Synthesis, Crystal Structures, and Physical Properties of the New Zintl Phases $A_{21}Zn_4Pn_{18}$ ($A = Ca, Eu$; $Pn = As, Sb$)— Versatile Arrangements of $[ZnPn_4]$ Tetrahedra

Nian-Tzu Suen, Yi Wang, and Svilen Bobev^{*}

Department of Chemistry and Biochemistry, University of Delaware,
Newark, Delaware 19716, U.S.A.

^{*} Corresponding author: Prof. Svilen Bobev; Department of Chemistry and Biochemistry
University of Delaware; Newark, DE 19716
Phone: (302) 831-8720 / Fax: (302) 831-6335 / e-mail: bobev@udel.edu

Abstract

Four new Zintl phases, $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ have been synthesized by metal flux reactions. Their structures have been established from single-crystal X-ray diffraction. Despite the similar chemical makeup and the identical formulae, the structures of the four compounds are not the same— $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ crystallize in the monoclinic space group $C2/m$ (No.12, $Z = 4$) with the $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ structure type, while $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ adopts the $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ structure type with the orthorhombic space group $Cmce$ (No.64, $Z = 8$). Both structures are based on ZnAs_4 or ZnSb_4 tetrahedra, linked in slightly different ways, and Ca^{2+} and Eu^{2+} cations that fill the space between them. The structural relationships between the title compounds and other known ternary phases with intricate structures are discussed. Electrical resistivity measurement on single-crystalline $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ suggests an intrinsic semiconductor behavior with a band gap of ca. 0.2 eV. The temperature dependent DC magnetization measurement on the same material indicates Curie-Weiss paramagnetism in the high-temperature regime, and a spontaneous antiferromagnetic ordering below 8 K. The calculated effective moments of Eu confirm the divalent Eu^{2+} ground state, as expected from the Zintl-Klemm concept.

Keywords: crystal structure, single-crystal X-ray diffraction, electronic structure calculations, calcium, europium, antimony, arsenic.

Introduction

Zintl phases formed between the alkali-, alkaline-earth, rare-earth metals and the groups 12–15 elements have generated much attention over the years [1-17]. The compositions, crystal structures and physical properties of Zintl phases are strongly related to each other and these relationships can be explained by Zintl concept [4]. Many Zintl phases such as $\text{Yb}_{14}\text{MnSb}_{11}$ [5], BaGa_2Sb_2 [6], and $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$ [7] have shown very promising potential as thermoelectric materials in the future. It has been pointed out that the bonding characteristics of such compounds are of critical importance to their superior thermoelectric properties [8].

Inspired by these discoveries, we embarked on a series of exploratory syntheses, investigations of the crystal chemistry, and magnetic and transport properties of new compounds in the ternary systems $A\text{--Mn--Pn}$, $A\text{--Zn--Pn}$ and $A\text{--Cd--Pn}$ (A = alkaline-earth metals, as well as the nominally divalent Eu and Yb from the lanthanide block; Pn = pnictogen elements) [9-17]. In recent years, our own research, as well as the research from other laboratories have confirmed that there are structural similarities among the Mn-, Zn- and Cd-ternary pnictides, whose structures are typically based on MnPn_4 , ZnPn_4 , and CdPn_4 tetrahedra. For example, the tetrahedral building units can be isolated like in $\text{Yb}_{14}\text{MnSb}_{11}$ [9], or interlinked in various ways as in the ribbons reported for $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ and $\text{Eu}_{11}\text{Zn}_6\text{Sb}_{12}$ [10]; the layers in $\text{Ba}_3\text{Cd}_2\text{As}_4$ and $\text{Ba}_3\text{Zn}_2\text{As}_4$ [11]; and the clusters in $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$ [12] and $\text{Ca}_{21}\text{Mn}_4\text{Bi}_{18}$ [13]. The above-named examples are not representative of the rich structural chemistry—there are a variety of other arrangements, as seen in $A\text{Mn}_2\text{Pn}_2$, $A\text{Zn}_2\text{Pn}_2$, and $A\text{Mn}_2\text{Pn}_2$ [15], as well as in $A_2\text{ZnPn}_2$ and $A_2\text{CdPn}_2$ (A = Ca, Sr, Ba, Eu, Yb; Pn = P, As, Sb) [16,17]. Interestingly, in the cases of $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$

[12] and $\text{Ca}_{21}\text{Mn}_4\text{Bi}_{18}$ [13], the polyanionic clusters made of MnSb_4 and MnBi_4 tetrahedra were considered, for some time, exclusive to the Mn-bearing compounds. Subsequently, our efforts to search for other possible analogous compounds in the $A\text{--Zn--Pn}$ and $A\text{--Cd--Pn}$ systems were successful, and we synthesized and structurally characterized $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$, $\text{Sr}_{21}\text{Cd}_4\text{Sb}_{18}$, $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$, and $\text{Ba}_{21}\text{Cd}_4\text{Bi}_{18}$ [14]. Notice that despite the fact that all four compounds are isoelectronic to each other, they are not isostructural. For example, $\text{Sr}_{21}\text{Cd}_4\text{Sb}_{18}$ crystallizes in the $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ structure type (monoclinic space group $C2/m$ (No.12, $Z = 4$)), while $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ adopts its own structure type (orthorhombic space group $Cmce$ (No.64, $Z = 8$)) [18]. Up until now, there were no other compounds known with the same structure, and the herein presented $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ is only the second known phase of this family. The other three reported Zintl phases— $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, and $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ are isotypic with $\text{Sr}_{21}\text{Cd}_4\text{Sb}_{18}$ [14]. The structural relationships between the title compounds and other related compounds such as $\text{Ca}_{11}\text{InSb}_9$ [19], $\text{Ca}_{10}\text{Mg}_2\text{Sb}_9$ [20], and $\alpha\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ [13] are included and discussed. The electrical resistivity and the magnetic susceptibility measurements for $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$, measured on a single-crystal from room temperature to 5 K, are presented as well.

Experimental

Synthesis

Calcium and Europium metals are sensitive to air, therefore all manipulations were carried out in an argon-filled glove box with $\text{O}_2/\text{H}_2\text{O}$ levels below 1 ppm, or under vacuum. The metals were purchased from commercial sources and were used as received: Ca (Aldrich, granules, 99.9%), Eu (Alfa, ingots, 99.9%), Zn (Alfa, shot,

99.999%), Sb (Alfa, shot, 99.99%) and Pb (Alfa, granules, 99.999%). The surface of the Eu ingot was cleaned with a blade before cutting into small pieces.

