pt triangular prisms (Pt2, Pt3, Pt4, Pt5/Pt55) and 3^6 net of Pt6 accommodating Eu3 atoms at z within 0.33–0.66 (perspective view along the c axis). Eu–Pt bonds within the block of trigonal prisms are omitted. (c) Perspective view of boron-centered Pt tetrahedra (B2 in $8f$ ($1/4, 1/4, 1/4$)) along the c axis. Eu1–Pt1 and Eu1–B2 bonds and atoms in split position are omitted.

structure. Both fragments are stacked via the hexagon formed by Pt1 atoms (Figure 2a, Table 1). The hexagonal face formed

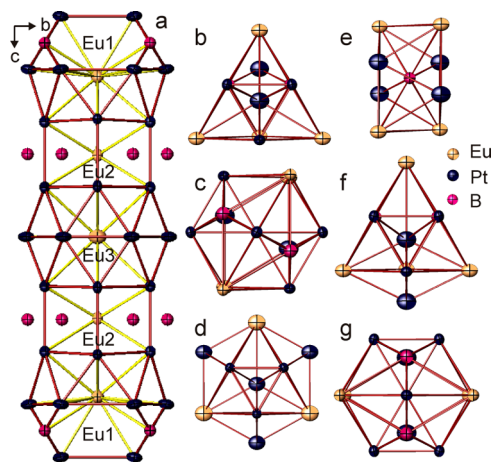


Figure 2. (a) Repeating block of Eu-centered polyhedra in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$. Eu2–B1 bonds are omitted. (b) Coordination polyhedron of Pt1. (c) Coordination polyhedron of Pt3 as representative of the atom environment for Pt2, Pt4, and Pt5. (d–g) Coordination polyhedra of Pt6 (d), B2 (e), Pt11 (f), and Pt55 (g).

by platinum atoms (Pt3 and Pt5) is capped by a Eu2 atom. The shapes of coordination polyhedra of Eu2 and Eu3 are similar: both atoms are coordinated by 12 Pt atoms forming two hexagonal faces of the coordination sphere. While in the Eu2 polyhedron they are linked by Pt2–Pt3 and Pt4–Pt5 contacts and form a hexagonal prism with the hexagonal faces capped by Eu atoms (Eu1 and Eu3), in the case of Eu3 the distances between the hexagonal faces are long (>0.4 nm) and preclude formation of Pt2–Pt2 and Pt4–Pt4 bonds. The coordination sphere of Eu3 includes also six Pt6 atoms located around the waist of an imaginary hexagonal prism; thus, those 18 platinum atoms form a cage elongated in the direction of the c axis

(pseudo-Frank–Kasper polyhedron, which can also be described as two face-connected hexagonal antiprisms) with the hexagonal faces capped by Eu2 atoms. In the case of Eu2, 6 boron atoms centering the rectangular faces of the hexagonal prism are located too far from the central atom to infer strong bonding (Eu2–B2 distances are 0.316 and 0.322 nm).

Pt1 has 10 atoms at coordination distances, and its polyhedron is derived from a tetragonal antiprism (Figure 2b). Pt2, Pt3, Pt4, and Pt5 (Figure 2c) are surrounded by distorted icosahedra with one additional platinum atom; for all four atoms the icosahedra are formed by three almost interperpendicular rectangles made of (i) 4 Pt, (ii) 2 Pt and 2 B, and (iii) 4 europium atoms. The coordination sphere of Pt6 resembles the coordination polyhedron of Cu ($2c$ ($1/3, 2/3, 0$)) in CaCu_5 and includes only platinum and europium atoms (in total 13, 2 of them are at a rather long distance Pt6–2Pt6, 0.3256 nm) (Figure 2d). B1 is coordinated by 6 Pt atoms forming a trigonal prism; three Eu atoms are located against the triangular faces of the trigonal prism (B1–Eu2 0.316 nm and B1–2Eu2 0.322 nm) (Figures 1b and 2a). B2 centers the tetrahedron made of near-neighboring platinum atoms; four Eu atoms complete the coordination sphere, forming a tetragonal antiprism (Figure 2e). The short distances between split positions (Pt1–Pt11 0.03682 nm and Pt5–Pt55 0.03021 nm) and their occupancies (0.80/0.20 for both Pt1/Pt11 and Pt5/Pt55) allow us to assume that on average the Pt1 and Pt5 atoms are present in four of five unit cells while one is filled with Pt11 and Pt55. Coordination spheres for the atoms when the split sites Pt11 and Pt55 are considered replicate the shape of those with (or for) Pt1 and Pt5 differentiating slightly in coordinating distances due to small shifts of atom positions, with the exception of Pt11 which has one more Pt11 in contact distance (Figure 2f and 2g).

EuPt₄B. Unit cell dimensions of the EuPt_4B single crystal and X-ray powder diffraction spectra recorded from both the annealed and the as-cast alloys suggested isotypism with CeCo_4B -type structure.^{1,2,9} Accordingly, the positions of Eu and Pt atoms obtained from structure solution in the space group $P6/mmm$ from the X-ray single-crystal data were consistent with the CeCo_4B type. The atom position of boron was derived from difference Fourier synthesis. Refinement of the structure with anisotropic displacement parameters converged to $R = 0.0259$ with residual electron densities smaller than $4940 \text{ e}^-/\text{nm}^3$ and revealed full occupancy of all atom sites (Table 2). The structure of EuPt_4B consists of CeCo_3B_2 - and CaCu_5 -type slabs alternating along the c axis. In the coordination sphere of boron (CeCo_3B_2 -type fragment), six Pt2 atoms are located at equal distance from the central atom, forming a regular triangular prism [BPT₂₆] (Figure 3a). Three europium atoms are located against the rectangular faces of the trigonal prism, revealing a B–Eu1 distance 0.32428(1) nm which is larger than the sum of atomic radii of the elements. The trigonal prisms share edges to form hexagonal channels accommodating the Eu1 atoms. Thus, Eu1 is surrounded by 12 Pt2 arranged in the shape of a hexagonal prism; two Eu2 atoms cap the hexagonal prisms of Eu1 at a distance of 0.3720 nm from the central atom (Figure 3b). Similar to the prototype structure and to $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$, Eu2 is located inside a rather large cage elongated along z ($d_{\text{Eu2-Pt2}} = 0.3611$ nm) and built of 18 platinum atoms, forming two face-connected hexagonal antiprisms; two Eu1 atoms cap the hexagonal faces. Both atoms in the CaCu_5 block (Eu2 and Pt1) reveal unusual thermal displacements: Eu2 exhibits a rather large thermal motion along the hexagonal axis with

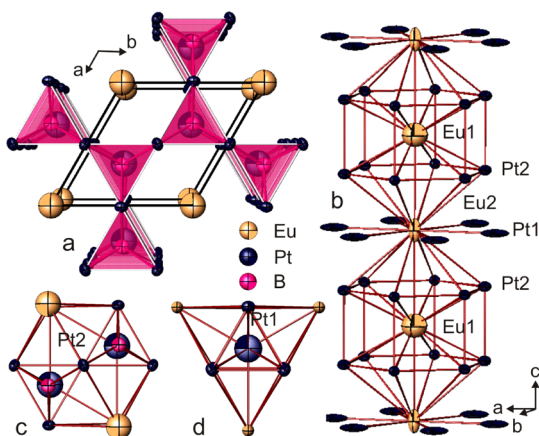


Figure 3. (a) Perspective view of the EuPt₄B structure along the *c*-axis direction emphasizing the boron-centered Pt₂ triangular prisms. Eu–Pt bonds are omitted. (b–d) Coordination spheres of Eu1 and Eu2 (b), Pt2 (c), and Pt1 (d). Atoms are represented by their thermal ellipsoids. For better visualization, the Pt1–Pt2 bonds are omitted in b.

