Structural and Physical Properties Diversity of New CaCu₅-Type Related Europium Platinum Borides

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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: EuPt₄B, CeCo₄B type, P6/mmm, a = 0.56167(2) nm, c = 0.74399(3) nm; EuPt₅B₂j, Ca₅Al₃Cu₂ type as an ordered variant of PuNi₃, R3m, a = 0.55477(2) nm, c = 2.2896(1) nm; and EuPt₃B₆·, a new unique structure type, Fmmn, a = 0.55813(3) nm, b = 0.95476(5) nm, c = 3.51578(2) nm. These compounds belong to the CaCu₅ family of structures, revealing a stacking sequence of CaCu₅-type slabs with different structural units: CaCu₅ and CeCo₃B₂ type in EuPt₄B; CeCo₃B₂ and Laves MgCu₂ type in EuPt₅B₂j; and CaCu₅, CeCo₃B₂ and site-exchange ThCr₂Si₂-type slabs in EuPt₃B₆·. The striking motif in the EuPt₃B₆· structure is the boron-centered Pt tetrahedron [BPt₄], 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, EuPt₄B and EuPt₅B₂j, were studied. Both compounds were found to order magnetically at 36 and 57 K, respectively. For EuPt₄B 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 EuPt₅B₂j was found to be extraordinarily large, on the order of 0.2 J/mol K².

INTRODUCTION

Phases with CaCu₅-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 CaCu₅-type fragments and slabs of Laves phases with MgZn₂ and MgCu₂ 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, RECo₅- or TbCu₂ type, where part of the atoms in the Ca site of the CaCu₅ 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 RE₃Co₁₇ revealing the intergrown CaCu₅- and Zr₆Al₃-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 CaCu₅ structure (space group P6/mmm; Ca in 1a (0,0,0), Cu in 2c (1/3,2/3,0), Cu₂ in 3g (1/2,0,1/2)) and formation of the ordered ternary substitution derivative CeCo₂B₂ (Ce in 1a, Co in 3g, and B in 2c).⁸ As relevant to the study presented herein, the CeCo₂B₂ 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 CeCo₂B₂ are stacked with slabs of the binary CaCu₅ type or Laves phases are frequently encountered among ternary rare-earth borides with Co and Ni.¹,²,⁹,¹⁰ 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 CaCu₅-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 CeCo₂B₂ and CaRh₂B₂ (ThCr₂Si₂) type were observed in Eu–Rh–B,¹³ Y–Os–B, and La–Ru–B systems;¹⁴ (ii) PrRh₄B₂ revealed CeCo₂B₂-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 CaCu₅-type derivatives concerns the crystal structure and physical properties studies for the REPt₄B series (CeCo₂B₂ 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 CaCu5-related structures. Our interest in this investigation was driven not only by the structural flexibility and diversity of CaCu5-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. Results presented herein expand knowledge on a family of CaCu5 derivative structures to (i) the EuPt1B6−x phase showing a new structural arrangement formed by stacking of inverse ThCrSi2-type slabs with CaCu5- and CeCo3B2-type fragments along the c-axis direction, (ii) a new member of rather simple structural series exhibiting the combination of CaCu5- and CeCo3B2-type slabs, namely, EuPt1B6 where a mixed-valence state of Eu has been observed, and (iii) a new compound EuPt1B6, composed of CeCo3B2- and Laves-phase (MgCu2) 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%, Ogasaw, 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 prepared 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 high vaporization of europium, Eu weight losses were compensated by adding carefully prepared 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 high vaporization of europium, Eu weight losses were compensated by adding carefully prepared extra amounts of Eu before melting. For homogeneity, samples were remelted several times. 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Table 1. X-ray Single-Crystal Structure Data* for Eu₁₈Pt₆₄B₁₈–ₓ

| Parameter | Value |
|-----------|-------|
| Nominal composition | Eu₁₈Pt₆₄B₁₈ |
| Structure type | Eu₅Pt₁₈B₆ (x = 1) |
| Range for data collection | 3.48° < θ < 29.95° |
| Crystal size | 35 × 35 × 15 µm³ |
| Rω² | 0.0331 |
| Mosaicity | 0.1073 |
| No. of variables | 52 |
| Residual density range for data collection | 3.48 ± 0.2 electrons/nm³ |