All reactions were done in the same fashion, using molten Pb as a flux. The corresponding elements in the ratio of $A:Zn:Pn:Pb = 21:4:18:100$ ($A = \text{Ca}$ or Eu ; $Pn = \text{As}$ or Sb) were loaded into 2 cm^3 alumina crucibles. The alumina crucibles were transferred into fused silica tubes and connected to a vacuum line. After the pressure reached below 10^{-3} torr, the samples were flame-sealed. The ampoules were placed in programmable muffle furnaces and were heated to 1273 K at a rate of 200 K/h, allowed to equilibrate at this temperature for 24 hrs, and then cooled down to 773 K at a rate of 4 K/h. The reactions were taken out from the furnace and the Pb flux was quickly removed by a centrifuge. The reactions products were small, irregular crystals with dark-silver luster. According to the powder X-ray diffraction patterns, however, the products were not single-phase materials. The latter is especially true for the As-containing reactions. This observation is most likely related to the low sublimation point of As (887 K) [21], accounting for the loss of some arsenic before the molten mixture reaches the reaction temperature. Attempts to run the reactions at lower temperatures were pursued but were unsuccessful.

In order to obtain phase-pure samples for property measurements, several other methods were employed. Among them, a two-steps synthesis method appeared to be advantageous. First, $\text{Zn-}Pn$ precursors ($Pn = \text{As}$ and Sb) were prepared by loading the elements in a ratio of 1:1. The mixtures were enclosed in evacuated fused silica tubes and were heated from room temperature to 793 K over 12 hours, held at 793 K for 24 hours, then cooled down to room temperature over 36 hours. The pre-reacted $\text{Zn-}Pn$ (Pn

= As and Sb) materials were ground into fine powders and loaded in alumina crucibles with the necessary amounts of Ca (or Eu) and Pn ($Pn = \text{As and Sb}$) in order to achieve the elemental ratio 21:4:18. After the mixtures were weighed and sealed in evacuated fused silica tubes, the reactions proceeded following the same scheme and heating profile mentioned above.

The obtained crystals were still small (*ca.* 0.5 mm in each dimension) and irregularly shaped; they were found to be moderately air-/moisture-sensitive and could not be handled freely in the ambient atmosphere. The small size of the available crystals, combined with small amounts of residual Pb flux, as well as the air-sensitivity hampered the property measurements. In particular, electrical resistivity measurements that require use of contacts were problematic.

To avoid the use of Pb flux, the synthesis conditions were modified and the reactions were ran “on stoichiometry” in welded Nb tubes. These experiments may have produced the desired phases, but lacked crystallographic quality crystals, and the interpretation of the powder patterns was not unambiguous. We also attempted to make the respective bismuthides, as well as the Yb-analogs of $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, (the ionic radii of Ca^{2+} and Yb^{2+} are very close, 1.00 Å and 1.02 Å, respectively [22]), but such reactions did not produce the targeted phases—work to identify the products is currently ongoing.

Powder X-ray Diffraction

X-ray powder diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer using filtered Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å). The data were gathered in θ – θ scan mode ($2\theta_{\text{max}} = 70^\circ$) with step-size 0.05° and 1 sec/step

counting time. The data were analyzed with the JADE 6.5 software package. It must be noted here, that due to the complex structures/large unit cells/low symmetry of title compounds, their diffraction patterns were very complicated—it is apparent that in order to resolve all Bragg peaks, much higher resolution instrument is needed. As a result, the presence of secondary phases could not be unequivocally ruled out based on the powder diffraction patterns alone. More clear evidence for the presence of some yet unidentified phases, as well as the common $\text{Ca}_{11}\text{Sb}_{10}$ and $\text{Eu}_{11}\text{Sb}_{10}$ binaries, was brought about by single-crystal X-ray work.

Since the tabletop powder diffractometer is operated in a glove-box, the sensitivity of the samples to air could be assessed by comparing the runs performed before and after exposure to air. The powder patterns after a few hours in air appear identical to the ones from the “fresh” samples, but peak broadening and intensity changes observed after a more prolonged exposure to air (ca. 1 week) suggest that the samples begin to decompose.

Single-crystal X-ray diffraction

For the purpose of collecting intensity data on the single-crystal diffractometer, the crystals were picked in the glove-box, and cut to desired dimensions under Paratone-N oil. Preliminary rotation images were acquired to index the unit cell and to estimate the crystal quality. Full spheres of reciprocal data (frame width 0.4° in ω at different θ settings) were collected on a Bruker *SMART* and *APEX II* CCD-based diffractometer diffractometer (monochromatized Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The temperature was kept at 200 K by cold nitrogen stream during the data collection. The programs *SMART* and *APEX II* [23] were used to acquire and process the data, and *SAINT* [24] was

used to reduce and integrate the raw data. *SADABS* [25] was used for semi-empirical absorption correction. The structures were solved by direct methods and refined with the full-matrix least squares on F^2 method, as implemented in *SHELXTL* [26]. Refined parameters included the scale factor and atomic positions with the corresponding anisotropic displacement parameters. For uniformity, before the final refinement steps, the atomic positions were standardized by *STRUCTURE TIDY* [27].

Important crystallographic information for $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ is provided in Table 1. The final atomic coordinates and equivalent isotropic displacement parameters are given in Tables 2-5. Selected interatomic distances are tabulated in Table 6. CIFs have also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers CSD-429152 for $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, CSD-429153 for $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, CSD-429154 for $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and CSD-429155 for $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$.

Lastly, we would like to note that the crystal structures reported herein are all obtained from crystals obtained via the flux-method (Pb in this case). As a result, one might be concerned about inadvertent flux inclusions. Since Pb is a very heavy element, we could argue that the single-crystal refinements can ascertain the lack of thereof. In all cases, freeing the site occupation factor for an individual site, while the remaining ones were kept fixed showed no signs for a possible homogeneity range, as all atomic positions were fully occupied. The final difference Fourier maps in all refined structures were flat, with highest maxima and deepest minima not larger than ca. $\pm 2\text{-}3\text{ e}^-/\text{\AA}^3$. The

residual density was highest for the $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$, reflecting the crystals' poorer quality.

Data collections for crystals from stoichiometric melts were also done to compare with the flux-grown crystals. The latter were of inferior quality and are not reported. Structure solutions and refinements in these cases did confirm the structure model with no indications of unaccounted for residual electron density.

Property Measurements

Field-cooled (FC) direct-current (dc) magnetization measurements on polycrystalline samples were performed in a Quantum Design PPMS. Large single-crystals of $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ were selected under a microscope from freshly prepared samples, and were ground into powders, which were then weighed and loaded in gel capsules. To prevent the material from moving under the magnetic field, the empty volume of the gel capsule was filled with cotton. Preparing the material was done in the glove-box, and once ready, the filled gel capsules were immediately transferred to the chamber of the PPMS. The measurements were carried out with an applied magnetic field of 5000 Oe in the temperature range 5 to 300 K. The raw data were corrected for the holder's diamagnetic contribution and converted to molar susceptibility ($\chi_m = M/H$).