$U_{33}:U_{11}(U_{22})$ of ca. 4:1, while Pt1 shows enlarged values U_{11} and U_{22} ($U_{11}(U_{22}):U_{33}$ of about 13). This behavior is illustrated by the thermal ellipsoids in Figure 3b. No fractional or partial occupancies for atom positions were observed from single-crystal data, and refinement of atoms on split positions was not successful. Trial refinements in the space group types with lower symmetry ($P\bar{6}2m$, $P\bar{6}m2$, $P6mm$, $P622$, $P6/m$, $P\bar{6}$, $P6$) yielded inferior results. Comparable features of thermal ellipsoids of atoms located in the channels formed by transition-metal atoms were hitherto also observed for the boride structures related to the CeCo_3B_2 type, such as $\text{In}_5\text{Ir}_9\text{B}_4$ ²⁸ ($P\bar{6}2m$, $a = 0.5590$ nm, $c = 1.0326$ nm) and LaNi_3B ²⁹ ($Imma$, $a = 0.4970$ nm, $b = 0.7134$ nm, $c = 0.8300$ nm); for the latter structure, the pronounced anisotropy of the atom thermal displacements preclude the symmetry change upon hydrogenation. In the case of EuPt₄B, a possible reason may be that in order to optimize the distance to its Pt₂ neighboring atoms Eu₂ is delocalized between the layers of Pt₂, consequently affecting (since Pt₁ and Eu₂ are at the same height) the thermal displacements of Pt₁. Enlarged displacement parameters of Eu₁ are probably indicative of a weak rattling of the europium atom within the 14-atom cage.

Eu₃Pt₇B₂. For Eu₃Pt₇B₂, systematic extinctions characteristic for the trigonal space group $R\bar{3}m$ and unit cell dimensions proposed isotypism with the $\text{Ca}_3\text{Al}_7\text{Cu}_2$ -type structure.¹¹ Structure solution by direct methods confirmed the arrangement of the heavy atoms analogous to that observed for $\text{Ca}_3\text{Ni}_7\text{B}_2$ ¹⁰ (Table 2). The boron position was successfully detected from difference Fourier synthesis. The structure is composed of CeCo_3B_2 - and MgCu_2 -type fragments alternating along *z*. Each successive block is shifted with respect to the former one in the (110) plane by a half unit cell. The perspective view of the Eu₃Pt₇B₂ unit cell along the *c* axis is presented in Figure 4a, showing triangular prisms formed by 6 Pt₁ around B. The CeCo_3B_2 -type slabs are formed by 12 Pt₁ and 2 Eu₁ atoms surrounding Eu₂ (Eu₂–Pt₁ 0.31525 nm, Eu₂–Eu₁ 0.32982 nm) to form the bicapped hexagonal prism (Figure 4c). Six boron atoms are located in front of the rectangular faces of the hexagonal prism at the distance 0.3203 nm, which is too long to assume bonding interaction (compare, for example, with $\text{Ca}_3\text{Ni}_7\text{B}_2$, where $d_{\text{Ca–B}} = 0.2978$ nm). The coordination polyhedron of Pt₂ exhibits a shape analogous to those of transition atoms in the binary

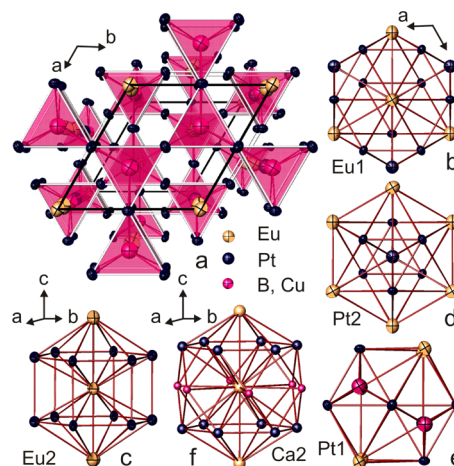


Figure 4. (a) Perspective view of the Eu₃Pt₇B₂ structure along the *c*-axis direction emphasizing the boron-centered Pt₁ triangular prisms. (b–e) Coordination spheres of Eu₁ (b), Eu₂ (c), Pt₂ (d), and Pt₁ (e). Atoms are represented by their thermal ellipsoids. (f) Twenty-membered cage capturing Ca₂ in the $\text{Ca}_3\text{Al}_7\text{Cu}_2$ structure.

MgCu_2 -type Laves phase: an icosahedron formed by 6Pt₁ and 6Eu₁ reveals interatomic distances (Table 2) which are comparable with distances in EuPt₂³⁰ (MgCu_2 type, Pt–6Pt 0.2727 nm, Pt–6Eu 0.3198 nm). The 16-vertices Frank–Kasper polyhedron [Pt₁₂Eu₄] of Eu₁ is slightly distorted in comparison with that of Eu in EuPt₂ (Figure 4b).

As compared to the prototype $\text{Ca}_3\text{Al}_7\text{Cu}_2$ structure,¹¹ significant changes in the coordination sphere of atoms are observed for the CeCo_3B_2 -type block: (i) the distance between the 3636 kagomé net formed by Al atoms is long (about 0.400 nm) in contrast to the corresponding distance between platinum atoms in Eu₃Pt₇B₂ ($d_{\text{Pt1–Pt1}} = 0.29959$ nm), thus delivering a different shape of the coordination polyhedron of Ca; (ii) due to the larger atomic radius of copper with respect to B, the distance Ca–Cu of 0.324 nm is sufficient to indicate bonding interaction, thus increasing the coordination number of Ca to CN = 20 (Figure 4f) as compared to CN Eu₂ = 14 in Eu₃Pt₇B₂. In contrast to EuPt₄B, in the present structure none of the atoms show significant anisotropy in their thermal vibration (Table 2).

STRUCTURAL RELATIONSHIPS

The investigated structures represent three families of structures revealing the CaCu_5 -type³¹ block in conjunction with other structural fragments. In the discussion below, the structures are arranged in order according to increasing complexity of structural arrangements.