Anisotropic thermal parameters were constrained for the atoms in split positions.

| Intertatomic distances (nm) | Eu₁–Eu₂: 0.3128(2) |
|-----------------------------|---------------------|
| Eu₁–Eu₂ | 0.3128(2) |
| Eu₁–P₄ | 0.3126(1) |
| Eu₁–P₅ | 0.3149(1) |
| Eu₁–P₆ | 0.3216(1) |
| Eu₁–P₇ | 0.3431(4) |
| Eu₁–Eu₂ | 0.3355(2) |
| Eu₁–Eu₃ | 0.3070(1) |
| Eu₁–Eu₄ | 0.3275(1) |
| Eu₁–Eu₅ | 0.3276(2) |
| Eu₁–Eu₆ | 0.3297(1) |
| Eu₁–Eu₇ | 0.3298(1) |
| Eu₂–P₄ | 0.3121(2) |
| Eu₂–P₅ | 0.3279(2) |
| Eu₂–P₆ | 0.3283(2) |
| Eu₂–P₇ | 0.3316(2) |
| Eu₂–Eu₃ | 0.3311(2) |
| Eu₂–Eu₄ | 0.3431(4) |
| Eu₂–Eu₅ | 0.3555(2) |
| Eu₂–Eu₆ | 0.3700(1) |
| Eu₂–Eu₇ | 0.3825(2) |

*Crystal structure data are standardized using the program Structure Tidy.*

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 Dataa for EuPt4B and Eu3Pt-B2

| parameter/com-pound | EuPt4B | Eu3Pt-B2 |
|---------------------|--------|----------|
| nominal composi-tion | Eu14Pt16B16.7 | Eu14Pt16B16.7 |
| space group | P63/mmm, No. 191 | R3m, No. 166 |
| structure type | CeCo4B | Ca2Al2Cu2 |
| formula from re-finement | EuPt4B | Eu3Pt-B2 |
| range for data col-lection | 2.09° < θ < 36.00° | 2.16° < θ < 29.98° |
| crys size | 40 × 40 × 25 μm³ | 35 × 35 × 15 μm³ |
| a [nm] | 0.56167(2) | 0.55477(2) |
| c [nm] | 0.74399(3) | 2.28963(11) |
| Z | 2 | 3 |
| reflax in refine-ment | 182 Fs > 4σ(Fs) of 1069 | 231 Fs > 4σ(Fs) of 777 |
| mosacity | <0.4 | <0.4 |
| no. of variables | 14 | 17 |
| R1 = Σ| | | |
| R1 [σ] = Fobs − Fcalc | 0.0259 (4) 0.0053(4) 0.0078(4) 0.0026(4) | 0.027 (4) 0.0053(4) 0.0078(4) 0.0026(4) |
| R2 | 0.035(2) | 0.0074(7) |
| GOF | 1.105 | 1.131 |
| extinction (Za-charaisen) | 0.0010(3) | 0.00050(6) |
| M1; occ. | Eu1 in 1a (0,0,0), 1.00; U1 = U2 = 0.042(1), 0.035(2), U3 = U4 = 0, 0.0209(6) |
| M1; occ. | Eu2 in 1b (0, 0, 1/2), 1.00; U1 = U2 = 0.0089(6), 0.0349(15), U3 = U4 = 0, 0.0044(3) |
| M3; occ. | Pt1 in 2d (1/3, 2/3, 1/2), 1.00; U1 = U2 = 0.0494(9), 0.0066(5), U3 = U4 = 0, 0.0248(3) |
| M4; occ. | Eu1 in 6i (1/2, 0, z), z = 0.19488(4), 1.00, 0.0102(3), 0.0070(3), 0.0068(4), U1 = U2 = 0, 0.0035(2) |
| M5; occ. | B in 2c (1/3, 2/3, 0), 1.00; U1 = U2 = 0.014(8), 0.002(11), U3 = U4 = 0, 0.007(4) |
| residual density, man. min [electrons/nm³] × 1000 | 4.94; −2.88 | 4.23; −4.66 |
| interatomic distances (nm) | | |
| Eu1–12Pt2 | 0.31605(3) | Eu1–3Pt3 | 0.32445(2) |
| Eu1–2Eu2 | 0.37200(2) | Eu1–3Pt1 | 0.32445(2) |
| Eu2–6Pt1 | 0.32428(1) | Eu2–3Pt1 | 0.32445(2) |
| Eu2–12Pt2 | 0.36113(4) | Eu2–3Pt1 | 0.32445(2) |
| Eu2–2Eu1 | 0.37200(2) | Eu2–12Pt2 | 0.31525(3) |
| Pt1–6Pt2 | 0.27896(4) | Eu2–2Eu1 | 0.33662(5) |
| Pt1–3Eu2 | 0.32428(1) | Pt1–2Eu1 | 0.31605(3) |
| Pt2–2B | 0.21751(4) | Pt2–2Eu1 | 0.31605(3) |
| Pt2–2Pt1 | 0.27896(4) | Pt2–2Eu1 | 0.31605(3) |
| Pt2–5Pt2 | 0.28999(1) | Pt2–3Eu2 | 0.33662(5) |
| Pt2–2Eu1 | 0.31613(4) | Pt2–12Pt2 | 0.31525(3) |
| Pt2–6Eu2 | 0.28908(4) | Eu1–3Eu1 | 0.33662(5) |
| Pt2–2Eu2 | 0.32982(12) | Eu2–12Pt2 | 0.31525(3) |
| B–6Pt2 | 0.21751(4) | Pt2–2Eu2 | 0.33662(5) |
| B–6Eu2 | 0.28908(4) | Pt2–12Pt2 | 0.31525(3) |
| B–6Eu2 | 0.32445(2) | Pt1–3Pt3 | 0.32445(2) |

