The New Zintl Phases $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$

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Abstract

Crystals of two new Zintl compounds, $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ have been synthesized using the molten metal flux method, and their structures have been established by single-crystal X-ray diffraction. Both compounds are isotypic and crystallize in the monoclinic space group $C2/m$ (No. 12, $Z = 4$). The structures are based on edge- and corner-shared MnSb_4 or CdSb_4 tetrahedra, which make octameric $[\text{Mn}_8\text{Sb}_{22}]$ or $[\text{Cd}_8\text{Sb}_{22}]$ polyanions. Homoatomic Sb–Sb bonds are present in both structures. The Eu atoms take the role of Eu^{2+} cations with seven unpaired $4f$ electrons, as suggested by the temperature-dependent magnetization measurements. The magnetic susceptibilities of $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ indicate that both phases order antiferromagnetically with Néel temperatures of ca. 7 K and ca. 10 K, respectively. The unpaired $3d$ electrons of the Mn atoms in $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ do contribute to the magnetic response, however, the bulk magnetization measurements do not provide evidence for long-range ordering of the Mn spins down to 5 K. Electrical resistivity measurements suggest that both compounds are narrow band gap semi-conductors.

Keywords: crystal structure, single-crystal X-ray diffraction, europium, antimony, Zintl phases.

Introduction

The compounds formed between the alkali- and alkaline-earth metals and the post-transition elements from groups 13–15 are known as Zintl phases [1, 2]. The boundaries of the Zintl family have been extended many times, and today's definition of Zintl phases includes some of the lanthanides, as well as some of the transition metals. The Zintl–Klemm concept explains their structures and bonding by assuming that electrons transfer from the less electronegative metals to the more electronegative ones, therefore each element achieves a closed shell state [3–5]. As a result, Zintl phases are nominally semiconductors (poor metals), and have been recognized for their excellent thermoelectric properties [6–11].

Our research group, in recent years, has studied and identified a large number of novel and peculiar structures among the ternary pnictides. Some relevant examples can be found in the “9–4–9” family alone [12–14], where a wealth of new compounds have been successfully synthesized and structurally characterized. Based on the above, it might be argued that the corresponding $AE-T-Pn$ systems ($AE = Ca, Sr, Ba, Eu, Yb$; $T = Mn, Zn, Cd$; $Pn = As, Sb, Bi$), which have been the subject of research interest for the past 2-3 decades, still present unexplored “phase space”.

Another testament to this conjecture is the series, which we can call the “21–4–18” family [15–17]. Since the discovery of the archetype $Sr_{21}Mn_4Sb_{18}$ in 2000 [18], the series has been extended by almost a dozen new compounds. We will draw the attention to the fact that $AE_{21}T_4Pn_{18}$ phases form with three different structures and the crystal chemistry was reviewed by us recently in a paper dealing with $Ca_{21}Zn_4As_{18}$, $Ca_{21}Zn_4Sb_{18}$, $Eu_{21}Zn_4As_{18}$ and $Eu_{21}Zn_4Sb_{18}$. What is peculiar about the “21–4–18”

family is the fact that except for α - and β - $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ [17], there is no evidence for polymorphism in any other $AE_{21}T_4Pn_{18}$ systems. For a given elemental mixture, one of the three structures is always realized, and the origins for the apparent structural preference are not yet understood. In the previous paper, we also noted the surprising observation that $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$, $\text{Ca}_{21}\text{Zn}_4\text{As}_{18}$ and $\text{Ca}_{21}\text{Zn}_4\text{Sb}_{18}$ are known, yet, their Yb-analogs are elusive—if one were to evoke a spatial argument for that, it can be easily countered by the fact that the ionic radii of Ca^{2+} and Yb^{2+} are almost identical, 1.00 Å and 1.02 Å, respectively [19].

In subsequent studies, we finally synthesized $\text{Yb}_{21}\text{Mn}_4\text{Sb}_{18}$, as well as its Eu-analog $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$. With this paper, we report on these experimental findings. In short, the magnetic response of these phases (*vide infra*) was difficult to interpret, which prompted us to seek the isostructural Eu- and Yb-based compounds with the magnetically-silent d^{10} metals Zn and Cd. $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ was successfully synthesized, but found to crystallize with the $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ structure type (orthorhombic space group *Cmce* (No. 64, $Z = 8$)) [16]. $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, in the other hand, were found to be isotypic with β - $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ [15] and $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$ [18] (monoclinic space group *C2/m* (No. 12, $Z = 4$)). Neither $\text{Yb}_{21}\text{Zn}_4\text{Sb}_{18}$ nor $\text{Yb}_{21}\text{Cd}_4\text{Sb}_{18}$ could be prepared during this study. Since the subject of the synthesis and thermoelectric properties of $\text{Yb}_{21}\text{Mn}_4\text{Sb}_{18}$ will be at the focus of a forthcoming paper, we will not discuss it in this article [20].