The resistivity measurement was done also in the PPMS by four probes method, using single-crystalline sample of $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ with dimensions $0.5 \times 0.5 \times 1$ mm. The measurement was carried out from 100 to 300 K with excitation current of 10 mA. Four platinum wires were connected to the crystal using EPO TEK H20 silver epoxy. Measurements both on heating and cooling were taken for the same specimen to ensure reproducibility.

Results and Discussion

Structures and chemical bonding

The four new ternary compounds $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ form with two different structure types. $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ crystallize with the $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ structure type [12,13] (monoclinic space group $C2/m$, No. 12; Pearson code $mC172$), while $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ adopts the $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ structure type [14] with the orthorhombic space group $Cmce$ (No. 164; Pearson code $oC344$). The two structures are depicted in Figure 1, using the crystallographic data for $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$, respectively. These two structure types have been studied in the past [12-14], therefore only a brief discussion will be provided below.

In $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ (Figure 1a), there are a total of 29 crystallographic sites in the asymmetric unit: 12 for Eu atoms, 3 for Zn atoms and 14 for As atoms (Table 4). This structure boasts a large unit cell with 84 Eu^{2+} cations, 16 As^{3-} anions (i.e., isolated atoms without any covalent bonds), 6 $[\text{As}_2]^{4-}$ dumbbells (one homoatomic bond), and two $[\text{Zn}_8\text{As}_{22}]^{48-}$ clusters of eight corner- and edge-shared $[\text{ZnAs}_4]$ subunits. One can also visualize these octameric species as being formed by 4 diborane-like $[\text{Zn}_2\text{As}_6]$ subunits, where two of them are symmetry-inequivalent and joined together through a corner-shared As atom into a $[\text{Zn}_4\text{As}_{12}]$ tetramer—an inversion symmetry generates the “other half” and connects the two via an As–As linker (Figure 2). This homoatomic bond accounts for the “48–” charge on the gigantic $[\text{Zn}_8\text{As}_{22}]^{48-}$ cluster (i.e., $8 \times \text{Zn}^{2+} + 20 \times \text{As}^{3-} + 2 \times \text{As}^{2-}$).

In the $[\text{As}_2]$ dimers and the $[\text{Zn}_8\text{As}_{22}]$ polyanions, the corresponding As–As distances are within the range of 2.464(5) Å–2.530(5) Å, while the Zn–As distances vary

from 2.529(2) Å to 2.778(3) Å, respectively. These numbers are close to the sum of the respective Pauling covalent radii ($r_{\text{As}} + r_{\text{As}} = 2.42$ Å; $r_{\text{Zn}} + r_{\text{As}} = 2.43$ Å) [28], which implies considerable covalent bonding character of the interactions within in these polyanions. Additionally, one can also notice that in $[\text{Zn}_8\text{As}_{22}]$, there are two distinctly different Zn–Zn interatomic distances, which are exemplified by $d_{\text{Zn2–Zn3}}$ (2.694(2) Å) and $d_{\text{Zn1–Zn1}}$ (3.582(2) Å). The relatively short Zn2–Zn3 distances suggest possible bonding interaction between these two Zn atoms (Pauling metallic radius for Zn is 1.339 Å [28]). This is not uncommon in this structure type, where some of the $[\text{ZnAs}_4]$ subunits are edge-shared ($\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$, $\text{Sr}_{21}\text{Cd}_4\text{Bi}_{18}$ and $\text{Eu}_{21}\text{Cd}_4\text{Bi}_{18}$ also have relatively short Mn–Mn and Cd–Cd contacts in the same crystallographic positions). Other structures, such as $\text{RE}_2\text{Zn}_5\text{Ti}$ ($\text{RE} = \text{Ce} - \text{Nd}$; $\text{Ti} = \text{Si, Ge, Sn}$) [29], also show Zn–Zn distances on the order of 2.7 Å, although these structures are based on polyhedral Zn fragments, and are arguably Zn-rich, where Zn–Zn bonding is essential to the overall stability.

The structure of $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ is very similar to that of $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ (Figure 1). There are also 29 crystallographic sites in the asymmetric unit: 12 for Eu atoms, 3 for Zn atoms and 14 for Sb atoms (Table 5). In $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$, one unit cell contains 168 Eu^{2+} cations, 32 isolated Sb^{3-} anions, 8 $[\text{Sb}_2]^{4-}$ dumbbells, and 8 $[\text{Zn}_4\text{Sb}_{12}]^{26-}$ polyanions. The Zn atoms are bound to four Sb atoms and form $[\text{ZnSb}_4]$ tetrahedra. These tetrahedra further link to each other to form diborane-like $[\text{Zn}_2\text{Sb}_6]$ subunits, and two $[\text{Zn}_2\text{Sb}_6]$ subunits joint together through a corner-shared Sb atom to built $[\text{Zn}_4\text{Sb}_{12}]$ polyanion.

The interatomic distances within the $[\text{Sb}_2]$ dimers and the $[\text{Zn}_4\text{Sb}_{12}]$ polyanions range from 2.824(1) Å to 2.895(1) Å, and from 2.720(1) Å to 2.936(1) Å, respectively.

Those values are in excellent agreement with the sum of Pauling covalent radii ($r_{\text{Sb}} + r_{\text{Sb}} = 2.78 \text{ \AA}$; $r_{\text{Zn}} + r_{\text{Sb}} = 2.60 \text{ \AA}$) [28], and comparable with those reported ternary zinc-antimony phases such as $\text{La}_6\text{ZnSb}_{15}$ [30], Ba_2ZnSb_2 [17], and $\text{Eu}_{11}\text{Zn}_6\text{Sb}_{12}$ [10], to name a few.

From the above description of the two structures, one can easily see that the most significant difference between the two structures are the polyanions $[\text{Zn}_8\text{As}_{22}]$ in $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $[\text{Zn}_4\text{Sb}_{12}]$ in $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$. Both are made of edge- or corner-shared $[\text{ZnPn}_4]$ tetrahedra, with the difference being that the As–As dumbbell bridges two $[\text{Zn}_4\text{As}_{12}]$ halves to form an octamer $[\text{Zn}_8\text{As}_{22}]$ in $\text{Eu}_{21}\text{Zn}_4\text{As}_{21}$, while the $[\text{Zn}_4\text{Sb}_{12}]$ unit in $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ is not dimerized, yet, it retains a dangling Sb_2 dumbbell on its side (Figure 1). Notice, however, that besides $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$, no other “21-4-18” phase is known to exhibit dimorphism [12-14].

