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Effect of Isovalent Substitution on the Structure and Properties of the Zintl Phase Solid Solution, $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ ($2 \leq x \leq 5$)

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Abstract

A novel Zintl phase structure type, $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ ($x = 2, 3, 4$ and 5), with the general formula $\text{Eu}_7\text{Cd}_4\text{Pn}_8$ (Pn = mixed occupancy Sb and As) has been synthesized by molten tin flux reaction. Its structure was determined using single-crystal X-ray diffraction methods. This structure type is only preserved for $2 \leq x \leq 5$ under our experimental conditions and efforts to synthesize samples with $x < 2$ or $x > 5$ resulted in other structure types. The mixed occupancy Sb and As can be thought of as a pseudoatom whose size, in this range of Sb/As ratios, fits the structure ideally. The title phase crystallizes in the *C*-centered monoclinic space group $C2/m$ (*No.* 12, $Z = 4$) with unit cell parameters ranging $a = 29.589(3) - 29.172(2)$ Å, $b = 4.677(4) - 4.6149(3)$ Å, $c = 19.723(17) - 19.455(13)$ Å, and $\beta = 125.651(1) - 125.53(1)^\circ$, depending on the Sb/As ratio. The structure can be described as parallel double pentagonal tubes resulting from Cd-Pn and Pn-Pn bonding. These double pentagons are formed through corner sharing of the Cd-centered CdPn_4 tetrahedra and a Pn-Pn interaction from two adjacent CdPn_4 tetrahedra. This structure type is closely related to the $\text{Sr}_{11}\text{Cd}_6\text{Sb}_{12}$ structure type as both share the same bonding features of Pn-Pn bonding and double pentagonal tubes. Electron microprobe analysis confirms the composition of these new Zintl solid solution phases. The As exhibits preferential substitution on specific sites, and site specificity trends are supported by lowest energy models from theoretical calculations. Theoretical calculations also predict that Sb-rich compounds should be metallic or semimetallic, and that they should become more insulating as As content increases. Members of the solid-solution order ferromagnetically between 5 K and 6 K, and exhibit relatively low electrical resistivity between 50 and 300 K, ranging from ~ 0.57 to ~ 26 mΩ·cm, increasing with increasing As content.

Keywords: Zintl phase, flux synthesis, transport properties, complex crystal structure, new structure type, solid solution, magnetism, intermetallic compounds, thermoelectric, density of states calculation

Introduction

Zintl phases are a class of polar intermetallic compounds that are traditionally comprised of electropositive Group 1 and 2 metal cations and electronegative main group anions. The electrons from metals are formally donated to the electronegative atoms, and as a result of an insufficient number of electrons transferred, the electronegative atoms covalently bond with one another in order to satisfy the octet rule.¹ This phenomenon leads to crystal structures that can be envisioned as polyanionic networks with isolated cations interspersed amongst them, which further results in Zintl phases occupying a wide range of diverse structure types. These structures, with varying degrees of structural complexity and chemical diversity, often exhibit interesting magnetic, electronic and thermoelectric properties.²⁻⁵ In recent years, traditional Zintl phase boundaries have been extended to include lanthanides and transition metals, especially those with d^0 , d^5 and d^{10} configurations. This expansion has resulted in an even larger breadth of compounds whose structural and electronic variety can yield unusual and favorable properties. An example is superconductivity that has been observed in the Zintl phases BaSn_3 ,⁶ $\text{Ba}_2\text{Sn}_3\text{Sb}_6$, and SrSn_3Sb_4 .⁷ In 2000, Mar and coworkers discovered the superconductivity of $\text{La}_{13}\text{Ga}_8\text{Sb}_{21}$ as part of their investigation of rare-earth gallium antimonides.⁸ The burgeoning field of thermoelectric materials has also been enriched by Zintl phases exhibiting high figure of merit zT ,⁹⁻¹² one of the most promising high temperature Zintl phase being $\text{Yb}_{14}\text{MnSb}_{11}$,¹³ demonstrating a thermoelectric figure of merit zT of ~ 1.0 at 1223 K. In addition, the $\text{A}_{14}\text{MnSb}_{11}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Eu}, \text{Yb}$) class of compounds has also yielded several materials displaying colossal magnetoresistance.¹⁴⁻¹⁶

Incorporation of transition metals in particular has resulted in a common structural feature: transition metal-centered MPn_4 tetrahedra bonded with pnictogen group elements that further bond to form complex structures. This is seen in a host of structural families including A_2MPn_2 ,¹⁷ CaAl_2Si_2 -type AM_2Pn_2 ,³ $\text{A}_2\text{M}_2\text{Pn}_3$,^{18,19} $\text{A}_3\text{M}_2\text{Pn}_4$,²⁰ and $\text{A}_{14}\text{M}_4\text{Pn}_{18}$ ²¹ (where $\text{A} = \text{Ca}, \text{Sr}$,

Ba, Eu and Yb, M = Zn and Cd, and Pn = P, As, Sb, and Bi). Amongst these structural families are several, such as $\text{Eu}_{11}\text{M}_6\text{Sb}_{12}$ ²² and $\text{Eu}_{10}\text{Cd}_6\text{Bi}_{12}$,²³ whose transition metal-centered tetrahedra combine similarly to form a double-pentagonal motif. The $\text{A}_{11}\text{M}_6\text{P}_{12}$ structure type (where A = Sr, Ca, Eu, M = Cd, Zn and P = Sb, As) was first synthesized as $\text{Sr}_{11}\text{Cd}_6\text{Sb}_{12}$,²⁴ and yielded several structural analogs including $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ and $\text{Eu}_{11}\text{Zn}_6\text{Sb}_{12}$,²² both of which have been investigated for potential thermoelectric applications.^{25,26}

Many Zintl phases have been proven to be amenable to various types of substitution given their structural flexibility; this substitution allows for tuning of certain properties toward optimization while maintaining the structure type.^{18,25,27-30} Here, we have synthesized the new Zintl phase solid solution $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ and investigated its crystal structure, electronic structure, magnetic properties, and low temperature electrical transport properties.