Experimental

Synthesis

Eu metal is fairly sensitive to air, therefore all handling of the materials was done inside an argon-filled glove box. The raw metals were purchased from Alfa or Aldrich and were used as received: Eu (ingots, 99.9%), Yb (ingots, 99.9%), Mn (pieces, 99.98%), Cd (shot, 99.999%), Sb (shot, 99.99%) and Pb (granules, 99.999%).

At the outset, we note that $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ can be obtained in reasonable yields only if Mn is used in 2- or 3-fold excess. This issue probably comes about from the high melting point of Mn, and/or its low solubility in the flux. For example, the most successful reaction in making this phase was an experiment loaded with the elemental ratio of $\text{Eu} : \text{Mn} : \text{Sb} : \text{Pb} = 21 : 10 : 18 : 100$. The very large quantity of Pb is to serve as a Pb flux. The mixture (contained in a 2 cm^3 alumina crucible covered on the top with quartz wool) was placed within a fused silica tube, which was then evacuated and flame-sealed. The reaction proceeded as follows: heating to 1273 K over 12 h; homogenization at this temperature for 24 h, and then cooling to 773 K at a rate of 10 K/h. Then, the excess of Pb flux was removed by decanting it. The fused silica ampoule was brought back into the glove box and opened. The reaction outcome consisted of many irregular grey crystals, later identified as $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ [21], and few darker, almost black irregular crystals, which were identified as $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$. Interestingly, the yield of $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ from the same elemental mixture, but using Sn as a flux, was almost quantitative, which may suggest that understanding the solubility of the reactants/products in the flux will be the key for optimizing the reaction conditions.

Variations of the stoichiometry and/or reaction temperature and cooling rates did not yield $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ as a single product. In addition to $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ [21], other side

products such as $\text{Eu}_{11}\text{Sb}_{10}$ [22] and EuMn_2Sb_2 [23] we also observed. $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ was also successfully synthesized through same method with typical by-products being $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ [24] and EuCd_2Sb_2 [25].

Powder X-ray diffraction

X-ray powder diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer using filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The data were analyzed with the JADE 6.5 software package. It must be noted here that the complex structures/large unit cells/low symmetry were the reason the diffraction patterns looked very complicated and the phase identification was hindered. For all structural work, single-crystal X-ray diffraction data was the method of choice. The powder patterns of fresh samples and samples left on the laboratory bench for 2-3 weeks were identical to the ones from freshly made samples. This suggests that the air-sensitivity of the title compounds is negligible over the specified period of time.

Single-crystal X-ray diffraction

For the intensity data collection on the single-crystal diffractometer, flux-grown crystals were picked and cut with a scalpel to the desired dimensions (less than $100 \text{ }\mu\text{m}$). This was done under a microscope in a drop of Paratone-N oil. In order to evaluate the crystal quality preliminary rotation images were acquired. The work was carried out on a Bruker *SMART* and APEX 2 CCD-based diffractometer (monochromatized $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). By using cold nitrogen stream, the temperature was kept at 200 K during the data collection—the Paratone-N oil hardens at these conditions and immobilizes the crystal during the experiment. The programs *SMART* and *SAINT* [26]

was used to acquire and process data. *SADABS* was used for the semi-empirical absorption correction [27]. The structures were easily solved by direct methods, and were refined with the full-matrix least squares on the F^2 method, as implemented in *SHELXTL* [28]. Refined parameters included the scale factor and atomic positions with the corresponding anisotropic displacement parameters. In the final step, the atomic positions were standardized by *STRUCTURE TIDY* [29].

Selected crystallographic information and refinement parameters for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ are summarized in Table 1. Final positional and equivalent isotropic displacement parameters are shown in Tables 2 and 3. Relevant interatomic distances and angles are listed in Table 4. 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-430851 for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and CSD-430852 for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$.

Property Measurements

Field-cooled (FC) direct-current (DC) magnetization measurements on polycrystalline samples were performed in a Quantum Design PPMS from 5 to 300 K in an applied magnetic field of 5000 Oe. The measured specimens were single-crystals of $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ or $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ that were selected under a microscope from freshly prepared samples, and then were ground into powders. The materials were weighed and loaded in gel capsules and filled with cotton to prevent them moving under the magnetic field. The raw magnetization data were corrected for the holder contribution and converted to molar susceptibility. The net effective moments were calculated from the linear fits of the inverse magnetic susceptibility versus temperature.