In a previous study on $A_{21}\text{Cd}_4\text{Pn}_{18}$ ($A = \text{Eu, Sr, Ba}$; $\text{Pn} = \text{Sb, Bi}$) [14], we had discussed the possible reason for having $[\text{Cd}_4\text{Pn}_{12}]$ polyanions preferred over $[\text{Cd}_8\text{Pn}_{22}]$ polyanions. With $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ being the sole structure featuring $[\text{Cd}_4\text{Sb}_{12}]$ and no apparent “cation” effects (as if the cations participating in the covalent bonding), we speculated that the most likely reason for this lies in a delicate balance between the sizes of the cations and the anions. Such geometric considerations, as also seen for $A_9\text{T}_{4+x}\text{Pn}_9$ ($A = \text{Ca, Sr, Eu, Yb}$; $T = \text{Zn, Cd, Mn}$; $\text{Pn} = \text{Sb, Bi}$) [31], can subtly influence the local environment and account for small changes in the Madelung energy that could be the discriminating factor here. The same conjecture can be applied here as well, recognizing that with larger cations ($\text{Eu}^{2+} = 1.31 \text{ \AA}$; $\text{Ca}^{2+} = 1.14 \text{ \AA}$) [22], “crystal packing” of molecular-like $[\text{Zn}_4\text{Pn}_{12}]$ fragments will be more flexible without the rigid linkers in

place. This reasoning could explain the difference between $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ and $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, however, it fails to explain the fact that $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$ are isostructural to each other. At present, this puzzling observation is not understood and we speculate that besides the “chemical pressure” effects of the cations (Figures 1 and 2, the cations colored in red, “pushing” on Zn2), one also needs to contemplate electronic effects at play. For example, a possible factor that needs to be considered is the difference in the electronegativities of As and Sb. Taking into account the Pauling scale ($\Delta\chi_{\text{Zn-As}} = 0.4$; $\Delta\chi_{\text{Zn-Sb}} = 0.3$) [28], we could argue that smaller size of As, combined with differences in the bond strengths of Zn–As/As–As and Zn–Sb/Sb–Sb is what sets the two apart. Of course, this discussion cannot be decoupled from the subtle difference between the electronegativities of Ca and Eu and the corresponding effects $\Delta\chi$ will have on the bonding—the roles of the cations in the bonding of Zintl phases has been a topic in many other articles [10-17].

Structural relationships

As mentioned earlier, $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ adopt the monoclinic $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ structure type [12] and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ crystallizes with the orthorhombic $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ structure type [14]. The structural similarities between these two structure types were already discussed (*vide supra*). In the following paragraphs, we will outline parallels to other structures, using $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ as an example.

To begin the discussion, we need to remind ourselves that the diversity among the ternary pnictides is truly amazing. There are so many phases with distinct connectivity modes of $[MPn_4]$ tetrahedra, where M includes many elements such as Mg, Ti, Nb, Mn,

group 12 and 13 elements [1-3; 9-17]. They all favor tetrahedral coordination, and the $[MPn_4]$ subunits further connect each other by sharing the corners or edges to form polyanions to be the backbone of those structures. Depending on the way these $[MPn_4]$ tetrahedra connect to each other the polyanions will have different conformations and therefore carry different formal charges.

For instance, the structures of $Ca_{11}InSb_9$ [19], $Ca_{10}Mg_2Sb_9$ [20], α - $Ca_{21}Mn_4Sb_{18}$ [13], and β - $Ca_{21}Mn_4Sb_{18}$ [12] share many common features (Figure 3). There are two universal subunits in these compounds—the $[MSb_4]$ tetrahedral, denoted as T hereafter, and $[NSb_6]$ octahedra denoted as O hereafter. Notice that some of the atoms can be ambivalent— $M = In, Mg$ (shown in yellow in the figure), Mn , and $N = Ca, Mg$ (shown in red in Figure 3).

If we use the tetrahedra (T) and the octahedra (O) to represent these structures, the $Ca_{11}InSb_9$ can be seen as repeating $[T \cdot O]$ units forming a chain, $Ca_{10}Mg_2Sb_9$ [20] can be visualized as a sequence of $[T \cdot T \cdot O \cdot O]$, and α - $Ca_{21}Mn_4Sb_{18}$ can be written as $[T \cdot T \cdot T \cdot T \cdot O]$. For β - $Ca_{21}Mn_4Sb_{18}$, the $[T \cdot T \cdot O \cdot T' \cdot T' \cdot O]$ formula best describes the connectivity, where the T' tetrahedra are the ones oriented in a direction orthogonal to the direction of the chain propagation. From the graphical representation, it may not be very clear that the octahedra in β - $Ca_{21}Mn_4Sb_{18}$ are more distorted compared to those of the other structures. This distortion is likely due to the two different orientations of the $[MnSb_4]$ tetrahedra, which is also the major difference between the α - $Ca_{21}Mn_4Sb_{18}$ and the β - $Ca_{21}Mn_4Sb_{18}$ structures—all four $[MnSb_4]$ tetrahedra in α - $Ca_{21}Mn_4Sb_{18}$ connect by sharing their edges, while part of the $[MnSb_4]$ tetrahedra in β - $Ca_{21}Mn_4Sb_{18}$ join each other through their corners (Figure 4). One can therefore envision the latter of the two structures as being

“derived” by replacing a Ca atom in α -Ca₂₁Mn₄Sb₁₈ (colored in red) with two Mn atoms (colored in black) within pentagonal prism (made of Ca and colored in green). The newly-formed [MnSb₄] tetrahedra (open frame) are connected to the other pair of edge-shared [MnSb₄] tetrahedra (pink) by via a common corner to become the polyanions in β -Ca₂₁Mn₄Sb₁₈. It is quite surprising that this “rearrangement” does not influence the neighboring Sb atoms in a significant way (only the positions of two Sb atoms move slightly) and without major interruption of the coordination of the Ca atoms. Ultimately, in both compounds, their structures adapt to the exact same number of valence electrons ($21 \times [\text{Ca}^{2+}]$, $4 \times [\text{Sb}]^{3-}$, $2 \times [\text{Sb}_2]^{4-}$, and $1 \times [\text{Mn}_4\text{Sb}_{10}]^{22-}$ for α -Ca₂₁Mn₄Sb₁₈; $42 \times [\text{Ca}]^{2+}$, $8 \times [\text{Sb}]^{3-}$, $3 \times [\text{Sb}_2]^{4-}$ and $1 \times [\text{Mn}_8\text{Sb}_{22}]^{48-}$ for β -Ca₂₁Mn₄Sb₁₈), in order to satisfy the electronic requirements for bonding in Zintl phases (*vide supra*).