Experimental

Synthesis. $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ was initially identified as a byproduct of a Sn flux reaction aimed at producing $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12-x}\text{As}_x$.²⁵ Samples with $x = 2, 3, 4$ and 5 were synthesized by reacting Eu (chunk, Stanford Metals, 99.99%), Cd (moss, Aldrich, 99.9+%), Sb (shot, Aldrich, 99.9999%) As (chunk, Johnson Matthey Chemicals, 99.9999+%) in a Sn (shot, Alfa Aesar, 99.8%) flux. All samples were handled in an argon- or a nitrogen-filled glovebox or under vacuum. Reactions were carried out in 5 cm³ alumina crucibles that had been cleaned by immersion in an aqua regia acid bath for 2-3 minutes, soaking in nanopure water for 3-4 hours, then drying in an oven at temperatures of over 200 °C overnight. Eu chunk was brushed with a wire brush to remove the oxide layer, then cut into small pieces. All other elements were used as purchased. Metals were loaded into alumina crucibles after weighing them according to an appropriate molar ratio ($\text{Eu}:\text{Cd}:\text{Sb}:\text{As}:\text{Sn} = 7:4:(8-x):x:20$, where $x = 0, 2, 3, 4, 5, 6$ and 8) scaled for 5 g of Sn flux. To prevent oxidation during heating, filled crucibles were sealed in fused silica tubes (20 mm inner diameter x 22 mm outer diameter) under vacuum (pressure < 200 mTorr). Excess tubing was cut away to ensure that vessels fit into the furnace, and resultant tubes measured between approximately 8 and 11 mm in length. The sealed tubes were placed in a box furnace and heated at 100 °C/h to 600 °C, allowed to dwell for 6 hours, then heated at 50 °C/h to 1000 °C

and allowed to dwell for 96 hours. Reactions were then cooled at 5 °C/h to 600 °C and allowed to dwell an additional 24 hours. To remove molten tin flux, reaction vessels were removed from the furnace at 600 °C, inverted, and spun in a centrifuge at 6500 rpm for 3-5 minutes. Crystals were harvested in a nitrogen filled glovebox equipped with an optical microscope. Metallic, silver, needle-like crystals of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ were observed as the product.

Single Crystal X-ray Diffraction. Crystals were selected from each sample, cut to desired dimensions under Paratone N oil, and mounted on MiTiGen microloops. Diffraction data were collected at 90 K on a Bruker Apex II diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and CCD area detector. Unit cell determination was carried out for more than 4 crystals of different shapes from each sample and structure determination was carried out on one crystal from each sample. Four sets of ω scans ($0.3^\circ/\text{frame}$) at different φ settings were collected under a N_2 stream. Unit cell determination, refinements and raw frame data integrations were accomplished using APEX II v2013.10-0 software. Space group determination was based on systematic absences using XPREP and semiempirical absorption correction based on symmetrically equivalent reflections was completed using SADABS. The structures were solved using direct methods from the SHELXTL Version 6.14. For $x = 5$, the difference between EMPA and As determined by refinement (4.28 vs 4.63) was significant. When the amount of As was restricted to the amount of As found by EMPA, R_1 and wR_2 values did not change, but there was a slight tendency for defects on the As sites. This suggests that the single crystal data is not properly accounting for vacancies in the structure. Therefore, for $x = 5$, the refinement of As was restricted to the EMPA value. In all other structures, As amount was freely refined.

Powder X-ray Diffraction. Powders of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ samples were loaded on a Bruker zero-background holder for powder X-ray diffraction (XRD). XRD data were collected by a Bruker D8 Advance Diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) with 2θ range of 20 to 80° with a step size between $0.013\text{--}0.016^\circ$ and scan rate of 1.2 s per step. Refinements of unit cell parameters were performed with the FullProf Suite³¹ using the profile matching mode.

Electron Microprobe Analysis. Several single crystals from each sample were examined for phase composition by electron microprobe analysis (EMPA) using a Cameca SX-100 Electron

Probe Microanalyzer equipped with a wavelength-dispersive spectrometer with 20 keV accelerating potential and a 10 nA beam current. Crystals were coated in epoxy and polished for analysis. The polished samples were mounted on 25 mm metal rounds with carbon tape and coated with carbon for conductivity. Characteristic X-rays generated by samples were qualitatively analyzed by wavelength-dispersive spectroscopy to determine compositions of samples using X-ray intensities of Eu, Cd, Sb, As and Sn as compared to calibrated standards EuPO_3 , Cd (metal), Sb (metal), GaAs, and Sn (metal). Elemental mapping was also performed to assess element homogeneity in each sample.

Electronic Structure Calculations. Electronic structure and total energies of various models of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ were calculated using the tight binding - linear muffin tin orbitals - atomic sphere approximation (TB-LMTO-ASA) program package.³² The unit cell parameters of $x = 0, 1$ and 8 could not be experimentally determined, so they were extrapolated based on linear fits of the experimentally determined unit cell parameters for samples $x = 2, 3, 4$, and 5 vs As content. For models of $x = 2$, experimentally determined unit cell parameters for sample $x = 2$ were used. For models $x = 0, 1$, and 2 , experimentally determined atomic positions for sample $x = 2$ were used, and for $x = 8$, experimentally determined atomic positions for $x = 5$ were used. Interstitial empty spheres were used to achieve complete filling of the space. The Barth-Hedin exchange potential was employed for LDA calculations. Radial scalar-relativistic Dirac equation was solved to obtain the partial waves. Empty spheres were necessary to achieve the LMTO volume criterion, and the overlap of the WS spheres was limited to no larger than 16%. The calculation was made for the grid of $12 \times 12 \times 6$ κ points with 242 κ -points in the irreducible Brillouin zone. Integration over the Brillouin zone was made by the tetrahedron method.³³ The basis set contained Eu (6s, 6p, 5d), Sb (5s, 5p), Cd (5s, 5p, 4d) and As (4s, 4p) with Eu(6p), Sb(5d, 4f), Cd(4f) and As(4d) functions being downfolded, while 4f electrons of Eu were treated as core electrons.

Magnetic Susceptibility Measurements. Magnetization measurements were performed in a Quantum Design MPMS SQUID magnetometer. Single crystals of each sample of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ were selected in a glove box under a microscope and the weight of each was measured. Each was secured on a strip of Mylar paper with Kapton tape and inserted into a commercial plastic straw for measurement. Each crystal was mounted with the a -axis parallel to the magnetic field

(the orientation of the crystal was determined by face-indexing during single-crystal X-ray diffraction). Zero field-cooled (ZFC) and field-cooled (FC) temperature-dependent magnetization was measured in a field of 0.1 T from 2-300K. Field-dependent magnetization was measured at 2K using fields from 0 T to 7 T for all samples and -7 T to 7 T for one $x = 2$ sample. Raw temperature-dependent data were converted to molar magnetic susceptibility ($\chi_m = M/(H \cdot \text{moles of sample})$) in emu/mol-Eu units. Raw field-dependent data were converted to Bohr magnetons (μ_B) per formula unit.

Transport Property Measurement. The electrical resistivity between 2 and 300 K was measured using a standard four-probe method with a physical property measurement system (PPMS, Quantum Design, Inc). Crystals were mounted on AC transport pucks using a low-background adhesive, and Pt wires were soldered to the puck and attached to crystals with silver paste.