The measurements of electrical resistivity as a function of temperature were also done in the PPMS. The four-probe method was utilized. For the purpose, four platinum wires (0.002") were attached to the surface of the measured specimens using EPO TEK H20 silver epoxy. The measurements were carried out with excitation current of 10 mA, and to ensure reproducibility, data were taken twice—both on heating and cooling. Band gaps were calculated from the linear fits of $\ln\rho$ with $1/T$.

Note that due to the lack of large enough single-crystals, sintered pellets made from polycrystalline $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ were used. The powders were pressed in a $\frac{1}{2}$ " dye under 10 tons, and then annealed in evacuated tubes at 1073 K for 3 days. This could have resulted in the formation of cracks or surface oxidation, which rendered the measurements impossible below ca. 200 K (due to the measured very high resistance values, particularly for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$).

Results and Discussion

Structure and bonding

$\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ both crystallize in the monoclinic space group $C2/m$ with the same structure as $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$ [15, 18]. The chemical bonding in this atomic arrangement has been well described in previous publications, therefore only a brief discussion will be provided herein.

There are a total of 29 crystallographic sites in the asymmetric unit of the structure: 12 for the Eu atoms, 3 for the Mn of Cd atoms, and 14 for the Sb atoms. The structure is fairly complicated (Figure 1) with a total of 84 Eu^{2+} cations, 16 Sb^{3-} anions, 6 $[\text{Sb}_2]^{4-}$ dumbbells, and 2 $[\text{Mn}_8\text{Sb}_{22}]^{48-}$ or $[\text{Cd}_8\text{Sb}_{22}]^{48-}$ polyanions in one unit cell. The latter moieties (Figure 1b) could be broken to two simpler $[\text{Mn}_4\text{Sb}_{11}]^{25-}$ or $[\text{Cd}_4\text{Sb}_{11}]^{25-}$

fragments, bridged by a Sb–Sb bond [30]. Note that the $[\text{MnSb}_4]^{10-}$ and $[\text{CdSb}_4]^{10-}$ tetrahedra are joined via edge- and corner-sharing. Assigning the formal charges in the polyanionic sub-lattice was done according to the Zintl-Klemm concept [1, 2], namely: $(4b\text{-Cd}^{2-})/(1b\text{-Sb}^{2-})/(2b\text{-Sb}^{1-})/(3b\text{-Sb}^0)$, where the abbreviations $1b$ -, $2b$ -, $3b$ -, and $4b$ - denote 1-, 2-, 3-, and 4-bonded atoms. Thus, $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ can be classified as Zintl phases and are expected to be semiconductors. Earlier work on the electronic structures of other compounds from this series confirms this notion.

The Cd–Sb distances in $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ are within the range 2.855(2)–3.010(1) Å. These distances are close (less than 10% larger) to the sum of the Pauling covalent radii ($r_{\text{Cd}} + r_{\text{Sb}} = 2.77$ Å) [30], which justifies the assumption that Cd and Sb are covalently bonded. The corresponding angles for the $[\text{CdSb}_4]^{10-}$ tetrahedra deviate from the ideal tetrahedral value of 109.5° , ranging from $82.53(4)^\circ$ to $126.53(3)^\circ$. The numerical values for the lengths of the Cd–Sb bonds and the Sb–Cd–Sb angles compare well with those reported for other ternary phases, such as $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ [24] and EuCd_2Sb_2 [25].

The Mn–Sb distances in $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ are within the range 2.758(1)–2.989(1) Å. These distances also match reasonably well the sum of Pauling covalent radii ($r_{\text{Mn}} + r_{\text{Sb}} = 2.57$ Å) [31], which also implies covalent bonding interactions between Mn and Sb and the rationalization of the $[\text{Mn}_8\text{Sb}_{22}]$ fragments as polyanions. The corresponding Sb–Mn–Sb angles for all tetrahedra range from $82.55(4)^\circ$ to $121.54(3)^\circ$. All structural metrics compare well with those reported for other structures based on MnSb_4 tetrahedra, for instance, $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ [21], EuMn_2Sb_2 [23], and $\text{Eu}_{14}\text{MnSb}_{11}$ [32].

Structural diversity

The “21–4–18” family encompasses three different structure types been exemplified by α -Ca₂₁Mn₄Sb₁₈ (*C2/c*), β -Ca₂₁Mn₄Sb₁₈ and Sr₂₁Mn₄Sb₁₈ (*C2/m*), and Ba₂₁Cd₄Sb₁₈ (*Cmce*). As mentioned already, what governs the structural preference is yet unclear.