Such structural parallels suggest that the arrangements of [MPn₄] tetrahedra are versatile, and that new polyanions made of [MPn₄] tetrahedra may still exist in these systems and await their discovery.

Magnetism and electrical resistivity

The $\chi_m(T)$ plot for Eu₂₁Zn₄Sb₁₈ is shown in Figure 5. We are interested in the magnetic properties of Eu₂₁Zn₄As₁₈ as well, however, the prepared sample were not homogenous. The temperature dependent DC magnetization measurements were done on cooling from 300 K to 5 K. In the high temperature range, the sample is paramagnetic, as expected for a material with Eu²⁺ cations which have 7 unpaired core 4f-electrons (electronic configuration [Xe]4f⁷) [32]. The data follow the Curie-Weiss law $\chi(T) = C/(T - \theta_p)$ [32], where C is the Curie constant ($N_A \mu_{\text{eff}}^2 / 3k_b$) and θ_p is the paramagnetic Weiss temperature. The effective magnetic moment of 7.88 μ_B can be calculated from the linear

fit of the $1/\chi_m(T)$ plot (inverse magnetic susceptibility vs temperature, shown as inset in Figure 5). The experimental value is close to the theoretical effective moment of free-ion Eu^{2+} ($7.94 \mu_B$) and confirms that Eu is divalent within the structure.

In the low temperature regime, the $\chi_m(T)$ plot shows the onset of antiferromagnetic ordering below ca. 8 K. The susceptibility reaches a maximum at this point and begins to drop as the temperature is lowered further. This is not surprising since the interatomic distances between individual Eu atoms are much longer than Eu in its elemental form (3.167 Å; hexagonal space group $P6_3/mmc$) [33]. However, we must note that the stipulated antiferromagnetic ordering is not in accordance with the positive value for θ_p of ca. 5 K. The low Weiss temperature indicates a weak coupling between the magnetic moments, but hints at the presence of possible ferromagnetic correlations. This warrants more precise experimental work at low temperature to fully understand the magnetic ground state in this material.

The electrical resistivity of single-crystalline $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ at room temperature is about $0.02 \Omega\cdot\text{m}$. The $\rho(T)$ data is shown in Figure 6, indicating that the resistivity increases exponentially with decreasing temperature, which suggests a typical semiconductor behavior. From the logarithmic $\rho(1/T)$ plot (inset in Figure 6), it is apparent that $\ln\rho$ increases linearly with $1/T$ in the measured interval. From fitting the data to a line, a band gap E_g of ca. 0.2 eV can be estimated. We did not compute the theoretical band gap for $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$, but note that this value is close to the calculated band gap for $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ ($E_g \approx 0.5$ eV) [14]; the calculations based on TM-LMTO-ASA method are known to overestimate the band gap.

The electrical resistivity for the remaining compounds could not be measured reliably because suitable single-crystals were not available. However, assuming they are also small band gap semiconductors, such intrinsic electronic properties, in combination with the complex crystal structure, suggest that the new materials presented herein, could be suitable for thermoelectric applications.

4. Conclusions

Reported were the synthesis and characterization of four new zinc-arsenides and zinc-antimonides. Based on their structures, it can be concluded that the selection of cations and anions affects the structural preference between the two different structure types. Comparison of the structures with other ternary pnictides, such as $\text{Ca}_{11}\text{InSb}_9$ and $\text{Ca}_{10}\text{Mg}_2\text{Sb}_9$ reveals very close relationships. This study suggests that the arrangements of ZnPn_4 tetrahedra are versatile, and that other new structure types may be discovered in the future within these systems. Magnetic susceptibility measurements on $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ show paramagnetic behavior through the entire range 10 to 300 K, and the onset of antiferromagnetic ordering at liquid helium temperatures. The calculated effective magnetic moment of $7.88 \mu_B$ indicates that the Eu metal is in its divalent state in the structure. From the electrical resistivity, the material shows a typical small-gap semiconductor behavior and a band gap E_g of ca. 0.2 eV. Currently, our efforts are focused on the syntheses and characterization of $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{As}_{18}$, the elusive members of this family, which are expected to show interesting magnetization arising from local moment magnetism due to both Eu^{2+} (7 unpaired 4f-electrons) and Mn^{2+} (5 unpaired 3d-electrons).

Acknowledgments

Svilen Bobev acknowledges financial support from the US Department of Energy-Basis Energy Sciences through a grant DE-SC0008885. The authors are indebted to Dr. H. He and Mr. G. Darone for help with some of the syntheses.

References

- [1] H. Schäfer, B. Eisenmann, W. Müller, *Angew. Chem. Int. Ed. Eng.* 12 (1973) 694.
- [2] B. Eisenmann, G. Cordier, in “Chemistry, Structure and Bonding of Zintl Phases and Ions”; S. M. Kauzlarich, Ed.; VCH Publishers: New York, (1996).
- [3] (a) H.-G. von Schnering, *Angew. Chem. Int. Ed. Eng.* 20 (1981) 33. (b) H. Schäfer, *Annu. Rev. Mater. Sci.* 15 (1985) 1.
- [4] E. Zintl, *Angew. Chem.* 52 (1939) 1.
- [5] S. R. Brown, S. M. Kauzlarich, F. Gascoin, G. J. Snyder, *G. J. Chem. Mater.* 18 (2006) 1873.
- [6] S. J. Kim, M. G. Kanatzidis, *Inorg. Chem.* 40 (2001) 3781.
- [7] F. Gascoin, S. Ottensmann, D. Stark, S. M. Haile, G. J. Snyder, *Adv. Funct. Mater.* 15 (2005) 1860.
- [8] (a) S. M. Kauzlarich, S. R. Brown, G. J. Snyder, *Dalton Trans.* 21 (2007) 2099; (b) G. J. Snyder, E. S. Toberer, *Nat. Mater.* 8 (2008) 105.
- [9] J. Y. Chan, M. M. Olmstead, S. M. Kauzlarich, *Chem. Mater.* 10 (1998) 3583.
- [10] B. Saparov, S. Bobev, A. Ozbay, E. R. Nowak, *J. Solid. State. Chem.* 181 (2008) 2690.
- [11] J. Wang, S. Q. Xia, X. T. Tao, *J. Solid. State. Chem.* 198 (2013) 6.
- [12] H. Kim, C. L. Condon, A. P. Holm, S. M. Kauzlarich, *J. Am. Chem. Soc.* 122 (2000) 10720.
- [13] S.-Q. Xia, S. Bobev, *Inorg. Chem.* 46 (2007) 874.
- [14] S.-Q. Xia, S. Bobev, *Inorg. Chem.* 47 (2008) 1919.
- [15] (a) P. Kluefers, H. Neumann, A. Mewis, H. U. Schuster, *Z. Naturforsch., B: Chem. Sci.* 35 (1980) 1317; (b) S.-Q. Xia, C. Myers, S. Bobev, *Eur. J. Inorg. Chem.* 27 (2008) 4262.