Results and Discussion

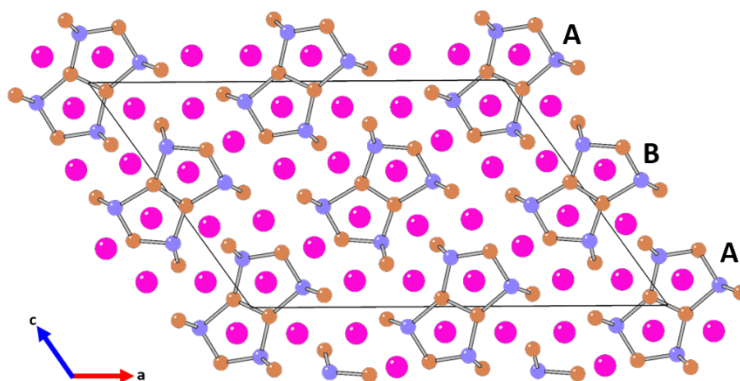


Figure 1: A view of the structure of $\text{Eu}_7\text{Cd}_4\text{Pn}_8$ ($\text{Pn} = \text{Sb/As}$) with one unit cell outlined. Eu, Cd, and Pn atoms are indicated by magenta, purple, and tan spheres, respectively. The crystallographically unique pentagonal motifs A and B are labeled.

Phase Synthesis and Purity. $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$, pictured in Figure 1, was synthesized by Sn flux synthesis, where x ranges from 2 to 5; under the presented conditions, this phase could only be synthesized as a mixed occupancy species with both Sb and As occupying pnictogen sites, so it will be generally referred to as $\text{Eu}_7\text{Cd}_4\text{Pn}_8$. Attempted syntheses of phases with $x < 2$ or $x > 5$ resulted in other phases that are not the focus of this manuscript. The title phase crystallizes in the monoclinic crystal system with the space group $C2/m$ (No. 12). The phase contains 19 crystallographically unique atom positions – eight pnictogen positions, seven Eu positions, and

four Cd positions – all in special positions ($4i$ Wyckoff site). There are no other reported compounds with the same atomic arrangement, making this a unique structure type based on a search of the reduced unit cell and Wyckoff sequence in the latest edition of the Inorganic Crystal Structure Database.³⁴ Single-crystal and powder x-ray diffraction as well as electron microprobe analysis were used to examine the products of each reaction. Structures were solved with $R_1 < 3.4\%$ and $wR_2 < 7.1\%$; details can be found in Table 1 and CIF files in the Supporting Information. There was no evidence of Sn incorporation into the structure according to electron microprobe analysis (EMPA) on single crystals (*vide infra*).

Powder X-ray diffraction was used to determine the phase purity of each sample. The whole pattern fitting for all samples based on refined single-crystal X-ray diffraction data is shown in Figure 2 including χ^2 values. In samples $x = 2, 3$, and 4 , no obvious impurity was detectable by X-ray diffraction. In sample $x = 5$, there were several unassigned peaks that were attributed to an impurity phase $\text{Eu}_2\text{CdSb}_{2-x}\text{As}_x$ (impurity peaks indicated with red arrows).

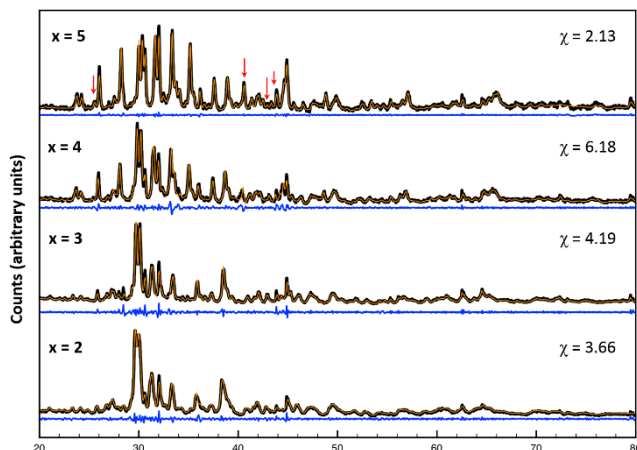


Figure 2. Powder X-ray diffraction patterns of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$, $x = 2, 3, 4$, and 5 . The data are shown in black, the calculated refinement in orange, and the difference is indicated below. Red arrows in $x = 5$ pattern indicate peaks attributed to an impurity phase, $\text{Eu}_2\text{CdSb}_{2-x}\text{As}_x$.

Figure 3a shows the amount of As in samples determined by EMPA. Both methods show similar amounts of incorporated As at low nominal x values, however the values begin deviate as the amount of As increases. Incorporated As estimated by x-ray diffraction is consistently lower than what is estimated by EMPA. When the amount of As was not allowed to freely refine, but was restricted to the amount of As found by EMPA, R_1 and wR_2 values did not change, only As occupancies. This suggests that the single crystal data is not properly accounting for vacancies in

the structure. Figure 3b shows elemental x-ray mapping of single crystals from each sample and the uniform color indicates that As is homogeneously distributed in each sample. Additionally, Figure S1 of the Supporting Information provides elemental mapping of Sn showing that residual Sn flux is not homogeneously distributed and appears in small amounts on each crystal.

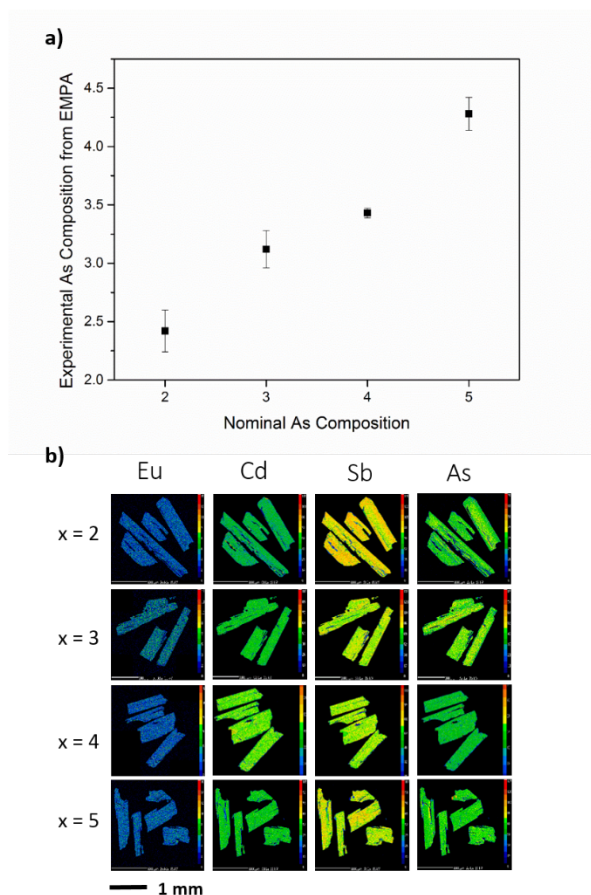
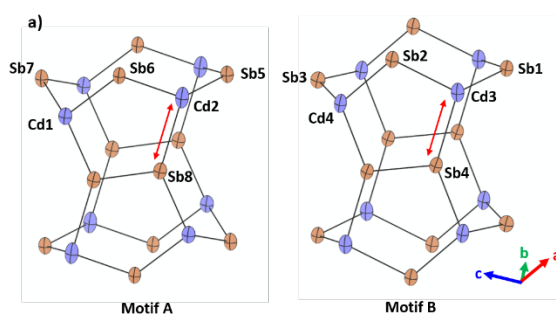