[a] Crystal structure data are standardized using the program Structure Tidy.25

[i] Isotropic (Uiso) and anisotropic atomic displacement parameters (Uij) are given in [10² nm²].

chains of edge-connected platinum tetrahedra interlinked via europium atoms (Figure 1c). Trigonal prisms are formed by platinum atoms centered by boron. The 3636 kagome 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 CaCa3.
Both fragments are stacked via the hexagon formed by Pt1 atoms (Figure 2a, Table 1). The hexagonal face formed 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−Pt3 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 perpendicular 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 CaCu3 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 0.033682 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).

**Figure 1.** (a) Crystal structure of EuPt6B6 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° 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.

**Figure 2.** (a) Repeating block of Eu-centered polyhedra in Eu5Pt18B6. 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).
the heavy atoms analogous to that observed for Ca₃Ni₇B₂

structure solution by direct methods con-

duction. In the case of EuPt₄B, a possible reason may be that

anisotropy of the atom thermal

value solution by direct methods con-

are located in front of the rectangular faces of the

bonds are omitted. (b–c) Coordination spheres of Eu₁ (b), Eu₂ (c), Pt₂ (d), and Pt₁ (e).

MgCu₂-type Laves phase: an icosahedron formed by 6Pt₁ and

As compared to the prototype Ca₃Al₂Cu₂ structure,¹¹ signifi-

cant changes in the coordination sphere of atoms are observed

for the CeCo₃B₂-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

Eu₂Pt₆ in Eu₁Pt₂₆. (f) Twenty-membered cage capturing Ca₂ in the Ca₃Al₂Cu₂ structure.