The EuPt₄B structure (CeCo_4B type^{1,2,9}) (Figure 5f) consists of alternating slabs of CaCu_5 type (A) (Figure 5a) and slabs of its ternary derivative CeCo_3B_2 type (B) (Figure 5b). It is a simplest representative of the structural series described in TYPIX²⁵ under the general formula $R_{m+n}T_{5m+3n}M_{2n}$ with $m = 1$, $n = 1$ (m and n correspond to number of CaCu_5 -type and CeCo_3B_2 -type blocks, respectively). Similar to the prototype structure, the hexagonal channels filled with Eu are formed by edge-connected trigonal prisms [BPt₆] in EuPt₄B and alternate with 18-membered platinum cages, capturing europium atoms along the *c* axis. While in the CeCo_4B structure the B atoms are located at 0.2889 nm from the central Ce atom and assume bonding, this distance is rather long in the europium isotype with platinum.

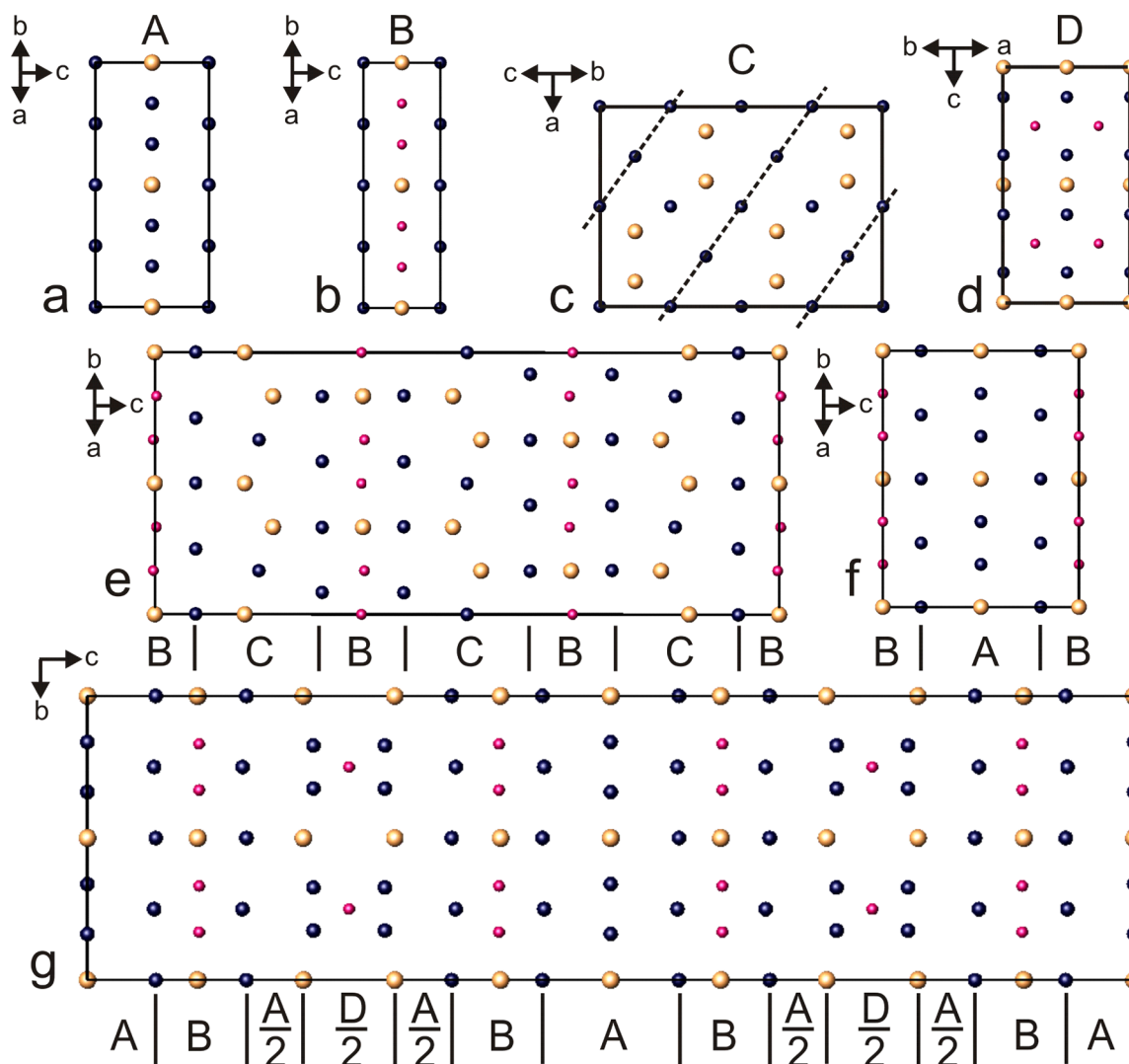


Figure 5. (a) CaCu_5 - and (b) CeCo_3B_2 -type structures (for both structures the origin is shifted by $0,0,1/2$). (c) EuPt_2 structure (MgCu_2 type, space group $Fd\bar{3}m$, origin shift $1/4, 0, 3/4$). Slabs of $\text{Eu}_3\text{Pt}_7\text{B}_2$ are outlined. (d) Inverse ThCr_2Si_2 -type structure.³⁶ (e–g) Structural relationships for (e) $\text{Eu}_3\text{Pt}_7\text{B}_2$, (f) EuPt_4B , and (g) $\text{Eu}_3\text{Pt}_{18}\text{B}_{6-x}$ structures. Relative arrangements of structural blocks are indicated with symbols A, B, C, and D.

In contrast to the relatively small unit cell and simple structure of EuPt_4B , the two remaining structures, $\text{Eu}_3\text{Pt}_7\text{B}_2$ and $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$, exhibit rather large unit cells and nontrivial stoichiometries.

$\text{Eu}_3\text{Pt}_7\text{B}_2$ is an ordered variant of the PuNi_3 type.³² This binary compound belongs to the rhombohedral branch of a structural series formed within composition range $\text{RM}_2\text{--RM}_5$ by stacking the fragments of CaCu_5 type and Laves phase and can be described by the formula $\text{R}_{2m+n}\text{M}_{4m+5n}\text{X}_{2n}$, where m accounts for the number of Laves-type slabs (R_2M_4) and n is a number of CaCu_5 -type slabs.^{1–3} Since only the structures with $m = 1$ have been observed for binary structures, the ternary representatives of this series which are built by combining CeCo_3B_2 - and Laves-type structural slabs ($\text{Ca}_3\text{Ni}_7\text{B}_2$,¹⁰ $\text{Ce}_2\text{Ir}_5\text{B}_2$ ¹²) follow the formula $\text{R}_{2+n}\text{M}_{4+3n}\text{X}_{2n}$: $2\text{MgCu}_2 + n\text{CeCo}_3\text{B}_2$. The ordered version of PuNi_3 was first identified in the Ca–Al–Cu system.⁹ In $\text{Ca}_3\text{Al}_7\text{Cu}_2$ -type structures with boron ($\text{Ca}_3\text{Ni}_7\text{B}_2$, $\text{Eu}_3\text{Pt}_7\text{B}_2$), the transition-metal atoms adopt the sites of aluminum in the MgCu_2 -type block and boron atoms replace copper in the CaCu_5 -type block. Figure 5e shows the arrangement of CeCo_3B_2 -type slabs (B) and MgCu_2 -type slabs (C) in the $\text{Eu}_3\text{Pt}_7\text{B}_2$ structure.