Figure 3: (a) The amount of As incorporated into each crystallized sample as determined by EMPA. **(b)** Elemental X-ray mapping images from electron microprobe analysis show the relative homogeneity of each element in single crystals of each sample. The scale bar of each image is 1 mm.

Structure. The structure of $\text{Eu}_7\text{Cd}_4\text{Pn}_8$ can be described as alternating double-pentagonal motifs that extend quasi-infinitely in the *b*-direction. These double-pentagons are comprised of CdPn_4 tetrahedra that are corner-shared as well as bridged by Sb_2 dimers to form two crystallographically unique double pentagonal motifs A and B (Figure 4a and b), which alternate as ABAB along the *c*-axis (shown in Figure 1). The double-pentagonal units are further corner shared to extend in the *b*-direction, forming tubes encapsulating Eu_2 and Eu_4 cations. The other four Eu cation positions are dispersed between the layers of double pentagonal tubes; Eu coordination environments are depicted in Figure 4c. As previously mentioned, under the

presented synthesis conditions, the compound can only be synthesized as a solid solution of Sb and As on pnictogen sites in which there is mixed occupancy in all sites. In this way, the combination of Sb/As can be thought of as a pseudoatom whose size matches this structure very well.

There are four unique Cd positions in the anionic network. The seven unique Eu^{2+} cations provide electrons to the anionic network and fill space, taking on two different coordination geometries (Figure 4b and c). Two of the sites, Eu2 and Eu4, take on a 10-coordinate geometry akin to that of eclipsed ferrocene, with the ten coordinating atoms being both Sb/As pseudoatoms and Cd atoms. The majority of the sites – Eu(1), Eu(3), Eu(5), Eu(6), and Eu(7) – take on a pseudo-octahedral coordination geometry, with six coordinating Sb/As pseudoatoms. According to the Zintl concept, the formal charges of the atoms in the polyanionic network can be assigned based on the number of bonds each has. In that way, the two three-bonded Sb/As pseudoatoms can be assigned as Sb^0/As^0 and the six two-bonded pseudoatoms can be assigned as $\text{Sb}^{-1}/\text{As}^{-1}$. Similarly, the four-coordinate Cd atom requires two electrons to complete its octet, and therefore can be assigned as Cd^{2-} . Thus, the compound can be described as a valence precise compound $(\text{Eu}^{2+})_7[(\text{Cd}^{2-})_4(2b\text{Sb}^{-1})_6(3b\text{Sb}^0)_2]$. Additionally, if we consider an ionic model in which the Cd atoms act as electropositive metals that will likely donate electrons to the structure (to yield Cd^{2+}), the compound can also be described as $(\text{Eu}^{2+})_7[(\text{Cd}^{2+})_4(\text{Sb}^{3-})_6[\text{Sb-Sb}]_2]^{2-}$.



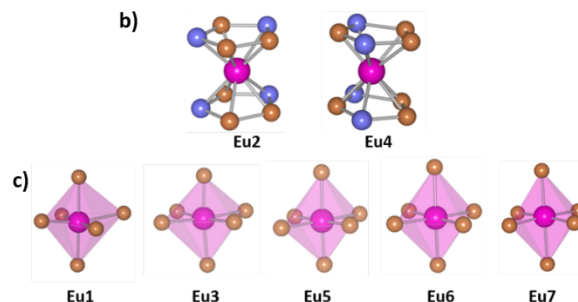


Figure 4: (a) Double pentagonal motif made of Cd(1)- and Cd(2)-centered tetrahedra (motif A) and Cd(3)- and Cd(4)-centered tetrahedra (motif B) represented as thermal ellipsoids at the 95% probability level, motif A. The unusually long contact in each is indicated with a red arrow. (b) Coordination environments of the two eclipsed ferrocene-like Eu sites. (c) Coordination environments of the other five Eu sites are pseudo-octahedral.

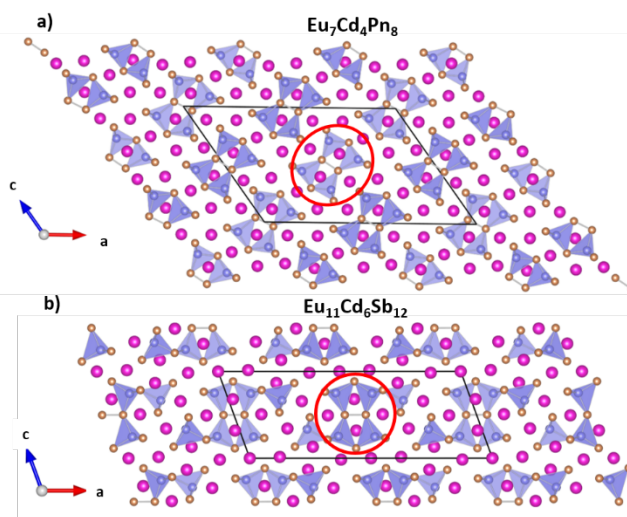


Figure 5: (a) The crystal structure of $\text{Eu}_7\text{Cd}_4\text{Pn}_8$ projected down the *b*-axis with one unit cell outlined. Eu, Cd and Sb atoms are shown in pink, purple and tan, respectively. As atoms, which occupy the same positions as Sb atoms, are hidden for clarity. (b) The crystal structure of $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ projected down the *b*-axis is shown for comparison with one unit cell is outlined. The double-pentagonal motif that both crystal structures share is circled.

The structure of $\text{Eu}_7\text{Cd}_4\text{Pn}_8$ is similar the structure of $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ (Figure 5a and b, respectively).²² The two structures share the same space group, $C2/m$, and the latter is also made up of Cd-centered tetrahedra that form double-pentagonal motifs and extend along the *b* direction. The double-pentagonal units in $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ contain an additional two CdSb₄ tetrahedra attached to Sb atoms.