■ STRUCTURAL RELATIONSHIPS

The investigated structures represent three families of struc-
tures revealing the Ca₃Cu₂-type 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 EuPt₂B₂ structure (CeCo₄B₂ type) (Figure 5f) consists of
alternating slabs of CaCu₃ type (A) (Figure 5a) and slabs of
its ternary derivative CeCo₂B₂ type (B) (Figure 5b). It is a
simplest representative of the structural series described in
TYPD₂²⁵ under the general formula Rₘ₀₃Tₙₐ₃Mₗₑ₉ with m = 1, n = 1 (m and n correspond to number of Ca₃Cu₂-type and
CeCo₂B₂-type blocks, respectively). Similar to the prototype
structure, the hexagonal channels filled with Eu are formed by
eedge-connected trigonal prisms [Bₙₐ₃] in EuPt₂B₂ and alternate with 18-membered platinum cages, capturing europium atoms
along the c axis. While in the CeCo₂B₂ 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 3. (a) Perspective view of the Eu₃Pt₇B₂ 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

(3). The boron position was successfully detected from

difference Fourier synthesis. The structure is composed of

CeCo₂B₂- and MgCu₂-type fragments alternating along

the 14-atom cage.

Eu₃Pt₇B₂. For Eu₂–Pt–B₂, systematic extinction characteristic for

the trigonal space group R₃m and unit cell dimensions proposed isotypism with the Ca₃Al₂Cu₂-type structure.¹¹ Structure

solution by direct methods confirmed the arrangement of the heavy atoms analogous to that observed for Ca₃Ni₂B₁₀

(Table 2). The boron position was successfully detected from
difference Fourier synthesis. The structure is composed of

CeCo₂B₂- and MgCu₂-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

Eu₂–Pt–B₂ unit cell along the c axis is presented in Figure 4a,
showing triangular prisms formed by 6 Pt₁ around B. The

CeCo₂B₂-type slabs are formed by 12 Pt₁ and 2 Eu 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 Ca₃Ni₂B₁₀

where dₙₐ₃ = 0.2978 nm). The coordination polyhedron of Pt₂
exhibits a shape analogous to those of transition atoms in the binary

U₁₁ = U₁₃ (U₁₃) of ca. 4:1, while Pt₁ shows enlarged values U₁₁

and U₁₃ (U₁₃/U₁₁ 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 (P6₂m, P6₃m, P6₃m, P6₁m, P6/m, 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 struc-
tures related to the CeCo₃B₂ type, such as In₅Ir₉B₄

(Table 2). The boron position was successfully detected from

difference Fourier synthesis. The structure is composed of

CeCo₃B₂- and MgCu₂-type Laves phase: an icosahedron formed by 6Pt₁ and

6Eu₁ reveals interatomic distances (Table 2) which are com-
parable with distances in Eu₁Pt₂₆ (MgCu₂ 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 Eu₁Pt₂₆ (Figure 4b).

As compared to the prototype Ca₃Al₂Cu₂ structure,¹¹ signifi-
cant changes in the coordination sphere of atoms are observed

for the CeCo₃B₂-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

Eu₂–Pt₁ in Eu₁Pt₂₆ (dₖₙ₉–ₙ₉ = 0.29959 nm), thus delivering a different shape of the coordination polyhedron of Ca₃ (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 Eu₁Pt₂₆.

In contrast to Eu₁Pt₂₆, in the present structure none of the
atoms show significant anisotropy in their thermal vibration
(Table 2).