With the addition of two new pieces to that “puzzle”, we would like to take another look at this conundrum. When considering α -Ca₂₁Mn₄Sb₁₈ (and Yb₂₁Mn₄Sb₁₈ in this case—see the electronic supporting information), [Mn₄Sb₁₀] linear tetramers made of all edge-shared MnSb₄ tetrahedra are noticed immediately. β -Ca₂₁Mn₄Sb₁₈ (and Eu₂₁Mn₄Sb₁₈ in this case) features [Mn₄Sb₁₁] fragments, which are actually two diborane-like [Mn₂Sb₆] subunits, conjoined through a common vertex. Mn–Sb distances and Sb–Mn–Sb angles in both structures are comparable. Therefore, the most reasonable assumption would be that filling the remaining space with cations is what differentiates the two structures.

Let us begin by attempting to represent both structures in polyhedral mode, where the polyhedra of the cations are also shown. The two chosen views (Figure 2a and 2b) show some remarkable similarities—note how the two Mn-centered tetrahedra (in red), which form [Mn₂Sb₆] subunits are aligned similarly, however, the other [Mn₂Sb₆] subunits are arranged in different directions (drawn in green for α -Ca₂₁Mn₄Sb₁₈ and in blue for Eu₂₁Mn₄Sb₁₈). Recall that in α -Ca₂₁Mn₄Sb₁₈, the green [Mn₂Sb₆] connects to the red one by edge-sharing, while for Eu₂₁Mn₄Sb₁₈, the blue [Mn₂Sb₆] is connected to red one through a common vertex.

More common units in the patterns are highlighted in red, as shown in detail in Figure 2. Focusing on the central parts, there are 3 cation sites and one [Mn₂Sb₆] (green

or blue). The “core” in both cases is decorated by four red $[\text{Mn}_2\text{Sb}_6]$ subunits. Careful comparing indicates that the blue and green $[\text{Mn}_2\text{Sb}_6]$ switch their positions (roles) in these two structures. The types of cations polyhedra are also slightly different—in $\alpha\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$, one octahedral (Ca1) and two pentagonal bi-pyramidal (Ca11) are forming the core, while for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, there is one pentagonal bi-pyramidal (Eu11) and two octahedral (Eu5) cations surrounding the blue $[\text{Mn}_2\text{Sb}_6]$ subunit. Based on the above, it is hard to rationalize the observations on the basis of atomic sizes alone.

Let us now look at the other structure, which is adopted by $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ only. There is no Mn-bearing compound known with the third structure, however, the atomic size of Mn and Zn are very close [31], thus, we can compare $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$. Generally, as discussed earlier, the major difference between these two structures is that the Sb–Sb dumbbell bridges two $[\text{Mn}_4\text{Sb}_{11}]$ fragments together to form an octamer $[\text{Mn}_8\text{Sb}_{22}]$, while the $[\text{Zn}_4\text{Sb}_{12}]$ unit has a dangling Sb atom, and is not dimerized. Figure 3 shows these polyanions. As shown in panel (a), $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ could be seen as stacking of slabs A and B with a repeating $[\text{A}\cdot\text{B}]$ unit, (to guide the eye, slabs A and B are shaded in yellow and light blue, respectively). Compared to $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ in panel (b), it is apparent that the sequence here is of repeating $[\text{A}]$ units (to help the reader see the difference, two adjacent slabs are shaded again in yellow and light blue, respectively). In some way, the two structures can be regarded as polytypes, although strong Sb–Sb bonds will have to be broken and re-formed in the process of “converting” one to the other. In a prior publication [16], we had speculated that since the tetrahedron, via which the dimerization occurs (or has the dangling bond to another Sb atom) is the most distorted one, it must be most sensitive to

its cation environment. This could have an effect, and be a significant factor for the observed structural preference, however, there must be a subtle electronic effect also at play here. For instance, comparing $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ with $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ —the former adopts the $\beta\text{-Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ structure type [15], while the latter crystallizes with $\text{Ba}_{21}\text{Cd}_4\text{Sb}_{18}$ structure type [16]. Zn is a little bigger than Mn, which means that the longer Zn–Sb bonds might make the corresponding ZnSb_4 tetrahedra more amenable to distortions. However, $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ are isostructural. Therefore, with all cations being the same, the structural difference might be due to the electronegativities ($\chi_{\text{Mn}} = 1.5$; $\chi_{\text{Zn}} = 1.6$; $\chi_{\text{Cd}} = 1.7$) [31]. The combination/synergy of the two factors is apparent, however, more experimental and theoretical work is needed to unravel it.