- [16] (a) J. Wang, M. Yang, M. Y. Pan, S.-Q. Xia, X. T. Tao, H. He, G. Darone, S. Bobev, *Inorg. Chem.* 50 (2011) 8020; (b) D. K. Wilson, B. Saparov, S. Bobev, *Z. Anorg. Allg. Chem.* 637 (2011) 2018.
- [17] B. Saparov, S. Bobev, *Inorg. Chem.* 49 (2010) 5173.
- [18] P. Villars, L. D. Calvert (Eds.), *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*, 2nd Ed., American Society for Metals, Materials Park, OH, USA 1991, and the desktop edition 1997.
- [19] G. Cordier, H. Schaefer, M. Stelter, *Z. Naturforsch., B: Chem. Sci.* 40 (1985) 868.
- [20] A. K. Ganguli, S. Gupta, J. D. Corbett, *Inorg. Chem.* 45 (2006) 196.
- [21] *CRC Handbook of Chemistry and Physics*, 83rd ed.; CRC Press LLC: Boca Raton, FL, 2002.
- [22] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr. B* 29 (1969) 925.
- [23] SMART, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- [24] SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- [25] SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- [26] SHEXLTL, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- [27] PLATON, Version 1.15, A. L. Spek, Utrecht University, Utrecht, The Netherlands, 2008.
- [28] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.
- [29] N.-T. Suen, S. Bobev, *Inorg. Chem.* 52 (2013) 9102.
- [30] O. L. Sologub, M. Vybornov, P. Rogl, K. Hiebl, G. Cordier, P. Woll, *J. Solid. State. Chem.* 122 (1996) 266.
- [31] (a) S. Bobev, J. D. Thompson, J. L. Sarrao, M. M. Olmstead, H. Hope, S. M. Kauzlarich, *Inorg. Chem.* 43 (2004) 5044; (b) S.-Q. Xia, S. Bobev, *J. Am. Chem. Soc.* 129 (2007) 10019.
- [32] (a) J. S. Smart, *Effective Field Theories of Magnetism*, Saunders, Philadelphia, PA, 1966. (b) C. Kittel, *Introduction to Solid-State Physics*, 7th ed., John Wiley & Sons Inc., New York, 1996.
- [33] K. Takemura, K. Syassen, *J. Phys.* F15 (1985) 543.

Figure Captions

Figure 1. Side-by-side comparison of the structures of $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ (a) and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ (b). Online color: the Zn atoms are drawn as purple spheres; As and Sb are shown as orange spheres. The Eu atoms are colored in green. In both representations, the Eu atoms shown in red, and the shaded cation polyhedra are to emphasize the subtle differences in the local environments (see text for further details).

Figure 2. A close view of the $[\text{Zn}_8\text{As}_{22}]$ polyanion in $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$. The black sphere located in the center of the tetrahedron shown as a frame, represents the position where the Zn2 atom would “flip” and break the $[\text{Zn}_8\text{As}_{22}]$ fragment into two $[\text{Zn}_4\text{As}_{12}]$ units, isosteric with the $[\text{Zn}_4\text{Sb}_{12}]$ polyanion in $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$. For relevant interatomic distances, please see Table 6.

Figure 3. A schematic representation of the structural relationship between $\text{Ca}_{11}\text{InSb}_9$, $\text{Ca}_{10}\text{Mg}_2\text{Sb}_9$, $\alpha\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$, and $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$. Different colors in the labels represent the corresponding elements in the structures.

Figure 4. A schematic representation of the hypothetical structural transformation between $\alpha\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ (see text for more information).

Figure 5. Temperature dependent magnetic susceptibility for polycrystalline $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$. The inset shows the temperature dependence of the inverse magnetic susceptibility. The solid line is the linear-fit of the data, according to the Curie-Weiss law. (T)

Figure 6. Temperature dependent electrical resistivity measurement for single-crystalline $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$. $\rho(T)$ (main panel) and $\ln\rho(1/T)$ (inset) are shown.

Table 1. Selected single-crystal data collection and structure refinement parameters for $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$.

Empirical formula	$\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$	$\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$	$\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$	$\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$
Formula weight, g mol^{-1}	2451.72	3294.66	4801.20	5644.14
Crystal system		Monoclinic		Orthorhombic
Space group		$C2/m$ (No.12)		$Cmce$ (No.64)
λ , Å		0.71073		
T , K		200(2)		
a , Å	16.3736(16)	17.3717(13)	16.958(6)	17.1256(11)
b , Å	15.5944(15)	16.5723(12)	16.166(6)	17.9312(12)
c , Å	16.1638(16)	17.0540(13)	16.668(6)	34.996(2)
β , °	92.190(2)	91.913(1)	92.008(6)	
V , Å ³	4124.2(7)	4906.9(6)	4567(3)	10746.7(12)
ρ_{calcd} , g cm^{-3}	3.949	4.460	6.983	6.977
μ (Mo $K\alpha$), cm^{-1}	192.51	138.33	433.4	346.9
GOF on F^2	1.039	1.017	1.031	1.161
R_1 [$I > 2\sigma(I)$] ^a	0.0467	0.0357	0.0463	0.0243
wR_2 [$I > 2\sigma(I)$] ^a	0.0919	0.0656	0.0954	0.0480
R_1 [all data] ^a	0.0784	0.0590	0.0731	0.0297
wR_2 [all data] ^a	0.1038	0.0741	0.1019	0.0494