U₃₀₃Tₙₐ₃Mₗₑ₉ with m = 1, n = 1 (m and n correspond to number of Ca₃Cu₂-type and
CeCo₂B₂-type blocks, respectively). Similar to the prototype
structure, the hexagonal channels filled with Eu are formed by
eedge-connected trigonal prisms [Bₙₐ₃] in Eu₁Pt₂₆ and alternate with 18-membered platinum cages, capturing europium atoms
along the c axis. While in the CeCo₂B₂ 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 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 Ca₃Al₂Cu₂ structure.
In contrast to the relatively small unit cell and simple structure of EuPt$_4$B, the two remaining structures, Eu$_3$Pt$_7$B$_2$ and Eu$_5$Pt$_{18}$B$_6$-$x$, exhibit rather large unit cells and nontrivial stoichiometries. Eu$_3$Pt$_7$B$_2$ is an ordered variant of the PuNi$_3$ type. This binary compound belongs to the rhombohedral branch of a structural series formed within composition range RM$_2$-$RM_5$ by stacking the fragments of CaCu$_5$ type and Laves phase and can be described by the formula $R_{2m}^nM_{4m+5}^n$, where $m$ accounts for the number of Laves-type slabs ($R_2M_4$) and $n$ is a number of CaCu$_5$-type slabs. 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$_3$B$_2$- and Laves-type structural slabs (Ca$_3$Ni$_7$B$_2$, Eu$_3$Pt$_7$B$_2$) follow the formula $R_{2+}^nM_{4+3}^nX_{2n}$: $2$MgCu$_2$ + $n$CeCo$_3$B$_2$. The ordered version of PuNi$_3$ was first identified in the Ca-Al-Cu system. In Ca$_2$AlCu$_2$-type structures with boron (Ca$_3$Ni$_7$B$_2$, Eu$_3$Pt$_7$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 5 shows the arrangement of CeCo$_3$B$_2$-type slabs (B) and MgCu$_2$-type slabs (C) in the Eu$_3$Pt$_7$B$_2$ structure.

The structure of Eu$_5$Pt$_{18}$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$_3$B$_2$ (B), and the third reveals the slab of the site-exchange variant of the ThCr$_2$Si$_2$ structure with B atoms adopting the sites of Cr (D). The body-centered structure of ThCr$_2$Si$_2$ (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). The unit cell of ThCr$_2$Si$_2$ 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 and particularly developed recently for pnictides due to discovery of superconductivity in the series of iron arsenides with ThCr$_2$Si$_2$ type. Ternary rare-earth borides with a ThCr$_2$Si$_2$-type structure are...
quite rare except for few representatives, such as \( \text{RECo}_2\text{B}_2 \) (\( \text{RE} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}−\text{Er} \)), \( \text{REFe}_2\text{B}_2 \) (\( \text{RE} = \text{Y}, \text{Gd}−\text{Tm}, \text{Lu} \)), and \( \text{BaRh}_2\text{B}_2 \). 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 \( \text{ThCr}_2\text{Si}_2 \) type \( \text{LaCo}_2\text{B}_2 \) (\( a = 0.36108 \text{ nm}, c = 1.02052 \text{ nm}, z = 0.3324(5) \)) revealed a relatively short Co−B bond (e.g., 0.20 \text{ nm}), indicating certain compression of the CoB layer along the c axis and an elongated La−B contact distance (0.308 \text{ nm}).

There are two BaAl\(_4\)-type derivative structures encountered for composition \( \text{RET}_2\text{X}_2 \): the structures of \( \text{ThCr}_2\text{Si}_2 \) (described above) and \( \text{CaBe}_2\text{Ge}_2 \), which is built by intergrowth of \( \text{ThCr}_2\text{Si}_2 \)-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., formation of compounds revealing only inverse \( \text{ThCr}_2\text{Si}_2 \)-type arrangement is rare; however, this arrangement occurs as slabs in intergrown structures (for example, in \( \text{CeNiSi}_2 \) and \( \text{CaRh}_2\text{B}_2 \)). Among borides, formation of inverse \( \text{ThCr}_2\text{Si}_2 \)-type structure was found for \( \text{ZnIr}_2\text{B}_2 \) where layers of edge-connected \([\text{BiR}_4]\) tetrahedra (Ir in 4\( \bar{e} \)) are separated by 4\( \bar{d} \) networks of zinc atoms (Zn in 2\( a \)). Similarly, in \( \text{Eu}_5\text{Pt}_{18}\text{B}_6 \), 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 \( \text{Eu}_5\text{Pt}_{18}\text{B}_6 \)-structure is 0.1978(1) \text{ nm} (and 0.2239(8) \text{ nm} for Pt11 in split position) as compared to the length of the Ir−B bond of 0.2150 nm in \( \text{ZnIr}_2\text{B}_2 \) showing the tetrahedral angles 2\( × \)137.07\( ^\circ \), 2\( × \)105.25\( ^\circ \), 2\( × \)90.27\( ^\circ \) in \( \text{Eu}_5\text{Pt}_{18}\text{B}_6 \) (2\( × \)126.09\( ^\circ \), 2\( × \)100.79\( ^\circ \), 2\( × \)102.91\( ^\circ \) for Pt11) and 4\( × \)121.68\( ^\circ \), 2\( × \)87.11\( ^\circ \) in \( \text{ZnIr}_2\text{B}_2 \). Because of limited spatial dimension of the \( \text{ThCr}_2\text{Si}_2 \) slab in the \( \text{Eu}_5\text{Pt}_{18}\text{B}_6 \)-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 Mulliken overlap population analysis suggested that the element with greater electronegativity is more strongly bound in the 4\( e \) site. The atoms site preferences in the structures of three discussed borides (i.e., \( \text{LaCo}_2\text{B}_2 \), \( \text{ZnIr}_2\text{B}_2 \), and \( \text{ThCr}_2\text{Si}_2 \)-type block in the \( \text{Eu}_5\text{Pt}_{18}\text{B}_6 \)-structure) 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 more strongly bound in the 4\( s \) site. Suggested that the element with greater electronegativity is more strongly bound along the c axis and an elongated La−B contact distance (0.308 \text{ nm}).