Physical Properties

The magnetic susceptibilities of both compounds were measured in the temperature range from 5 K to 300 K. The magnetic responses (Figure 4) appear similar to that of $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ we reported previously [17]. The temperature dependent DC magnetization data show that in the high temperature range, both samples are paramagnetic. At very low temperatures, the magnetic susceptibilities begin to drop, although not sharply, which likely indicate antiferromagnetic (AFM) ordering. The Néel temperature for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ is ca. 10 K and for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ is ca. 7 K respectively. Both are comparable to the Néel temperature for $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ (8 K) [17].

Above ca. 30–40 K, the plots of the inverse susceptibilities vs the temperature show near perfect linearity. Linear fits of the data (Figure 4, insets) confirm the expected Curie–Weiss type paramagnetic behavior ($\chi(T) = C/(T - \theta_p)$) [33], where C is the Curie constant and θ_p is the paramagnetic Weiss temperature. The determined

values for θ_P are as follow: $\theta_P = -1.4$ K for and $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$, $\theta_P = -2.0$ K for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ respectively, which are in agreement with the apparent AFM ordering.

The calculation of the effective magnetic moments was done using the formula $\mu_{\text{eff}} = \sqrt{7.99C}$, where the value of C was taken from the linear fits. For $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$, which only contains magnetic Eu^{2+} (ground state $J = 7/2$ and theoretical free-ion moment of $7.94 \mu_B$) [33], the calculated effective magnetic moment is $7.93 \mu_B$ per Eu-atom ($36.4 \mu_B$ per formula unit). The agreement between the experimental and the calculated moments is nearly perfect. For $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, contributions to the effective moment from both Eu^{2+} and Mn^{2+} ought to be expected. If one assumes that Mn^{2+} has the high spin configuration (d^5) and spin-only magnetism (ground state $S = 5/2$ and theoretical free-ion moment of $5.9 \mu_B$), μ_{eff} per formula unit should be $39.0 \mu_B$ ($21 \times \text{Eu}^{2+} + 4 \times \text{Mn}^{2+}$). μ_{eff} derived from the linear fit is $38.8 \mu_B$ per formula unit. Why the experimental value is slightly lower than the expected moment is yet unknown, and one might speculate that $3d$ and $4f$ spins interact in some way [34]. It is worth mentioning here that $\text{Eu}_{10}\text{Mn}_6\text{Sb}_{13}$ [21], another ternary compound based on the same elements, but with a layered structure, also shows slightly reduced net effective moment ($27.9 \mu_B$, while the expected value based on $10 \times \text{Eu}^{2+}$ and $6 \times \text{Mn}^{2+}$ is $29.0 \mu_B$). This phase is also a small gap semiconductor, but the Eu^{2+} moments in this kind of layered arrangement are ordered ferromagnetically [21]. Another useful parallel can be drawn with the isostructural $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$ [19], which should show the characteristic $3d$ magnetic response of this structure. This material is suggested to behave as a free-electron Pauli paramagnet. The original paper, however, makes a note that the susceptibility of $\text{Sr}_{21}\text{Mn}_4\text{Sb}_{18}$ has field dependence and shows an upturn at 12 K,

therefore, the magnetic data are not easily interpreted [18]. Similarly intricate Mn-based magnetism has been reported for $\text{Yb}_9\text{Mn}_4\text{Sb}_9$ [14], Sr_2MnSb_2 [35], CaMn_2Sb_2 [36], among others. The data we present here for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ are yet another clue that interesting low temperature physics is likely to be found in these systems, and call for further physical characterization work to understand the origins of this unusual behavior.

Resistivity data as a function of temperature were obtained on polycrystalline pellets as no large enough single-crystals were available. Figure 5 shows the electrical resistivity on both compounds. From the $\rho(T)$ plots, it is evident that the resistivity at room temperature is relatively low, but quickly increases with decreasing the temperature. This semiconductor-like behavior is of course expected, as both compounds were rationalized in the previous section as Zintl phases with closed-shell electronic configurations for all atoms ($\text{Mn}^{2+} - d^5$, and $\text{Cd}^{2+} - d^{10}$, within the framework of the Zintl formalism can be considered as pseudo-group II elements). From the $\ln\rho(1/T)$ plots (insets in Figure 5), it is apparent that $\ln\rho$ increases linearly with $1/T$. Calculations following the Arrhenius activation law suggest experimental band gaps of 0.26 eV for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and 0.08 eV for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$. The smaller gap for the latter correlates with its resistivity value at room temperature ($0.0015 \Omega\cdot\text{m}$), which is almost 1,000 times smaller than the corresponding ρ_{300} for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$. Of course, as stated in the Experimental part, the reported values are for pellets that may not have achieved more than 2/3 of the theoretical density of the bulk solid, and thus, should be used with caution. Nonetheless, the two compounds are semiconductors with the right band gaps for thermoelectric applications. Being materials with very complex structures and showing no apparent sign of degradation in ambient air over several weeks, the charge-

and heat-transport properties of $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and especially $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ are worthy of a more detailed investigation.