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$; A, B – weight coefficients.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}^a for $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Ca1	8j	0.0816(1)	0.1543(1)	0.3503(1)	0.0117(4)
Ca2	8j	0.0849(1)	0.1632(1)	0.1448(1)	0.0116(4)
Ca3	8j	0.1103(1)	0.1204(1)	0.5769(1)	0.0130(4)
Ca4	8j	0.1189(1)	0.3729(1)	0.0559(1)	0.0143(4)
Ca5	8j	0.1580(1)	0.3389(1)	0.4365(1)	0.0113(4)
Ca6	8j	0.2538(1)	0.3214(1)	0.2435(1)	0.0130(4)
Ca7	8j	0.3661(1)	0.3682(1)	0.0592(1)	0.0162(4)
Ca8	8j	0.4300(1)	0.1663(1)	0.1579(1)	0.0121(4)
Ca9	8j	0.4461(1)	0.1258(1)	0.3811(1)	0.0123(4)
Ca10	4i	0.2505(2)	0	0.4197(2)	0.0138(6)
Ca11	4i	0.2625(2)	0	0.0931(2)	0.0131(6)
Ca12	4i	0.5969(2)	0	0.2567(2)	0.0148(6)
Zn1	8j	0.2645(1)	0.1149(1)	0.2515(1)	0.0120(2)
Zn2	4i	0.0004(1)	0	0.7946(1)	0.0151(4)
Zn3	4i	0.1590(1)	0	0.7557(1)	0.0130(3)
As1	8j	0.0803(1)	0.3182(1)	0.2567(1)	0.0102(2)
As2	8j	0.2577(1)	0.1940(1)	0.1031(1)	0.0103(2)
As3	8j	0.2671(1)	0.1936(1)	0.3896(1)	0.0107(2)
As4	8j	0.4279(1)	0.3612(1)	0.2395(1)	0.0110(2)
As5	4i	0.0450(1)	0	0.4399(1)	0.0112(3)
As6	4i	0.0542(1)	0	0.0560(1)	0.0130(3)
As7	4i	0.1495(1)	0	0.2517(1)	0.0104(3)
As8	4i	0.2457(1)	0	0.6253(1)	0.0109(3)
As9	4i	0.3792(1)	0	0.2586(1)	0.0107(3)
As10	4i	0.4308(1)	0	0.5320(1)	0.0101(3)
As11	4i	0.4664(1)	0	0.0698(1)	0.0118(3)
As12	4i	0.7408(1)	0	0.1156(1)	0.0107(3)
As13	4h	0	0.2456(1)	1/2	0.0104(3)
As14	4g	0	0.2461(1)	0	0.0100(3)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}^a for $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Ca1	8j	0.0837(1)	0.1563(1)	0.3512(1)	0.0108(4)
Ca2	8j	0.0855(1)	0.1627(1)	0.1459(1)	0.0100(4)
Ca3	8j	0.1118(1)	0.1204(1)	0.5769(1)	0.0141(4)
Ca4	8j	0.1182(1)	0.3724(1)	0.0571(1)	0.0157(4)
Ca5	8j	0.1574(1)	0.3377(1)	0.4356(1)	0.0119(4)
Ca6	8j	0.2536(1)	0.3276(1)	0.2431(1)	0.0131(4)
Ca7	8j	0.3631(1)	0.3668(1)	0.0579(1)	0.0138(4)
Ca8	8j	0.4281(1)	0.1698(1)	0.1570(1)	0.0113(4)
Ca9	8j	0.4464(1)	0.1247(1)	0.3817(1)	0.0116(4)
Ca10	4i	0.2531(2)	0	0.4189(2)	0.0136(6)
Ca11	4i	0.2643(2)	0	0.0935(2)	0.0137(6)
Ca12	4i	0.5916(2)	0	0.2542(2)	0.0158(6)
Zn1	8j	0.2649(1)	0.1200(1)	0.2481(1)	0.0131(2)
Zn2	4i	0.0008(1)	0	0.7967(1)	0.0149(3)
Zn3	4i	0.1539(1)	0	0.7566(1)	0.0135(3)
Sb1	8j	0.0793(1)	0.3181(1)	0.2560(1)	0.0094(1)
Sb2	8j	0.2569(1)	0.1977(1)	0.0992(1)	0.0102(1)
Sb3	8j	0.2690(1)	0.1963(1)	0.3894(1)	0.0108(1)
Sb4	8j	0.4296(1)	0.3595(1)	0.2399(1)	0.0101(1)
Sb5	4i	0.0500(1)	0	0.4358(1)	0.0113(2)
Sb6	4i	0.0610(1)	0	0.0571(1)	0.0113(2)
Sb7	4i	0.1522(1)	0	0.2524(1)	0.0106(2)
Sb8	4i	0.2472(1)	0	0.6276(1)	0.0103(2)
Sb9	4i	0.3786(1)	0	0.2592(1)	0.0107(2)
Sb10	4i	0.4259(1)	0	0.5353(1)	0.0101(2)
Sb11	4i	0.4637(1)	0	0.0758(1)	0.0110(2)
Sb12	4i	0.7401(1)	0	0.1162(1)	0.0100(2)
Sb13	4h	0	0.2450(1)	1/2	0.0093(2)
Sb14	4g	0	0.2447(1)	0	0.0089(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}^a for $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Eu1	8j	0.0834(1)	0.1521(1)	0.3488(1)	0.0107(2)
Eu2	8j	0.0862(1)	0.1622(1)	0.1463(1)	0.0113(2)
Eu3	8j	0.1102(1)	0.1206(1)	0.5782(1)	0.0117(2)
Eu4	8j	0.1221(1)	0.3713(1)	0.0549(1)	0.0135(2)
Eu5	8j	0.1592(1)	0.3382(1)	0.4371(1)	0.0107(2)
Eu6	8j	0.2553(1)	0.3217(1)	0.2427(1)	0.0106(2)
Eu7	8j	0.3710(1)	0.3730(1)	0.0606(1)	0.0140(2)
Eu8	8j	0.4298(1)	0.1655(1)	0.1595(1)	0.0114(2)
Eu9	8j	0.4463(1)	0.1256(1)	0.3792(1)	0.0102(2)
Eu10	4i	0.2518(1)	0	0.4184(1)	0.0122(3)
Eu11	4i	0.2613(1)	0	0.0935(1)	0.0117(3)
Eu12	4i	0.5999(1)	0	0.2552(1)	0.0139(3)
Zn1	8j	0.2635(1)	0.1143(1)	0.2509(1)	0.0119(4)
Zn2	4i	0.0010(2)	0	0.7903(2)	0.0163(7)
Zn3	4i	0.1580(2)	0	0.7553(2)	0.0113(6)
As1	8j	0.0803(1)	0.3180(1)	0.2575(1)	0.0105(4)
As2	8j	0.2576(1)	0.1943(1)	0.1033(1)	0.0099(4)
As3	8j	0.2682(1)	0.1927(1)	0.3854(1)	0.0099(4)
As4	8j	0.4298(1)	0.3668(1)	0.2401(1)	0.0100(4)
As5	4i	0.0430(1)	0	0.4420(2)	0.0110(5)
As6	4i	0.0485(2)	0	0.0578(2)	0.0142(5)
As7	4i	0.1510(1)	0	0.2493(2)	0.0094(5)
As8	4i	0.2465(1)	0	0.6277(2)	0.0099(5)
As9	4i	0.3726(1)	0	0.2562(2)	0.0099(5)
As10	4i	0.4329(1)	0	0.5308(2)	0.0103(5)
As11	4i	0.4678(1)	0	0.0673(2)	0.0114(5)
As12	4i	0.7424(1)	0	0.1215(2)	0.0100(5)
As13	4h	0	0.2456(1)	1/2	0.0094(5)
As14	4g	0	0.2460(1)	0	0.0090(5)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}^a for $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Eu1	16g	0.12345(2)	0.38980(2)	0.27700(2)	0.0138(1)
Eu2	16g	0.13279(2)	0.13937(2)	0.28160(2)	0.0135(1)
Eu3	16g	0.15471(2)	0.08991(2)	0.07533(2)	0.0107(1)
Eu4	16g	0.16062(2)	0.09681(2)	0.17680(2)	0.0094(1)
Eu5	16g	0.17242(2)	0.43573(2)	0.16981(2)	0.0105(1)
Eu6	16g	0.32789(2)	0.26390(2)	0.12899(2)	0.0108(1)
Eu7	16g	0.33680(2)	0.16089(2)	0.03187(2)	0.0106(1)
Eu8	16g	0.37990(2)	0.39087(2)	0.03887(2)	0.0124(1)
Eu9	16g	0.12438(2)	0.44978(2)	0.06010(2)	0.0101(1)
Eu10	8f	0	0.09896(3)	0.37708(2)	0.0143(1)
Eu11	8f	0	0.25507(3)	0.04084(2)	0.0118(1)
Eu12	8f	0	0.26850(3)	0.20393(2)	0.0112(1)
Zn1	16g	0.11856(5)	0.26998(5)	0.12692(3)	0.0129(2)
Zn2	8f	0	0.01032(7)	0.14687(4)	0.0159(3)
Zn3	8f	0	0.35497(7)	0.37245(4)	0.0124(3)
Sb1	16g	0.19469(3)	0.27387(3)	0.05746(2)	0.0102(1)
Sb2	16g	0.19824(3)	0.26732(3)	0.20118(2)	0.0097(1)
Sb3	16g	0.31782(3)	0.08740(3)	0.12205(2)	0.0083(1)
Sb4	16g	0.36391(3)	0.43941(3)	0.12998(2)	0.0089(1)
Sb5	8f	0	0.04931(4)	0.03146(2)	0.0107(1)
Sb6	8f	0	0.06457(4)	0.22213(2)	0.0103(1)
Sb7	8f	0	0.07339(4)	0.48277(2)	0.0094(1)
Sb8	8f	0	0.15921(4)	0.12449(2)	0.0087(1)
Sb9	8f	0	0.25561(4)	0.43523(2)	0.0093(1)
Sb10	8f	0	0.25781(4)	0.31034(2)	0.0092(1)
Sb11	8f	0	0.37973(4)	0.12223(2)	0.0091(1)
Sb12	8f	0	0.47421(4)	0.20964(2)	0.0111(1)
Sb13	8e	1/4	0.01286(4)	1/4	0.0077(1)
Sb14	8d	0.24540(4)	0	0	0.0086(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6. Selected interatomic distances (Å) and angles (°) in $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$, $\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$.