The structure of $\text{Eu}_3\text{Pt}_{18}\text{B}_{6-x}$ represents a new type of ternary borides. It can be considered as an intergrowth of three kinds of

structure blocks (Figure 5g): one is a CaCu_5 type (A), the second having the atom arrangement of its ordered ternary derivative CeCo_3B_2 (B), and the third reveals the slab of the site-exchange variant of the ThCr_2Si_2 structure with B atoms adopting the sites of Cr (D). The body-centered structure of ThCr_2Si_2 (space group $I4/mmm$, Th in 2a: $0, 0, 0$; Cr in 4d: $0, 1/2, 1/4$, Si in 4e: $0, 0, z$), an ordered variant of BaAl_4 , is widely distributed among RET_2X_2 compounds (T = transition metal, X = p element).³³ The unit cell of ThCr_2Si_2 can be described as a stacking of infinite layers of interconnected tetragonal $[\text{Cr}_4]$ pyramids around the Si atom (Wyckoff position 4e, commonly named as pyramidal site) running perpendicular to the c axis with a layer of thorium atoms between these pyramids. Cr atoms are tetrahedrally surrounded by four Si atoms (Wyckoff position 4d, tetrahedral site). Chemical bonding, atomic site preferences as a function of electronegativity of the constituent elements, size effect with respect to the structural stability, phase widths, and physical properties have been studied for different combinations of the elements^{34–41} and particularly developed recently for pnictides due to discovery of superconductivity in the series of iron arsenides with ThCr_2Si_2 type.^{42–44} Ternary rare-earth borides with a ThCr_2Si_2 -type structure are

quite rare except for few representatives, such as RECo_2B_2 ($\text{RE} = \text{Y, La, Pr, Nd, Sm, Gd-Er}$),^{45–47} REFe_2B_2 ($\text{RE} = \text{Y, Gd-Tm, Lu}$),⁴⁸ and BaRh_2B_2 .⁴⁹ In all these structures the transition metal occupies the atom site of Cr and boron is placed in the position of Si. Accordingly, each T atom is coordinated by four B atoms; a recent reinvestigation of the ThCr_2Si_2 type LaCo_2B_2 ($a = 0.36108$ nm, $c = 1.02052$ nm, $z = 0.3324(5)$) revealed a relatively short Co–B bond (e.g., 0.20 nm), indicating certain compression of the CoB layer along the c axis and an elongated La–B contact distance (0.308 nm).⁵⁰

There are two BaAl_4 -type derivative structures encountered for composition RET_2X_2 : the structures of ThCr_2Si_2 (described above) and CaBe_2Ge_2 , which is built by intergrowth of ThCr_2Si_2 -type slabs and slabs of its site-exchange variant along the [001] direction (and thereby one-half of T and X atoms occupy the tetrahedral and pyramidal sites and vice versa, respectively). As reported by Parthe et al.,³⁶ formation of compounds revealing only inverse ThCr_2Si_2 -type arrangement is rare; however, this arrangement occurs as slabs in intergrown structures (for example, in CeNiSi_2 , BaCuSn_2 , $\text{La}_3\text{Co}_2\text{Sn}_7$). Among borides, formation of inverse ThCr_2B_2 -type structure was found for ZnIr_2B_2 where layers of edge-connected $[\text{BIR}_4]$ tetrahedra (Ir in $4e$ (0, 0, z , $z = 0.37347$), B in $4d$ (0, 1/2, 1/4)) are separated by 4^+ networks of zinc atoms (Zn in $2a$ (0, 0, 0)).⁵¹ Similarly, in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ four atoms of platinum form tetrahedra around boron atoms, however exhibiting a higher degree of compression along the b axis: the Pt1–B distance in the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ is 0.1978(1) nm (and 0.2239(8) nm for Pt11 in split position) as compared to the length of the Ir–B bond of 0.2150 nm in ZnIr_2B_2 showing the tetrahedral angles $2 \times 137.07^\circ$, $2 \times 105.25^\circ$, $2 \times 90.27^\circ$ in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ ($2 \times 126.09^\circ$, $2 \times 100.79^\circ$, $2 \times 102.91^\circ$ for Pt11) and $4 \times 121.68^\circ$, $2 \times 87.11^\circ$ in ZnIr_2B_2 . Because of limited spatial dimension of the ThCr_2Si_2 slab in the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ structure (i.e., one-half a unit cell cut along (111)), the tetrahedra do not form infinite layers but are arranged in one-dimensionally linked chains running infinitely along the a axis. Previous theoretical studies based on Mülliken overlap population analysis suggested that the element with greater electronegativity is more strongly bound in the $4e$ site.^{52,53} The atoms site preferences in the structures of three discussed borides (i.e., LaCo_2B_2 , ZnIr_2B_2 , and ThCr_2Si_2 block in the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$) are consistent with the electronegativity on the Pauling scale of boron, relative to those of transition elements Co, Ir, and Pt.

Among a large family of reported ternary rare-earth transition-metal borides, the Eu phases are usually missing. For only a few CaCu_5 -type derivative ternary borides with europium have the precise structural parameters and physical properties been investigated. These are (i) the $\text{Eu}_2\text{Rh}_5\text{B}_4$ and $\text{Eu}_3\text{Rh}_8\text{B}_6$ structures composed of the CeCo_3B_2 - and CaRh_2B_2 -type fragments,⁵⁴ (ii) $\text{Eu}_3\text{Ni}_7\text{B}_2$ of CeCo_4B type exhibiting one nickel site partially occupied by a mixture of europium and nickel atoms.⁵⁵ In both $\text{Eu}_2\text{Rh}_5\text{B}_4$ and $\text{Eu}_3\text{Rh}_8\text{B}_6$ compounds, the Eu atoms have been found in the divalent state, revealing magnetic moments only slightly smaller than the theoretical value of $7.94 \mu_B$.⁵⁴ EuIr_2B_2 of CaRh_2B_2 type can be considered as a metal-deficient derivative structure of CeCo_3B_2 ; according to a plot of the unit cell volumes vs lanthanide atomic number, Eu was found to be divalent.⁵⁶ Comparing the interatomic distances and relating them to the magnetic properties, one can see that in both $\text{Eu}_2\text{Rh}_5\text{B}_4$ and $\text{Eu}_3\text{Rh}_8\text{B}_6$ (Eu $4f^7$) the Eu–Eu distances are 0.3207, 0.3654 nm and 0.3113, 0.3614 nm respectively, while Eu–Rh distances vary between 0.3079 and 0.3256 and 0.3054 and 0.3279 nm. EuIr_2B_2 shows similar distance variations: the Eu–Eu bond is

0.3852 nm, and the distances Eu–Ir are 0.3058 and 0.3313 nm. The differences in bond length analogous to $\text{Eu}_2\text{Rh}_5\text{B}_4$, $\text{Eu}_3\text{Rh}_8\text{B}_6$, and EuIr_2B_2 can be found in EuPt_4B , where one Eu atom, namely, Eu1 (CeCo_3B_2 -type block) exhibits rather short contacts with Pt2 of 0.31605 nm, whereas Eu2 (CaCu_5 -type block) exhibits Pt neighbors at 0.32428 and 0.36113 nm. There is one rather long bond between europium atoms Eu1–Eu2 0.3720 nm in EuPt_4B . The deviations of the lattice parameters of the europium compound from the lanthanoid contraction in the REPt_4B series also confirm the assumption that Eu is not trivalent in EuPt_4B (Figure 6).