4. Conclusions

Two new Zintl phases, $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ have been successfully synthesized, and their structures have been determined by single-crystal X-ray diffraction. Both compounds crystallize in the monoclinic space group $C2/m$. The structure consists of edge- and corner-shared tetrahedra, which form complex $[\text{Mn}_8\text{Sb}_{22}]$ and $[\text{Cd}_8\text{Sb}_{22}]$ polyanions. Temperature-dependent magnetization measurements show the Eu^{2+} moments in both $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ to be weakly anti-ferromagnetically coupled below ca. 10 K and 7 K, respectively. Electrical resistivity measurements confirm that both compounds are small gap semiconductors. Currently, our efforts are focused on scaling up the syntheses and detailed properties characterization of these, and some other members of this family.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc..... The information consists of additional X-ray crystallographic data for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, as well as CIF for $\text{Yb}_{21}\text{Mn}_4\text{Sb}_{18}$.

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Figure Captions

Figure 1. Polyhedral views of $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, unit cell (a), and close up view of the $[\text{Mn}_8\text{Sb}_{22}]$ subunit (b). Online color: the Eu, Mn and Sb atoms are drawn as green, blue and orange spheres, respectively.

Figure 2. Structural relationships between $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ ($C2/c$) and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ ($C2/m$). Shown is the three-dimensional packing in $\text{Ca}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$, with the similarities and differences highlighted. Online color: Mn centered tetrahedra colored in red, green and blue to distinguish the different orientations of the $[\text{Mn}_2\text{Sb}_6]$ di-borane like units. The cations are shown in grey.

Figure 3. Structural relationships between $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ ($Cmce$) and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ ($C2/m$). Panel (a) shows the polyanionic sub-network of the $\text{Eu}_{21}\text{Zn}_4\text{Sb}_{18}$ structure. Panel (b) shows the polyanionic sub-network of the $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ structure.

Figure 4. Temperature dependent magnetic susceptibility for polycrystalline $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ (a) and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ (b). 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.

Figure 5. Temperature dependent electrical resistivity for polycrystalline $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ (a) and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ (b). The linear fits of $\ln\rho$ vs $1/T$ are shown as insets.

Table 1. Selected single-crystal data collection and structure refinement parameters for $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$. Both structures are with the monoclinic space group $C2/m$ (No. 12) with four formula units per cell.

Empirical formula	$\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$	$\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$
Formula weight, $\text{g}\cdot\text{mol}^{-1}$	5832.26	5602.42
Radiation	graphite-monochromated Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$	
Temperature, K	200(2)	200(2)
Crystal dimensions (μm)	$90 \times 60 \times 60$	$70 \times 60 \times 50$
a , $\text{\AA}$	18.068(4)	18.0227(10)
b , $\text{\AA}$	17.228(4)	17.1988(9)
c , $\text{\AA}$	17.651(4)	17.5981(9)
β , $^\circ$	91.942(4)	91.876(1)
V , $\text{\AA}^3$	5491(2)	5451.9(5)
ρ_{calcd} , $\text{g}\cdot\text{cm}^{-3}$	7.06	6.83
μ (Mo $K\alpha$), cm^{-1}	337.5	333.6
2θ (Mo $K\alpha$) range	2.30° – 56.16°	2.32° – 59.14°
Unique data with $F_o^2 > 2\sigma(F_o^2)$	5749 ($R_{\text{int}} = 0.044$)	7374 ($R_{\text{int}} = 0.023$)
Variables	216	216
GOF on F^2	0.991	1.204
R_1 [$I > 2\sigma(I)$] ^a	0.028	0.021
wR_2 [$I > 2\sigma(I)$] ^a	0.050	0.045
R_1 [all data] ^a	0.039	0.024
wR_2 [all data] ^a	0.053	0.046
$(\Delta\rho)_{\text{max}} / (\Delta\rho)_{\text{min}}$, $\text{e}\cdot\text{\AA}^{-3}$	2.32 / -1.63	1.56 / -1.33

^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. In the case of $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$: $A = 0.0152$ and $B = 0$; for $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$: $A = 0.013$ and $B = 54.516$. For additional information, the reader is referred to the CIFs in the Supporting Information.