It should be noted that, in both $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$ and $\text{Eu}_7\text{Cd}_4\text{Pn}_8$, the double-pentagonal motifs do not form perfect pentagons and the two sides of the pentagons are asymmetrical in length. This is due to both structures containing an unusually long Cd-Sb contact. In $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12}$,

the long Cd-Sb distance is 3.1965(8) Å, and Eu₇Cd₄Pn₈ there is one in each of the crystallographically unique double-pentagonal motifs; Cd(3)-Sb(4) and Cd(2)-Sb(8) which fall in the range 3.152(8)-3.1262(6) Å and 3.2004(8)-3.2283(7) Å throughout the solid solution, respectively. In both structures, these bonds are nearly 20% longer than the sum of the covalent radii.³⁵ This is especially unusual considering the remaining bond lengths in the Eu₇Cd₄Pn₈ structure, which range from 2.594(6) Å – 2.943(3) Å throughout the solid solution compare well to distances reported for other ternary A-Cd-Pn arsenides and antimonides with structures based on Cd-centered tetrahedra.^{17,22,36,37} Selected bond lengths are listed in

Table 2 and a completed list is given in the Supporting Information. Bobev and coworkers noted the same long Cd-Sb contact in pentagonal motifs in both Ba₁₁Cd₆Sb₁₂ and Sr₁₁Cd₆Sb₁₂.³⁸ They further conclude that this unusually long contact should not be treated as a typical 2-center-2-electron bond because of the elongation of the Cd thermal ellipsoids (also seen in Eu₇Cd₄Pn₈ structure, Figure 4a). They additionally find that Sb₂ dimers with distances shorter than 2.85 Å are found in the literature³⁹ and generally connected to two Cd atoms; however, Sb₂ dimers that are four-connected are less common and have longer distances (around 2.95 Å).

We also note that the two motifs within Eu₇Cd₄Pn₈ behave differently with respect to this long contact. Both motif A and motif B have an elongated thermal ellipsoid pointing in the direction of the Sb₂ dimer (see Figure 4a and b), however only the former exhibits a shorter Sb₂ distance associated with two-bonded dimers in the literature (2.7346(1) – 2.5894(9) Å). Motif B has a longer Sb₂ distance within the dimer associated with the less common four-bonded dimer (2.803(1) – 2.6907(8) Å). Furthermore, throughout the solid solution, in motif A the Cd(2)-Sb(8) bond increases in length as the unit cell size shrinks (from 3.2004(8) to 3.2283(7) Å), whereas the analogous Cd(3)-Sb(4) length in motif B decreases with the decreasing unit cell size (from 3.152(8) to 3.1262(6) Å).

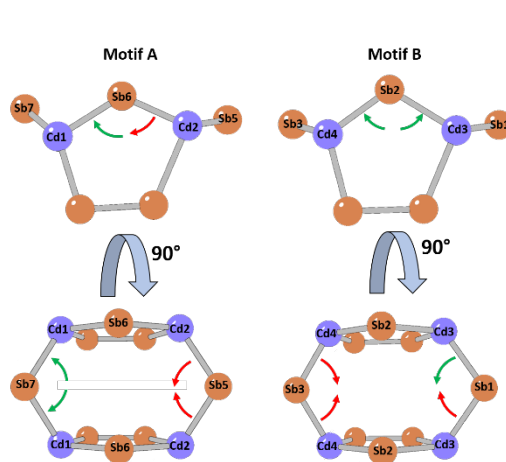


Figure 6: Representation of a single pentagon from both Motif A and Motif B with arrows indicating how each bond angle changes with increasing As substitution. Green arrows indicate increasing bond angle and red arrows indicate decreasing bond angle.

When examining selected bond angles within the pentagonal motif (listed in

Table 2), it becomes apparent that even though motifs A and B seem identical, their bond angles change in different manners. There are several competing interactions here, depicted in Figure 6: The angles at the apex of the pentagon of Motif A does not change consistently while in Motif B, the angle increases steadily. Furthermore, within each motif, there are two angles that determine the distance between the stacked pentagonal units in the *b* direction. In Motif A, one angle increases while the other decreases. In motif B, however, one angle increases, while the other does not change consistently. These competing trends may be responsible in part for the limited range of this solid solution and, therefore, reinforce the idea of the Sb/As pseudoatom in this range being the ideal size to fit the structure.

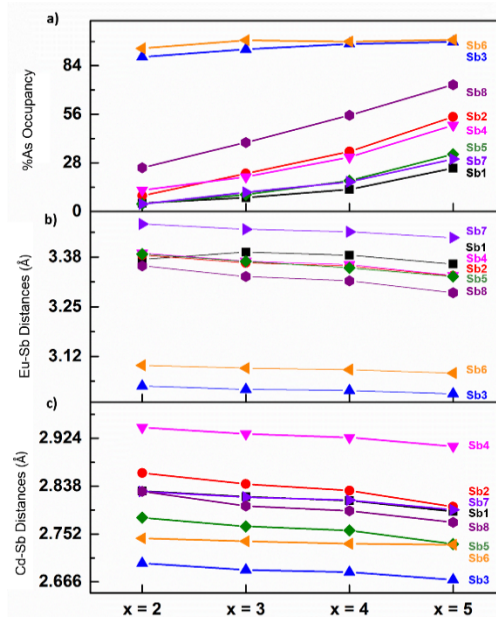


Figure 7: Graphs showing (a) the percentage of As incorporated per Sb site, (b) the average distances between Sb and Eu sites (up to 3.5 Å) and (c) the average distances between Sb and Cd sites (up to 3 Å) vs composition.

We also analyzed each Pn site environment by considering its distance from the other substituent elements Eu and Cd. The average Sb-Eu distances shown in Figure 7b show that Sb-Eu distances increase in the following order: Sb6 < Sb3 << Sb8 < Sb2~Sb4 < Sb1 < Sb5 < Sb7. Notably, sites Pn3 and Pn6 have considerably shorter Eu-Pn distances as compared to distances between Eu and other Pn sites. The average Cd-Sb distances in Figure 7c indicate that Cd-Sb distance increases in the following order: Sb3 < Sb6 < Sb5 < Sb8 < Sb7~Sb1 < Sb2 << Sb4.

Site Preference. As the As content increases in the solid solution, the lattice parameters decrease, which is consistent with the smaller covalent radius of As (1.19 Å) compared to Sb (1.39 Å)³⁵ and structural data in Table 1. The structure contains eight crystallographically unique Sb sites into which As may substitute. It is expected that, in an ideal solid solution, As would uniformly distribute throughout the Sb positions. However, refined site occupancies from single-crystal diffraction data show that As atoms preferentially substitute on certain sites, known as the “coloring problem”.⁴⁰ Figure 7a shows experimentally determined site occupancy percentages of As incorporated into each pnictogen site plotted as a function of nominal As content. In all samples, preferential substitution occurs at sites Sb6, Sb3 and Sb8.