In order to obtain the electronic configuration (EC) of the Eu ions and thus the magnetic state, the magnetization of \( \text{EuPt}_4\text{B} \) 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 6.** Lattice constants of the \( \text{REPt}_4\text{B} \) series. Values for \( \text{La}−\text{Pr} \) and \( \text{Nd} \) are taken from the literature. For the europium compound, lattice parameters were obtained from Rietveld refinement of single-phase \( \text{EuPt}_4\text{B} \) alloy used for physical properties measurements.

Similarly, in \( \text{Eu}_3\text{Pt}_{7}\text{B}_2 \), the Eu−Eu contacts are long and the distances between Eu and Pt atoms are rather heterogeneous, ranging within 0.3128 and 0.3611 \text{ nm}.

**Magnetic Properties**

In order to obtain the electronic configuration (EC) of the Eu ions and thus the magnetic state, the magnetization of \( \text{EuPt}_4\text{B} \) 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 \( \text{EuPt}_4\text{B} \) 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 \text{ T} above the ordering temperature being indicative that the samples are free from magnetic impurities and other...
Both EuPt4B and Eu3Pt7B2 are found to order ferromagnetically. Eu3Pt7B2 shows a transition at 57 K, while EuPt4B 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 $\chi = \chi_0 + C/(T - \theta)$. The paramagnetic Curie temperatures $\theta$ for EuPt4Bc are 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 Eu3Pt7B2 and EuPt4Bc, respectively (solid lines, Figure 7), with a temperature-independent susceptibility $\chi_0$ of about $3 \times 10^{-6}$ cm$^3$/g for both compounds. While the paramagnetic moment of Eu3Pt7B2, recounted per one europium atom is almost that expected for the theoretical value of the free Eu$^{3+}$ ion ($\mu_{\text{eff}} = 7.94 \mu_B$) the effective moment obtained for EuPt4Bc is significantly smaller, pointing to a mixed- or -intermediate valence state of Eu. The fact that Eu in EuPt4B 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 EuPt4Bc can be represented as $\mu_{\text{eff}} = \sqrt{\mu_{\text{Eu}^{2+}}^2 + (1-x)\mu_{\text{Eu}^{3+}}^2}$. 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$^{3+}$ 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 EuPt4B 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 magneto-crystalline anisotropy due to the CaCu5 building blocks. On the contrary, there is hardly any difference for ZFC and field cooling detectable even in the low-field regime for Eu3Pt7B2 yielding also reversible magnetic isotherms without a significant hysteresis, which means the coercivity is 3 orders of magnitude smaller than for EuPt4Bc.