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

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Eu(1)	8j	0.0849(1)	0.1547(1)	0.3500(1)	0.0140(2)
Eu(2)	8j	0.0876(1)	0.1622(1)	0.1465(2)	0.0134(2)
Eu(3)	8j	0.1131(1)	0.1211(1)	0.5761(3)	0.0156(2)
Eu(4)	8j	0.1193(1)	0.3710(1)	0.0568(3)	0.0165(1)
Eu(5)	8j	0.1561(1)	0.3378(1)	0.4352(1)	0.0139(1)
Eu(6)	8j	0.2533(1)	0.3254(1)	0.2431(1)	0.0146(1)
Eu(7)	8j	0.3667(1)	0.3701 (1)	0.0608(1)	0.0164(1)
Eu(8)	8j	0.4285(1)	0.1693(1)	0.1568(1)	0.0140(1)
Eu(9)	8j	0.4455(1)	0.1262(1)	0.3801(1)	0.0139(1)
Eu(10)	4i	0.2544(1)	0	0.4193(1)	0.0154(1)
Eu(11)	4i	0.2639(1)	0	0.0913(1)	0.0152(1)
Eu(12)	4i	0.5914(1)	0	0.2539(1)	0.0170(1)
Cd(1)	8j	0.2663(1)	0.1216(1)	0.2475(1)	0.0149(1)
Cd(2)	4i	0.0003(1)	0	0.7907(1)	0.020(1)
Cd(3)	4i	0.1571(1)	0	0.7530(1)	0.0160(1)
Sb(1)	8j	0.0794(1)	0.3178 (1)	0.2558(1)	0.0125(1)
Sb(2)	8j	0.2570(1)	0.1995(1)	0.0948(1)	0.0133(1)
Sb(3)	8j	0.2690(1)	0.1970(1)	0.3922(1)	0.0139(1)
Sb(4)	8j	0.4301(1)	0.3541(1)	0.2422(1)	0.0133(1)
Sb(5)	4i	0.0466(1)	0	0.4374(1)	0.0146(1)
Sb(6)	4i	0.0576(1)	0	0.0568(1)	0.0158(1)
Sb(7)	4i	0.1535(1)	0	0.2524(1)	0.0135(1)
Sb(8)	4i	0.2515(1)	0	0.6242(1)	0.0135(1)
Sb(9)	4i	0.3817(1)	0	0.2559(1)	0.0130(1)
Sb(10)	4i	0.4289(1)	0	0.5341(1)	0.0130(1)
Sb(11)	4i	0.4651(1)	0	0.0732(1)	0.0140(1)
Sb(12)	4i	0.7392(1)	0	0.1174(1)	0.0133(1)
Sb(13)	4h	0	0.2449(1)	½	0.0125(1)
Sb(14)	4g	0	0.2437(1)	0	0.0121(1)

^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 $\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$.

atom	site	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Eu(1)	8j	0.0839(1)	0.1558(1)	0.3497(1)	0.0110(1)
Eu(2)	8j	0.0864(1)	0.1636(1)	0.1465(1)	0.0102(1)
Eu(3)	8j	0.1119(1)	0.1207(1)	0.5768(1)	0.0131(1)
Eu(4)	8j	0.1199(1)	0.3715(1)	0.0564(1)	0.0139(1)
Eu(5)	8j	0.1587(1)	0.3370(1)	0.4363(1)	0.0108(1)
Eu(6)	8j	0.2543(1)	0.3229(1)	0.2428(1)	0.0114(1)
Eu(7)	8j	0.3662(1)	0.3702(1)	0.0587(1)	0.0137(1)
Eu(8)	8j	0.4284(1)	0.1700(1)	0.1590(1)	0.0109(1)
Eu(9)	8j	0.4462(1)	0.1248(1)	0.3802(1)	0.0107(1)
Eu(10)	4i	0.2525(1)	0	0.4221(1)	0.0120(1)
Eu(11)	4i	0.2634(1)	0	0.0882(1)	0.0118(1)
Eu(12)	4i	0.5942(1)	0	0.2541(1)	0.0145(1)
Mn(1)	8j	0.2638(1)	0.1116(1)	0.2491(1)	0.0110(1)
Mn(2)	4i	0.0001(1)	0	0.7903(1)	0.0133(3)
Mn(3)	4i	0.1559(1)	0	0.7560(1)	0.0107(2)
Sb(1)	8j	0.0800(1)	0.3184(1)	0.2567(1)	0.0094(1)
Sb(2)	8j	0.2571(1)	0.1949(1)	0.0999(1)	0.0102(1)
Sb(3)	8j	0.2689(1)	0.1929(1)	0.3877(1)	0.0107(1)
Sb(4)	8j	0.4292(1)	0.3618(1)	0.2398(1)	0.0093(1)
Sb(5)	4i	0.0467(1)	0	0.4367(1)	0.0116(1)
Sb(6)	4i	0.0557(1)	0	0.0596(1)	0.0120(1)
Sb(7)	4i	0.1505(1)	0	0.2506(1)	0.0097(1)
Sb(8)	4i	0.2476(1)	0	0.6277(1)	0.0102(1)
Sb(9)	4i	0.3785(1)	0	0.2554(1)	0.0097(1)
Sb(10)	4i	0.4281(1)	0	0.5340(1)	0.0099(1)
Sb(11)	4i	0.4651(1)	0	0.0736(1)	0.0109(1)
Sb(12)	4i	0.7407(1)	0	0.1200(1)	0.0098(1)
Sb(13)	4h	0	0.2454(1)	1/2	0.0091(1)
Sb(14)	4g	0	0.2445(1)	0	0.0086(1)