$\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$		$\text{Eu}_{21}\text{Zn}_4\text{As}_{18}$	
Atomic pair	Distance	Atomic pair	Distance
As5–As5	2.485(3)	As5–As5	2.464(5)
As6–As6	2.486(3)	As6–As6	2.491(5)
As10–As10	2.525(3)	As10–As10	2.529(5)
As11–As11	2.548(3)	As11–As11	2.530(5)
Zn1–As2	2.696(2)	Zn1–As2	2.778(3)
Zn1–As3	2.547(1)	Zn1–As3	2.573(3)
Zn1–As7	2.599(2)	Zn1–As7	2.655(3)
Zn1–As9	2.595(1)	Zn1–As9	2.615(3)
Zn2–As4 ×2	2.532(1)	Zn2–As4 ×2	2.529(2)
Zn2–As6	2.607(2)	Zn2–As6	2.683(4)
Zn2–As7	2.540(2)	Zn2–As7	2.606(4)
Zn3–As4 ×2	2.593(3)	Zn3–As4 ×2	2.620(2)
Zn3–As8	2.586(2)	Zn3–As8	2.645(4)
Zn3–As12	2.599(2)	Zn3–As12	2.614(4)
Zn1–Zn1	3.582(2)	Zn1–Zn1	3.695(3)
Zn2–Zn3	2.694(2)	Zn2–Zn3	2.778(4)
As6–Zn2–As7	84.91(6)	As6–Zn2–As7	85.2(1)
As6–As6–Zn2	114.45(9)	Zn2–As6–As6	121.2(2)
$\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$		$\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$	
Sb5–Sb5	2.839(2)	Sb5–Sb5	2.824(1)
Sb6–Sb6	2.830(2)	Sb6–Sb12	2.886(1)
Sb10–Sb10	2.878(2)	Sb7–Sb7	2.895(1)
Sb11–Sb11	2.915(2)	Zn1–Sb1	2.759(1)
Zn1–Sb2	2.845(1)	Zn1–Sb2	2.936(1)
Zn1–Sb3	2.720(1)	Zn1–Sb8	2.842(1)
Zn1–Sb7	2.793(1)	Zn1–Sb11	2.832(1)
Zn1–Sb9	2.805(1)	Zn2–Sb4 ×2	2.7198(9)
Zn2–Sb4 ×2	2.720(1)	Zn2–Sb6	2.808(2)
Zn2–Sb6	2.736(2)	Zn2–Sb8	2.782(1)
Zn2–Sb7	2.733(2)	Zn3–Sb4 ×2	2.7805(9)
Zn3–Sb4 ×2	2.745(1)	Zn3–Sb9	2.829(2)
Zn3–Sb8	2.777(2)	Zn3–Sb10	2.786(2)
Zn3–Sb12	2.798(2)		
Zn1–Zn1	3.978(1)	Zn1–Zn1	4.061(1)
Zn2–Zn3	2.795(2)	Zn2–Zn3	2.867(2)
Sb6–Zn2–Sb7	83.46(5)	Sb6–Zn2–Sb8	86.08(4)
Sb6–Sb6–Zn2	109.04(5)	Zn2–Sb6–Sb12	125.57(4)

Figure1

[Click here to download high resolution image](#)

FIGURES

Figure2
[Click here to download high resolution image](#)

Figure3

[Click here to download high resolution image](#)

Figure4

[Click here to download high resolution image](#)

$\alpha\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$

$\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$

Figure5

[Click here to download high resolution image](#)

Figure6

[Click here to download high resolution image](#)