Table 1: Selected diffraction data.

Nominal x Value	x = 2	x = 3	x = 4	x = 5
Empirical Formula	Eu ₇ Cd ₄ Sb _{5.53} As _{2.47} (3)	Eu ₇ Cd ₄ Sb _{4.67} As _{3.33} (3)	Eu ₇ Cd ₄ Sb _{4.35} As _{3.65} (2)	Eu ₇ Cd ₄ Sb _{3.38} As _{4.62} (2)
FW (g/mol)	2371.65	2331.49	2316.27	2270.90
T (K)	90			
Radiation	Mo K α , λ = 0.71073 Å			
Space Group	C 2/m (No. 12)			
Z	4			
Crystal System	Monoclinic			
Unit cell dimensions (Å/°)	a = 29.589(3) b = 4.677(4) c = 19.723(17) β = 125.651(1)	a = 29.427(18) b = 4.6558(3) c = 19.629(12) β = 125.595(1)	a = 29.346(2) b = 4.6468(4) c = 19.558(16) β = 125.4943(9)	a = 29.172(2) b = 4.6149(3) c = 19.455(13) β = 125.53(1)
Volume (Å ³)	2218.0(3)	2186.9(2)	2171.4(3)	2131.4(2)
ρ_{calc} (g/cm ³)	7.102	7.081	7.085	7.077
μ (Mo K α , cm ⁻¹)	334.41	341.69	345.08	354.41
GOF on F ²	1.061	1.050	1.020	1.097
R_1 [$I > 2\sigma(I)$] ^a	0.0208	0.0279	0.0213	0.0192
wR_2 [$I > 2\sigma(I)$] ^a	0.0420	0.0669	0.0437	0.0422
R_1^a [all data]	0.0250	0.0335	0.0265	0.0214
wR_2^a [all data]	0.0433	0.0703	0.0457	0.0431
Largest peak/hole (e/ $\text{\AA}^3$)	1.61/-1.749	2.864/-2.326	1.571/-1.804	2.002/-1.975

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

Table 2: Selected bond distances (Å) and angles (°).

	Eu ₇ Cd ₄ Sb _{5.53} As _{2.47} (3)	Eu ₇ Cd ₄ Sb _{4.67} As _{3.33} (3)	Eu ₇ Cd ₄ Sb _{4.35} As _{3.65} (1)	Eu ₇ Cd ₄ Sb _{3.38} As _{4.615} (2)
Pn4-Cd3	3.152(8)	3.138(1)	3.138(7)	3.1262(6)
Pn4-Cd4	2.9416(7)	2.932(1)	2.9257(7)	2.9097(6)
Pn4-Pn4	2.803(1)	2.766(1)	2.7446(9)	2.6907(8)
Pn8-Pn8	2.7346(1)	2.671(2)	2.647(1)	2.5894(9)
Pn8-Cd1	2.8269(7)	2.802(1)	2.7937(7)	2.7730(6)
Pn8-Cd2	3.2004(8)	3.207(1)	3.209(2)	3.2283(7)
Cd3-Pn1-Cd3	111.47(2)	111.32(3)	111.43(2)	111.439(18)
Cd4-Pn2-Cd3	112.63(2)	112.86(3)	112.91(2)	113.496(1)
Cd4-Pn3-Cd4	120.08(3)	120.04(4)	119.95(3)	119.60(2)
Cd2-Pn5-Cd2	114.48(3)	114.63(3)	114.76(2)	115.13(2)
Cd2-Pn6-Cd1	123.53(3)	123.43(4)	123.36(3)	123.73(2)

Preferential As substitution occurs in the following site order: Sb6, Sb3, Sb8, Sb2~Sb4, Sb5~Sb7~Sb1 (Figure 7a). We looked to simple structural reasoning to understand what governs the site specificity phenomenon in this phase. In previous research examining site preference in isovalent substitution in $\text{Eu}_{13}\text{AMnSb}_{11}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}, \text{and Yb}$), it was found that the smaller Yb and Ca prefer to substitute into the most geometrically symmetrical sites; e.g. octahedrally coordinated Eu sites nearest to perfect octahedral geometry had the highest amounts of Yb or Ca substitution.⁵ It follows that, since As is smaller than Sb, it may also prefer to substitute into more geometrically symmetric sites. However, in this structure there is no common geometrical coordination (octahedral, tetrahedral, etc.) to compare amongst the Sb sites, so this logic is not easily applied. Another proposed reasoning is that the more electronegative As atoms will preferentially substitute into Sb sites with more negative formal charges. However, all but two of the Sb sites are assigned the same formal charge, yet these sites all contain very different amounts of As.

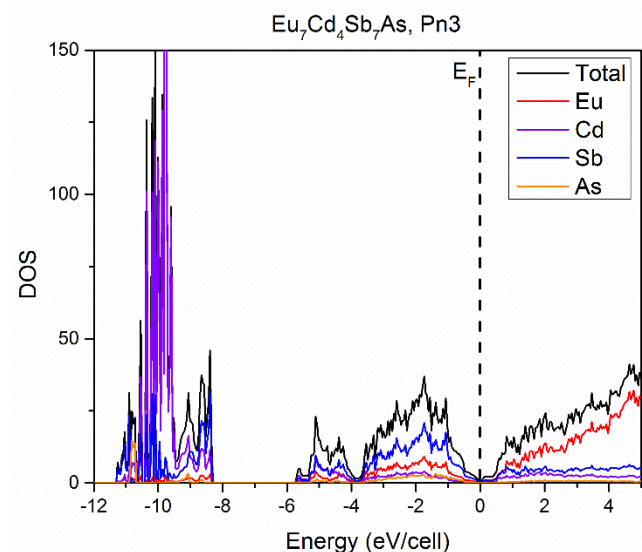


Figure 8: Projected density of states (DOS) for the lowest energy hypothetical compound $\text{Eu}_7\text{Cd}_4\text{Sb}_7\text{As}$ in which As fully occupies Pn3.