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

Table 4. Selected interatomic distances (Å) and angles (°) in Eu₂₁Cd₄Sb₁₈ and Eu₂₁Mn₄Sb₁₈.

Eu ₂₁ Cd ₄ Sb ₁₈		Eu ₂₁ Mn ₄ Sb ₁₈	
Cd1–Sb2	3.010(1)	Mn1–Sb2	2.989(1)
Cd1–Sb3	2.865(1)	Mn1–Sb3	2.811(1)
Cd1–Sb7	2.927(1)	Mn1–Sb7	2.804(1)
Cd1–Sb9	2.956(1)	Mn1–Sb9	2.821(1)
Cd2–Sb4	2.880(1) ×2	Mn2–Sb4	2.758(1) ×2
Cd2–Sb6	2.921(1)	Mn2–Sb6	2.856(2)
Cd2–Sb7	2.855(2)	Mn2–Sb7	2.781(1)
Cd3–Sb4	2.970(1) ×2	Mn3–Sb4	2.832(1) ×2
Cd3–Sb8	2.889(2)	Mn3–Sb8	2.841(1)
Cd3–Sb12	2.907(1)	Mn3–Sb12	2.824(1)
Sb6–Sb6	2.841(2)	Sb6–Sb6	2.857(1)
Sb2–Cd1–Sb3	126.53(3)	Sb2–Mn1–Sb3	121.54(3)
Sb2–Cd1–Sb7	109.12(3)	Sb2–Mn1–Sb7	109.12(3)
Sb2–Cd1–Sb9	112.26(3)	Sb2–Mn1–Sb9	111.68(3)
Sb3–Cd1–Sb7	106.78(3)	Sb3–Mn1–Sb7	109.62(3)
Sb3–Cd1–Sb9	106.63(3)	Sb3–Mn1–Sb9	107.52(3)
Sb7–Cd1–Sb9	88.97(3)	Sb7–Mn1–Sb9	93.83(3)
Sb4–Cd2–Sb4	121.65(4)	Sb4–Mn2–Sb4	119.07(5)
Sb4–Cd2–Sb6	110.99(3) ×2	Sb4–Mn2–Sb6	110.90(3) ×2
Sb4–Cd2–Sb7	111.99(3) ×2	Sb4–Mn2–Sb7	113.80(3) ×2
Sb6–Cd2–Sb7	82.53(4)	Sb6–Mn2–Sb7	82.55(4)
Sb4–Cd3–Sb4	115.70(4)	Sb4–Mn3–Sb4	114.20(5)
Sb4–Cd3–Sb8	110.49(3)	Sb4–Mn3–Sb8	110.52(3)
Sb4–Cd3–Sb12	107.82(3)	Sb4–Mn3–Sb12	108.92(3)
Sb8–Cd3–Sb12	103.76(4)	Sb8–Mn3–Sb12	103.15(4)

Figures

Figure 1

Figure 2

(a)

(b)

Figure 3

(a)

(b)

Figure 4

Figure 5

Graphical Abstract

$\text{Eu}_{21}\text{Mn}_4\text{Sb}_{18}$ and $\text{Eu}_{21}\text{Cd}_4\text{Sb}_{18}$ have complex monoclinic structures, based on MnSb_4 and CdSb_4 tetrahedra, both edge- and corner-shared. A perspective of the crystal structure is shown, as viewed along the b axis.