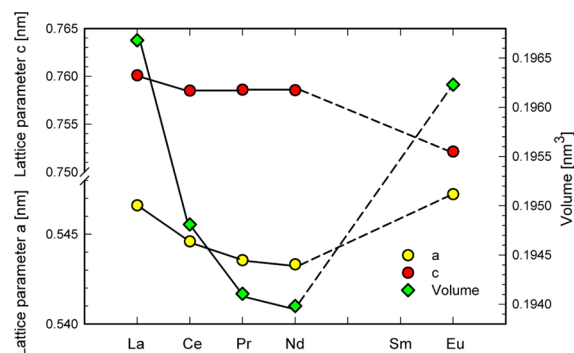


Figure 6. Lattice constants of the REPt_4B series. Values for La–Pr and Nd are taken from the literature.¹⁶ For the europium compound, lattice parameters were obtained from Rietveld refinement of single-phase EuPt_4B alloy used for physical properties measurements.

Similarly, in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ the Eu–Eu contacts are long and the distances between Eu and Pt atoms are rather heterogeneous, ranging within 0.3128 and 0.3611 nm.

MAGNETIC PROPERTIES

In order to obtain the electronic configuration (EC) of the Eu ions and thus the magnetic state, the magnetization of EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$ was measured and analyzed in detail. The temperature dependence of the magnetization and susceptibility for various fields is presented in Figures 7 and 8, respectively.

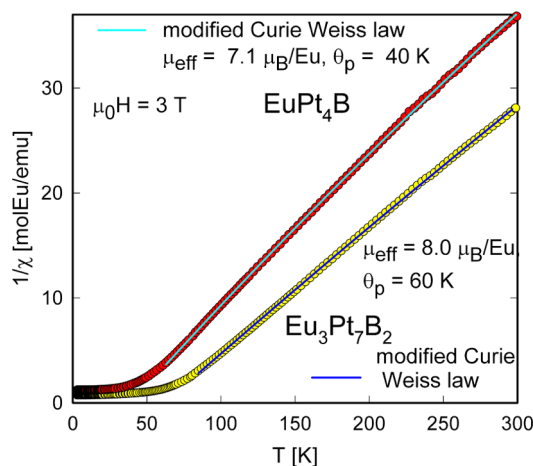


Figure 7. Temperature-dependent inverse magnetic susceptibility of EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$. Solid lines are fits according to the modified Curie–Weiss law.

Magnetic susceptibility data $\chi = M/H$ scale pretty well for 0.1, 1, and 3 T above the ordering temperature being indicative that the samples are free from magnetic impurities and other

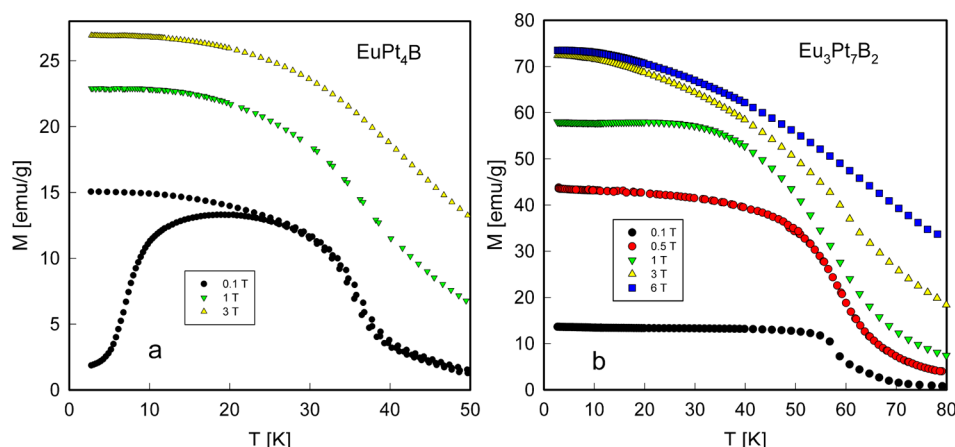


Figure 8. Temperature-dependent magnetization of EuPt_4B (a) and $\text{Eu}_3\text{Pt}_7\text{B}_2$ (b).

magnetic secondary phases; data are displayed in Figure 7 as χ^{-1} vs T for the 3 T run, only.

Both EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$ are found to order ferromagnetically. $\text{Eu}_3\text{Pt}_7\text{B}_2$ shows a transition at 57 K, while EuPt_4B orders below 36 K as determined from low-field magnetization measurements and corresponding Arrott plots (see below). The magnetic susceptibility in the paramagnetic region is accounted for by the modified Curie–Weiss law $\chi = \chi_0 + C/(T - \theta_p)$. The paramagnetic Curie temperatures $\theta_p = 60$ and 40 K together with effective magnetic moments $\mu_{\text{eff}} = 8.0$ and $7.1 \mu_B$ per Eu atom (derived from the Curie constant, C), were obtained as a result of least-squares fits to the susceptibility data of $\text{Eu}_3\text{Pt}_7\text{B}_2$ and EuPt_4B , respectively (solid lines, Figure 7), with a temperature-independent susceptibility χ_0 of about $3 \times 10^{-6} \text{ cm}^3/\text{g}$ for both compounds. While the paramagnetic moment of $\text{Eu}_3\text{Pt}_7\text{B}_2$ recounted per one europium atom is almost that expected for the theoretical value of the free Eu^{2+} ion ($\mu_{\text{eff}} = 7.94 \mu_B$) the effective moment obtained for EuPt_4B is significantly smaller, pointing to a mixed- or intermediate valence state of Eu. The fact that Eu in EuPt_4B possesses two inequivalent lattice sites suggests that the more static case (i.e., mixed valence) might account. In such a case, the system can be treated as a mixture of Eu^{2+} and Eu^{3+} atoms located either at the 1(a) or the 1(b) site. Following this approach, the paramagnetic moment of Eu in EuPt_4B can be represented as $\mu_{\text{eff}} = \sqrt{x\mu_{\text{Eu}^{2+}}^2 + (1-x)\mu_{\text{Eu}^{3+}}^2}$. Here we use a mean literature value for the effective moment of Eu^{3+} with $\mu_{\text{Eu}^{3+}} = 3.5 \mu_B$ ^{57,58} rather than the theoretically vanishing effective magnetic moment of a pure Eu^{3+} state. The fraction x of Eu atoms in the 2+ state is thus estimated to be $x = 0.75$, whereas a vanishing effective moment for the Eu^{3+} state gives a fraction of 80% in the Eu^{2+} state. Although the latter is presumably an overestimate, analysis of the saturation magnetization and heat capacity (see below) supports these assumptions.