In order to further probe As site preference, eight models of the theoretical compound “ $\text{Eu}_7\text{Cd}_4\text{Sb}_7\text{As}$ ” were calculated, each having As fully occupy one of the eight pnictogen sites (Pn1 through Pn8). A procedure similar to work done on $\text{Eu}_{11}\text{Cd}_6\text{Sb}_{12-x}\text{As}_x$ was followed.²⁵ Figure 8 shows the density of states of the lowest energy model, $\text{Eu}_7\text{Cd}_4\text{Sb}_7\text{As}$ with As fully occupying

Pn3. States closest to the Fermi level are predominantly Sb $5p$ and Eu $5d$ orbitals which indicates significant cation-anion mixing and, furthermore, implies that Eu-Sb interactions are not completely ionic, suggesting that the Zintl count is oversimplified. States between -12 eV and -8 eV correspond to filled Cd- d orbitals with some contribution of Sb and As- s orbitals. States between -6 eV and -4 eV predominantly consist of Sb- p states with contributions from Eu- d and Eu- s states as well as Cd- s states. States between -4 eV and the Fermi level are Sb- p and Eu- d atomic functions with some contribution from Cd- p . Each of the Eu sites contributes to the DOS approximately equally. Sb5 and Sb7, which connect double-pentagonal units (motif A) along the b direction, have the highest contribution at the Fermi level, whereas the 3-bonded Sb8 and Sb4, which are shared between pentagons in the ac -plane, have the smallest contribution. Figure S2 of the Supporting Information compares density of states plots of each the models and shows that changing the site occupied by As has little impact on the electronic structure, especially in the vicinity of the Fermi energy.

Figure 9 shows the difference in relative total energy of each model with respect to the lowest energy model (Pn3, set at 0 eV/cell) compared to the experimentally determined percent occupancy of As in $x = 2$. According to the total energies, As substitution should follow the order: Pn3 > Pn8 > Pn4 > Pn6 > Pn7 > Pn1 > Pn2 > Pn5. This order roughly correlates to the percent occupancy of As: sites that were preferentially occupied by As yield models with lower total energies than sites less preferred by As. Although the trend roughly matches that of site preference, the magnitude in energy difference does not correspond with the magnitude in percent occupancy differences. For example, site Pn6 has the largest percentage of As, but is only slightly lower in energy than four other Pn sites, and remains much higher in energy than two others. To examine the possibility that multiple site substitution leads to additional stabilization, two models of $\text{Eu}_7\text{Cd}_4\text{Sb}_6\text{As}_2$ were calculated: one in which both Pn1 and Pn5 (the least occupied Pn sites) were fully occupied by As, and one in which Pn3 and Pn6 (the most occupied Pn sites) were fully occupied by As. ΔE between the two models is ~ 2.289 eV/cell, with the Pn3Pn6 model being lower in energy. This suggests that in addition to some sites favoring As occupation, there exists additional stabilization when sites are occupied simultaneously. It should be noted that these calculations are performed using unit cell

parameters extrapolated from experimentally determined parameters to $x=1$, as well as experimentally determined fractional coordinates for atom positions. These parameters may oversimplify the results because they have not been geometrically optimized. However, the results still suggest that the pseudoatom is important for structural stability.

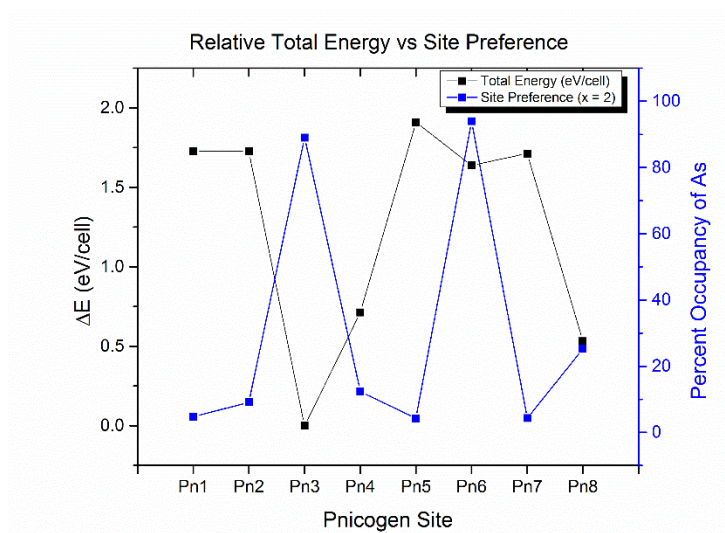


Figure 9: Relative total energies of calculated models of $\text{Eu}_7\text{Cd}_4\text{Sb}_7\text{As}$ with As singly occupying each of the eight pnictogen position versus experimentally determined site occupancy of As in $x = 2$.

Models for the theoretical end members of the solid solution “ $\text{Eu}_7\text{Cd}_4\text{Sb}_8$ ” and “ $\text{Eu}_7\text{Cd}_4\text{As}_8$ ” were also calculated. The band structure calculated for the hypothetical compound $\text{Eu}_7\text{Cd}_4\text{Sb}_8$ (Figure 10a) suggests that samples should have metallic character since in its band structure, there are several conduction band valleys crossing the Fermi level consistent with the pseudogap. The band structure for hypothetical compound $\text{Eu}_7\text{Cd}_4\text{As}_8$ (Figure 10b) shows that there is a band gap opening along all directions except Γ -A where there is a band valley crossing the Fermi level, which results in the non-zero DOS at the Fermi level. This trend is in line with the larger polarity of As-Cd bonds as compared to Sb-Cd bonds, and also is reflected in the resistivity measurements discussed below.

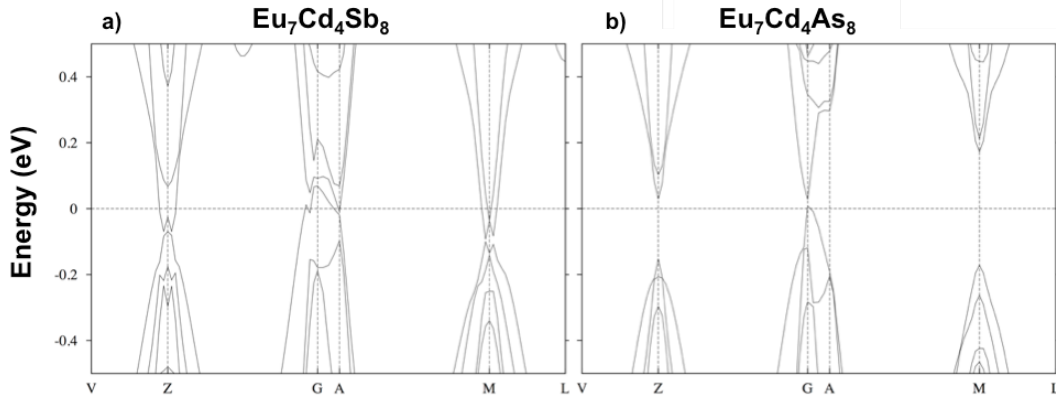


Figure 10: Calculated band structures of hypothetical compounds a) $\text{Eu}_7\text{Cd}_4\text{Sb}_8$ and b) $\text{Eu}_7\text{Cd}_4\text{As}_8$. The former shows metallic character, while the latter shows opening of the band gap with complete occupation of As.