A comparison of the magnetic isotherms of both compounds is shown in Figure 10, where the isotherms are displayed as $M$ versus $H$ plots (Arrott plots). It should be noted that in the case of EuPt4Bc with pronounced hysteresis only the de-magnetization 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 59 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 EuPt4B (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.
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 59). Using this simple estimate we obtain for Eu$_3$Pt$_7$B$_2$ 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 Eu$_3$Pt$_7$B$_2$ $M_S = 7.43 \mu_B$/mol-Eu and $M_0 = 7.24 \mu_B$/mol-Eu and for EuPt$_4$B $M_S = 5.13 \mu_B$/mol-Eu and $M_0 = 3.85 \mu_B$/mol-Eu. Both the saturation as well as the spontaneous magnetization of Eu$_3$Pt$_7$B$_2$ is well above the value expected for a Eu$^{2+}$ ion ($M_s = g_j \mu_B$), indicative that a substantial 5d conduction electron polarization contributes to the total moment. The significant smaller saturation and spontaneous moment of EuPt$_4$B 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 Eu$^{2+}$ state in EuPt$_4$B, while a somewhat smaller fraction of about 53% is obtained using the ratio of the spontaneous moments. This latter is an underestimate caused presumably by the large high-field susceptibility of EuPt$_4$B also visible in the larger slope of the Arrott plot in comparison to that of Eu$_3$Pt$_7$B$_2$.

**SPECIFIC HEAT**

Further information on the ground state properties of EuPt$_4$B and Eu$_3$Pt$_7$B$_2$ can be gained from specific heat measurements. Experimental results are shown in Figure 11.

Both EuPt$_4$B and Eu$_3$Pt$_7$B$_2$ exhibit distinct $\lambda$-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 $\delta C_p = 56 \text{ J/mol}\cdot\text{K}$ in the case of Eu$_3$Pt$_7$B$_2$ corresponds well to a mean-field-like transition of a $j = 7/2$ system [$\delta C_p = N^*g_0j(j+1)/((2j^2 + 2j + 1))$, where $N$ is the number of RE atoms/mol. Considering three Eu$^{2+}$ atoms per mole yields $\delta C_p = 60.39 \text{ J/mol}\cdot\text{K}$, in fair agreement with experiment. The jump of the specific heat of EuPt$_4$B right at the magnetic phase transition temperature is only about 13 J/mol\cdotK 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% Eu$^{2+}$ and 35% Eu$^{3+}$), which is in line with the broad range of estimates from the magnetic data where we obtained 53% Eu$^{2+}$ as a lower and 80% Eu$^{3+}$ as an upper limit.

Low-temperature heat capacity data were analyzed in terms of a ferromagnetic spin wave model including a spin wave gap $\Delta$, i.e., $C_p = \gamma T + \beta T^3 + \delta T^{5/2} \exp(-\Delta/T)$ with $\gamma$ the Sommerfeld value and $\beta$ proportional to the low-temperature Debye temperature $T_D^{\beta} \theta_D^{\beta} = (1944 N/\rho)^{1/2}$. 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 mJ/mol-K$^2$, resulting in an effective 68 mJ/mol-K$^2$ per europium atom, $\beta = 0.000222$ and 0.000702 J/mol-K$^2$, $\delta = 0.36$ and 0.46 J/mol-K$^3/2$, and $\Delta = 12.6$ and 10 K for EuPt$_4$B$_2$ and Eu$_3$Pt$_7$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 Eu$_3$Pt$_7$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$_3$Co$_6$, Gd$_3$Rh$_6$ and Gd–Ni$_6$ binaries.

**ELECTRICAL RESISTIVITY**

We studied the electrical resistivity $\rho$ of EuPt$_4$B$_2$ and Eu$_3$Pt$_7$B$_2$ from 0.3 K to room temperature (see Figure 12). Data evidence metallic behavior in both cases with rather low overall resistivities. Unlike Eu$_3$Pt$_7$B$_2$, in the resistivity curve of EuPt$_4$B$_2$ a slight change of slope is observed 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 Eu$_3$Pt$_7$B$_2$ and EuPt$_4$B$_2$. Although the anomaly in both compounds is of ferromagnetic origin, application of a magnetic field causes differential responses of the resistivity. The resistivity of EuPt$_4$B$_2$ decreases slightly in the entire temperature range studied, and the $\rho(T)$ anomaly is suppressed by fields of 6 T. Magnetoresistance of Eu$_3$Pt$_7$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 Eu$_3$Pt$_7$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 Eu$_3$Pt$_7$B$_2$ as compared to EuPt$_4$B$_2$ might follow from the fact that the overall resistivity, specifically the residual resistivity, is much lower here than in the case of EuPt$_4$B$_2$.