The temperature-dependent magnetization, displayed in Figure 8 for various fields, exhibits for EuPt_4B significant irreversibilities of the magnetization for zero-field cooling (ZFC) and field cooling (FC) which disappear only for fields larger than 1 T. These irreversibilities can be attributed to domain wall pinning associated with a remarkable hysteresis and a coercivity of 0.32 T at 2.8 K (see Figure 9) as a consequence of the magnetocrystalline anisotropy due to the CaCu_5 building blocks. On the contrary, there is hardly any difference for ZFC and field cooling detectable even in the low-field regime for $\text{Eu}_3\text{Pt}_7\text{B}_2$ yielding also

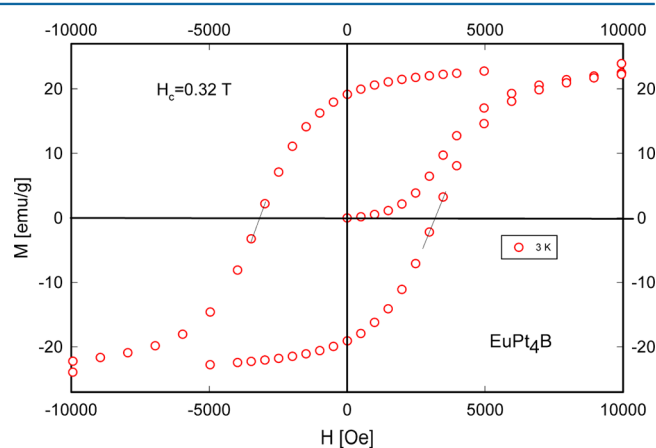


Figure 9. Hysteresis in magnetization of EuPt_4B .

reversible magnetic isotherms without a significant hysteresis, which means the coercivity is 3 orders of magnitude smaller than for EuPt_4B .

A comparison of the magnetic isotherms of both compounds is shown in Figure 10, where the isotherms are displayed as M^2 versus H/M plots (Arrott plots). It should be noted that in the case of EuPt_4B with the pronounced hysteresis only the demagnetization data, where the rotation of the magnetization plays the dominant role, are used for the Arrott plots. Deviations from the expected linear behavior of the Arrott plots are observed frequently, see, e.g., ref S9 and references therein, in particular with a curvature symmetrical with respect to T_c , i.e., a negative curvature at $T < T_c$ and a positive curvature at $T > T_c$. This is indeed observed for EuPt_4B (Figure 10a), and such symmetrical deviations about T_c can be attributed to spatial variations of the magnetization and/or spin fluctuations. As we have a stoichiometric compound these deviations may arise from fluctuating moments associated with significant thermal motions of Eu2 along the hexagonal axis and/or with the proposed weak rattling of the Eu1 atoms within the 14-atoms cage rather than from a heterogeneous magnetization. On the other hand, it was shown that a substantial uniaxial magnetocrystalline anisotropy causes a remarkable downturn of the Arrott plots below T_c .⁶⁰ In this model, the negative curvature of the Arrott plots below T_c can be accounted for as a result of domain rotations in the non-oriented crystallites and against the random but uniaxial anisotropy fields H_A . A rather simple way to estimate H_A in terms of this model is to extrapolate the linear part of the Arrott plot backward

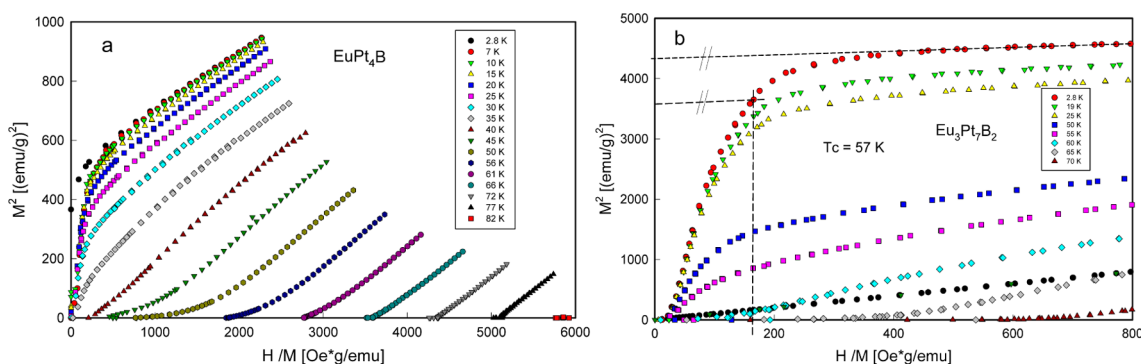


Figure 10. Arrott plots of EuPt₄B (a) and Eu₃Pt₇B₂ (b). Dashed lines are used to estimate H_A through the procedure explained below.

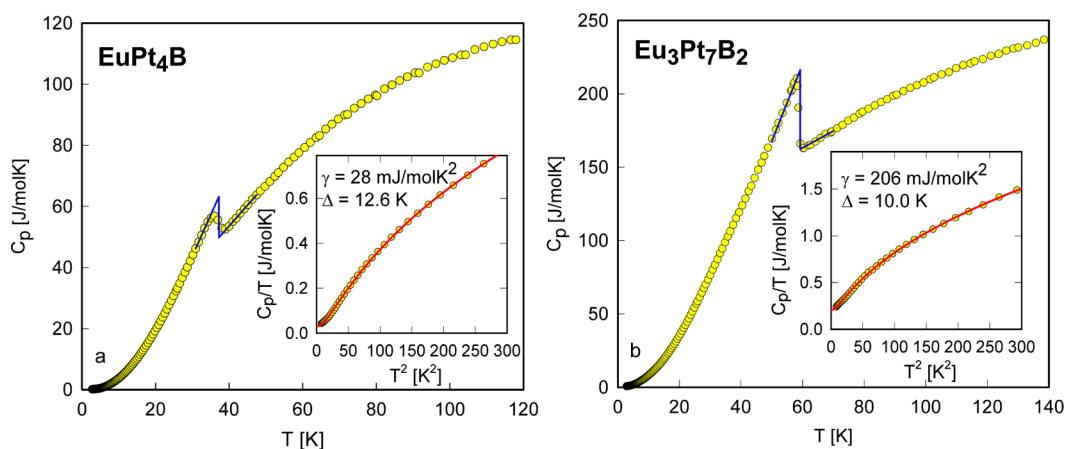


Figure 11. Temperature-dependent specific heat C_p of EuPt₄B (a) and Eu₃Pt₇B₂ (b). Solid lines idealize the ferromagnetic phase transition. (Insets) Low-temperature details together with least-squares fits (solid lines) based on a ferromagnetic spin wave model.

to obtain the spontaneous magnetization, and taking 91.3% of that value gives with a parallel forward extrapolation an intersection with the experimental Arrott plot, yielding a value for H/M where this particular field corresponds to the anisotropy field H_A (see the dashed lines in Figure 10b; for further details see ref S9). Using this simple estimate we obtain for Eu₃Pt₇B₂ an anisotropy field of about 1 T which arises from the uniaxial anisotropy of the building blocks.