To quantitatively evaluate $\rho(T)$ of Eu$_3$Pt$_7$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 Eu$_3$Pt$_7$B$_2$ can be described by

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

where $\rho_{\text{BG}} = C(T^\delta/(\theta_d^5))(e^{\delta/\theta_d}(e^{\theta_d/\Delta} - 1))$ is the Bloch–Grüneisen term corresponding to the resistivity originating from scattering of conduction electrons on phonons and $\rho^\text{mag} = \rho_0 + \rho_{\text{mag}}$, with $\rho_{\text{mag}}$ describing the interaction of conduction electrons with localized magnetic moments. In the absence of crystalline electric field effects, $\rho_{\text{mag}}$ is temperature independent in the paramagnetic temperature range. $\rho_0$ is the residual resistivity. A Debye temperature $\theta_d = 312$ K and $\rho_0^\text{mag}$ are 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 $\omega \approx k^5$ 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 $\rho = \rho_0 + AT^2$, $\rho_0 = 7.64 \mu\Omega$-cm was obtained.

The low-temperature part of the resistivity of EuPt$_4$B$_2$ is in good agreement with the temperature dependence of a ferromagnetic material. Experimental data are well accounted for by $\rho = \rho_0 + B\Delta(1 + (2T/\Delta)e^{-\Delta/T})$ with $\Delta = 12.8$ 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 CaCu₅-type derivative family of structures, revealing three different structural series. Eu₅Pt₄B forms a CeCo₁₂B type and is composed of CaCu₅- and CeCo(B₂)₅-type fragments stacked along the c axis; Eu₄Pt₂B₂ is built of CeCo₁₂B₂- and MgCu₆-type slabs and exhibit an ordered variant of PuNi₂, namely, Ca₃Al₃Cu₂ 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 [BP₆].

Unique stacking of Ca₃Cu₂-, CeCo₁₂B₂-, and ThCr₂Si₂-type slabs has been uncovered in the Eu₅Pt₁₈B₆₋ₓ structure; the atom arrangement in the ThCr₂Si₂-type block is rare for the distribution of Pt and B atoms on Si and Cr atom sites, respectively (BaAl₂-type derivative structures), thus changing the coordination of the transition metal as compared to other representatives of a large family of ThCr₂Si₂-type compounds and exhibiting chains of edge-connected platinum tetrahedra [BP₄] running along the a-axis direction. With respect to Eu–Eu linkage, the europium atoms are interconnected infinitely along the c axis in both Eu₅Pt₂B and Eu₄Pt₂B₂ structures. The Eu₅Pt₁₈B₆₋ₓ structure exhibits the repeating blocks of 5 fused polyhedra of Eu linked in a sequence —ThCr₂Si₂—CeCo₁₂B₂—CaCu₅—CeCo₁₂B₂—ThCr₂Si₂—; the units are shifted for a 1/2 along the b-axis direction with respect to each other, forming blocks which are interlinked via ThCr₂Si₂-type fragment along the c axis. Positioning of the B atom on the Cr Wyckoff site in the ThCr₂Si₂-type slab and consequently its nearest tetrahedral coordination plays a decisive role in formation of Eu₅Pt₁₈B₆₋ₓ structure, serving as a linking entity (Figure 14) for the repeating structural units of fused Eu polyhedra.

Although Eu₅Pt₂B 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% Eu³⁺ and 50% Eu²⁺ 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 Eu₄Pt₂B₂ 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 mJ/mol·K², 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 Eu₅Pt₂B, Eu₄Pt₂B₂, and Eu₅Pt₁₈B₆₋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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