Although the magnetization at 7 T at 2.8 K is not in a fully saturated state for both compounds we use that value for the saturation magnetization M_s , while the spontaneous magnetization M_0 is obtained from the backward extrapolation of the Arrott plot as mentioned above. This yields for Eu₃Pt₇B₂ $M_s = 7.43 \mu_B/\text{mol-Eu}$ and $M_0 = 7.24 \mu_B/\text{mol-Eu}$ and for EuPt₄B $M_s = 5.13 \mu_B/\text{mol-Eu}$ and $M_0 = 3.85 \mu_B/\text{mol-Eu}$. Both the saturation as well as the spontaneous magnetization of Eu₃Pt₇B₂ is well above the value expected for a Eu²⁺ ion ($M_s = gJ = 7 \mu_B$), indicative that a substantial 5d conduction electron polarization contributes to the total moment. The significant smaller saturation and spontaneous moment of EuPt₄B indicate, in line with results for the effective moments, a mixed-valence state. Under the assumption that the conduction electron polarization is of similar magnitude in both compounds, the ratio of their saturation moments indicates that 69% of the Eu ions are in the Eu²⁺ state in EuPt₄B, while a somewhat smaller fraction of about 53% is obtained using the ratio of the spontaneous moments. The latter is an underestimate caused presumably by the large high-field susceptibility of EuPt₄B also visible in the larger slope of the Arrott plot in comparison to that of Eu₃Pt₇B₂.

SPECIFIC HEAT

Further information on the ground state properties of EuPt₄B and Eu₃Pt₇B₂ can be gained from specific heat measurements. Experimental results are shown in Figure 11.

Both EuPt₄B and Eu₃Pt₇B₂ exhibit distinct λ -like anomalies around 35 and 57 K, respectively, idealized in Figure 11 by solid lines, which can be attributed to a second-order phase transition of magnetic origin. A nonmagnetic isostructural compound to be used as an analogue was not available for a full comparative analysis. However, it is easily seen that the height of the anomaly $\delta C_p = 56$ J/mol·K in the case of Eu₃Pt₇B₂ corresponds well to a mean-field-like transition of a $j = 7/2$ system ($\delta C_p = N^*SR[j(j+1)/(2j^2 + 2j + 1)]$), where N is the number of RE atoms/mol. Considering three Eu²⁺ atoms per mole yields $\delta C_p = 60.39$ J/mol·K, in fair agreement with experiment. The jump of the specific heat of EuPt₄B right at the magnetic phase transition temperature is only about 13 J/mol·K in comparison with the expected value of 20.13 J/mol·K. This reveals that only a fraction of the Eu ions is involved in magnetic ordering (i.e., 65% Eu²⁺ and 35% Eu³⁺), which is in line with the broad range of estimates from the magnetic data where we obtained 53% Eu²⁺ as a lower and 80% Eu²⁺ as an upper limit.

Low-temperature heat capacity data were analyzed in terms of a ferromagnetic spin wave model including a spin wave gap Δ , i.e., $C_p = \gamma T + \beta T^3 + \delta T^{3/2} \exp(-\Delta/T)$ with γ the Sommerfeld value and β proportional to the low-temperature Debye temperature θ_D^{LT} ($\theta_D^{\text{LT}} = ((1944N)/\beta)^{1/3}$). Such an analysis should hold for temperatures well below the Curie temperature.

Results of least-squares fits are shown as solid lines in the insets of Figure 11, revealing excellent agreement with $\gamma = 28$ and $206 \text{ mJ/mol}\cdot\text{K}^2$, resulting in an effective $68 \text{ mJ/mol}\cdot\text{K}^2$ per europium atom, $\beta = 0.000222$ and $0.000702 \text{ J/mol}\cdot\text{K}^4$, $\delta = 0.36$ and $0.46 \text{ J/mol}\cdot\text{K}^{3/2}$, and $\Delta = 12.6$ and 10 K for EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$, respectively. The corresponding Debye temperatures are 370 and 321 K , respectively. Both Eu-based compounds are characterized by Sommerfeld values well beyond simple metals, pointing to strong electron correlations induced by intra-atomic $4f$ – $5d$ exchange in Eu^{2+} ions in combination with a significant hybridization of Eu and Pt $5d$ orbitals. The latter is also corroborated by the high saturation magnetization of $\text{Eu}_3\text{Pt}_7\text{B}_2$ which significantly exceeds the expected saturation moment of free Eu^{2+} ions. We note that largely enhanced Sommerfeld values due to f – d exchange have been reported for various Gd intermetallics such as Gd_3Co ,⁶¹ Gd_3Rh ,⁶² and Gd-Ni ⁶³ binaries.

ELECTRICAL RESISTIVITY

We studied the electrical resistivity ρ of EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$ from 0.3 K to room temperature (see Figure 12). Data evidence

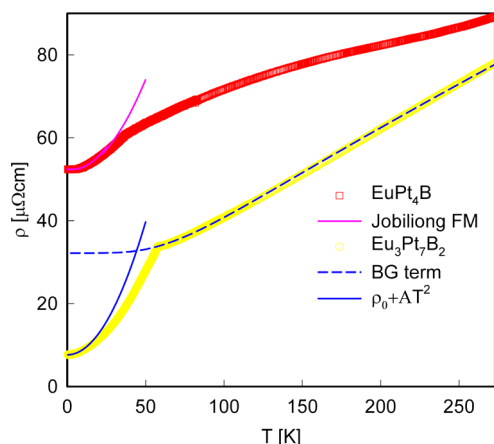


Figure 12. Temperature-dependent electrical resistivity ρ of EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$. Lines correspond to models mentioned in the text.⁶⁴

metallic behavior in both cases with rather low overall resistivities. Unlike $\text{Eu}_3\text{Pt}_7\text{B}_2$, in the resistivity curve of EuPt_4B a slight change of slope is observed at around 240 K , pointing to some additional, unanticipated scattering processes. For both compounds, anomalies of $\rho(T)$ characterize the magnetic phase transition.

Figure 13 represents the magnetic field dependence of the resistivity of $\text{Eu}_3\text{Pt}_7\text{B}_2$ and EuPt_4B . Although the anomaly in both compounds is of ferromagnetic origin, application of a magnetic field causes different responses of the resistivity. The resistivity of EuPt_4B decreases slightly in the entire temperature range studied, and the $\rho(T)$ anomaly is suppressed by fields of 6 T . Magnetoresistance of $\text{Eu}_3\text{Pt}_7\text{B}_2$, on the other hand, is positive at low temperatures as well as in the high-temperature paramagnetic range and negative only in a narrow region around the transition temperature. Despite the ferromagnetic ground state of $\text{Eu}_3\text{Pt}_7\text{B}_2$ leading, in general, to a negative magnetoresistance, the classical magnetoresistance can overcompensate the one originated by magnetic interactions, resulting in an increase of $\rho(T)$ with increasing magnetic fields, at least for certain temperature ranges. The dominance of the classical magnetoresistance in $\text{Eu}_3\text{Pt}_7\text{B}_2$ as compared to EuPt_4B might follow from the fact that the overall resistivity, specifically the

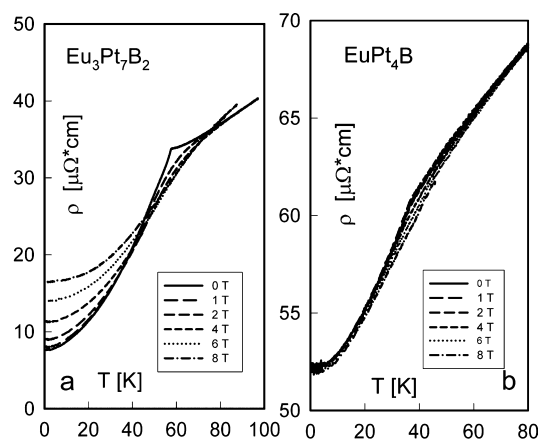


Figure 13. Temperature-dependent electrical resistivity of $\text{Eu}_3\text{Pt}_7\text{B}_2$ (a) and EuPt_4B (b) as a function of magnetic field.

residual resistivity, is much lower here than in the case of EuPt_4B .

To quantitatively evaluate $\rho(T)$ of $\text{Eu}_3\text{Pt}_7\text{B}_2$, experimental data were first split into two parts, i.e., a low-temperature region (below the magnetic phase transition) and a high-temperature paramagnetic part. In the paramagnetic regime the behavior of the resistivity of $\text{Eu}_3\text{Pt}_7\text{B}_2$ can be described by

$$\rho = \rho_0^* + \rho_{\text{BG}}$$

where $\rho_{\text{BG}} = C(T^5/\theta_D^5) \int_0^{(\theta_D/T)} (x^5/((e^x-1)(1-e^{-x})))$ is the Bloch–Grüneisen term corresponding to the resistivity originated from scattering of conduction electrons on phonons and $\rho^* = \rho_0 + \rho_{\text{mag}}$, with ρ_{mag} describing the interaction of conduction electrons with localized magnetic moments. In the absence of crystalline electric field effects, ρ_{mag} is temperature independent in the paramagnetic temperature range. ρ_0 is the residual resistivity. A Debye temperature $\theta_D = 312 \text{ K}$ and $\rho^* = 32 \mu\Omega\cdot\text{cm}$ were obtained from a least-squares fit in a temperature region over 80 K (dashed line, Figure 12). In the low-temperature region, the resistivity of a ferromagnetic material with spin wave dispersion $\omega \approx k^2$ is expected to behave like $\sim T^2$. Moreover, as a consequence of the enlarged gamma value, derived from the specific heat measurements, the electron–electron scattering should also be taken into account and in turn be proportional to T^2 at low temperatures as well, making it impossible to distinguish between both phenomena. As a result of the fit using $\rho = \rho_0 + AT^2$, $\rho_0 = 7.64 \mu\Omega\cdot\text{cm}$ was obtained.

The low-temperature part of the resistivity of EuPt_4B is in good agreement with the temperature dependence of a ferromagnetic material. Experimental data are well accounted for by⁶⁴ $\rho = \rho_0 + BT\Delta(1 + (2T/\Delta))e^{-\Delta/T}$ with $\Delta = 12.8 \text{ K}$ as the width of the gap in ferromagnetic spin wave spectrum. The high-temperature part, on the other hand, displays some characteristic curvature observed in systems strongly influenced by the crystalline electric field, supporting the mixed-valence hypothesis.

SUMMARY

Three new ternary phases have been observed for the first time in the Eu–Pt–B system from arc-melted alloys annealed at 1020 K . Crystal structures have been studied by X-ray single-crystal diffraction and validated by Rietveld refinements of X-ray powder diffraction data. The results beautifully illustrate

the structural diversity and versatility of a CaCu_5 -type derivative family of structures, revealing three different structural series.

EuPt_4B forms a CeCo_4B type and is composed of CaCu_5 - and CeCo_3B_2 -type fragments stacked along the c axis; $\text{Eu}_3\text{Pt}_7\text{B}_2$ is built of CeCo_3B_2 - and MgCu_2 -type slabs and exhibit an ordered variant of PuNi_3 , namely, $\text{Ca}_3\text{Al}_2\text{Cu}_2$ type with Al and Cu atom sites occupied by Pt and B atoms, respectively. In both compounds the nearest coordination for boron atom is trigonal prism $[\text{BPt}_6]$.

Unique stacking of CaCu_5 -, CeCo_3B_2 -, and ThCr_2Si_2 -type slabs has been uncovered in the $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ structure; the atom arrangement in the ThCr_2Si_2 -type block is rare for the distribution of Pt and B atoms on Si and Cr atom sites, respectively (BaAl_4 -type derivative structures), thus changing the coordination of the transition metal as compared to other representatives of a large family of ThCr_2Si_2 -type compounds and exhibiting chains of edge-connected platinum tetrahedra $[\text{BPt}_4]$ running along the a -axis direction. With respect to Eu–Eu linkage, the europium atoms are interconnected infinitely along the c axis in both EuPt_4B and $\text{Eu}_3\text{Pt}_7\text{B}_2$ structures. The $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ structure exhibits the repeating blocks of 5 fused polyhedra of Eu linked in a sequence ...– ThCr_2Si_2 – CeCo_3B_2 – CaCu_5 – CeCo_3B_2 – ThCr_2Si_2 –...; the units are shifted for a $1/2a$ along the b -axis direction with respect to each other, forming blocks which are interlinked via ThCr_2Si_2 -type fragment along the c axis. Positioning of the B atom on the Cr Wyckoff site in the ThCr_2Si_2 -type slab and consequently its nearest tetrahedral coordination plays a decisive role in formation of $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ structure, serving as a linking entity (Figure 14) for the repeating structural units of fused Eu polyhedra.

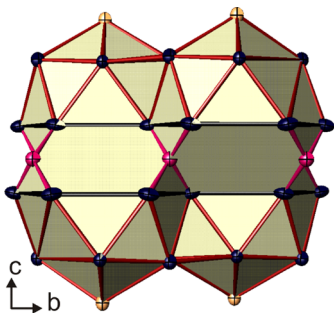


Figure 14. Eu1 polyhedra fused by B-atoms in $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$.

Although EuPt_4B exhibits a ferromagnetic ordering at relatively high temperature of 36 K, a mixed-valence state for Eu is observed. In a static case of valence distribution one would expect 50% Eu^{3+} and 50% Eu^{2+} as a consequence of obvious difference between the coordination polyhedra for two Eu atoms unlike our case, where magnetic and specific heat measurements purpose more complex valence behavior. Time-dependent studies are needed to distinguish between a static and a more complex dynamic case of mixed-valence state.

In $\text{Eu}_3\text{Pt}_7\text{B}_2$, the Eu atoms are in the 2+ state and the compound orders ferromagnetically at around 57 K. The electron part of specific heat was found to be $206 \text{ mJ/mol}\cdot\text{K}^2$, pointing to the existence of strong electron correlations.

■ ASSOCIATED CONTENT

Supporting Information

Single-crystal refinement data for three compounds in CIF format; figures of Rietveld refinements of the X-ray powder diffraction patterns of EuPt_4B , $\text{Eu}_3\text{Pt}_7\text{B}_2$, and $\text{Eu}_5\text{Pt}_{18}\text{B}_{6-x}$ ($x = 1$).

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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