AC Resistivity. Figure 11 shows the resistivity of each sample as a function of temperature. Each sample's resistivity decreases with decreasing temperature, however each shows an upturn in resistivity at low temperatures ($T < 30$ K). The abrupt decrease in resistivity in $x = 2, 3$ can be attributed to the superconducting transition of residual Sn flux ($T_c \sim 3.7$ K). The resistivity is affected by the amount of As substitution in each sample and as As substitution increases, resistivity also increases. This is in line with previously discussed band structure calculations predicting a lower density of states at the Fermi level for the hypothetical As-only phase. The low temperature behavior is also affected by As substitution: as As content increases, the low temperature upturn in resistivity is more pronounced.

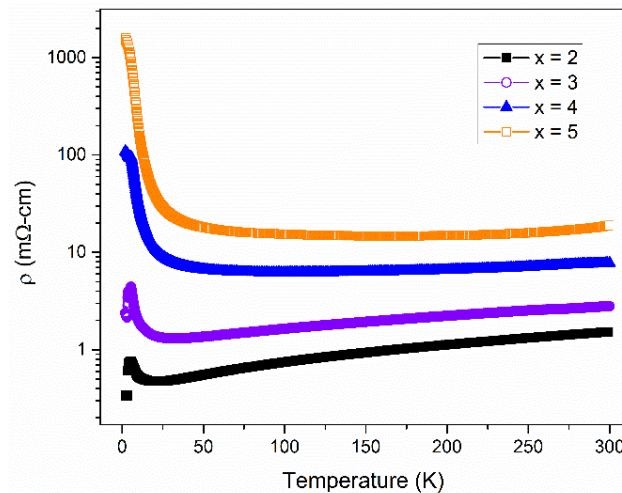


Figure 11: Electrical resistivity measurements below room temperature for $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$, $x = 2, 3, 4$ and 5 . Each sample exhibits metallic/semi-metallic resistivity between about 30 K and room temperature and resistivity increases as As content increases.

Magnetic Properties. Figure 12 shows zero field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility as a function of temperature for $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$, $x = 2$. Magnetic data for samples $x = 3, 4$, and 5 (including $1/\chi$) are shown in Figures S3 and S4 of the Supporting Information. All samples exhibit ferromagnetic ordering as indicated by the increase in magnetic susceptibility at low temperatures for the FC measurement and the positive Weiss constant (given in Table 3) which suggests a ferromagnetically ordered system. The inset in Figure 12 shows a bifurcation in the FC/ZFC measurements. The transition temperature increases from $x = 1$ to $x = 2$, which is expected as the unit cell contracts with increasing As , however, for $x \geq 3$, the T_C then plateaus at $T_C = 5.75$ suggesting that magnetic interactions are no longer affected by the contraction of the unit cell. Above about 50 K, each sample exhibits paramagnetic behavior. The effective magnetic moment of each sample was calculated from a fit to a modified Curie-Weiss law in the paramagnetic regime, and resultant parameters are listed in Table 3. Experimental magnetic moments agree well with calculated values based on the spin-only effective magnetic moment for Eu^{2+} . Sample $x = 2$ gives a slightly higher number of Eu^{2+} (7.56 moles per formula unit) than is expected from the formula unit, and $x = 3$ and 5 are slightly smaller. The $x = 2$ sample was measured with two crystals from different sample batches, and both gave amounts of Eu^{2+} slightly higher than 7. This could be attributed to either a slightly different formula or a small amount of a secondary phase present in each of these samples. The slightly lower moments in $x = 3$ and 5 could be due to small amounts of Sn flux inclusion. Overall, these results suggest that Eu is divalent and orders ferromagnetically around 5.75 K, and also confirm the formula of the compounds.

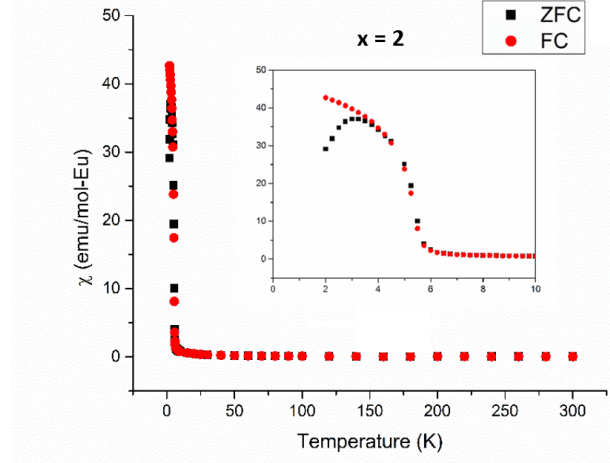


Figure 12: χ vs temperature of $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ samples $x = 2$ measured under a field of 100 Oe. All samples exhibit ferromagnetic ordering and are fitted to a modified Curie-Weiss law in the paramagnetic regime after 50 K.

Table 3. Magnetic data for $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$, $2 \leq x \leq 5$.

	$x = 2$	$x = 3$	$x = 4$	$x = 5$
Experimental x (determined from single-crystal XRD)	2.47	3.33	3.66	4.62
MW (g/mol)	2374.123	2331.624	2329.868	2271.0145
χ_0^a (emu/mol)	-0.0077(48)	-0.00423(18)	-0.0023(32)	-0.0055(2)
C^a	59.6(1.1)	50.80(38)	55.26(67)	50.85(53)
$\mu_{\text{eff, theoretical}} (\mu_B)^b$	21.01	21.01	21.01	21.01
$\mu_{\text{eff, experimental}} (\mu_B)^c$	21.83(19)	20.15(15)	21.02(12)	20.16(72)
θ (K) a	1.71(79)	3.78(32)	4.39(51)	4.10(44)
Number of Eu^{2+} /f.u.	7.56(13)	6.44(9)	7.01(8)	6.44(46)
T_C (K)	5.25	5.75	5.75	5.75
Fit range (K)	50-300	50-300	50-300	50-300

Data were fitted to a modified Curie-Weiss law, $\chi(T) = \chi_0 + (C/T - \vartheta)$ in the paramagnetic regime (50-300K), where χ_0 is the diamagnetic correction, C is the curie constant, T is temperature and ϑ is the Weiss constant. a Obtained from fitting the data to equation, $\chi(T) = \chi_0 + (C/T - \vartheta)$. b Calculated as the spin-only effective magnetic moment for Eu^{2+} using $\mu_{\text{eff}} = \sqrt{n(n+2)}$, where n is the number of unpaired electrons. c Using the equation $\mu_{\text{eff}} = (8C)^{1/2}$

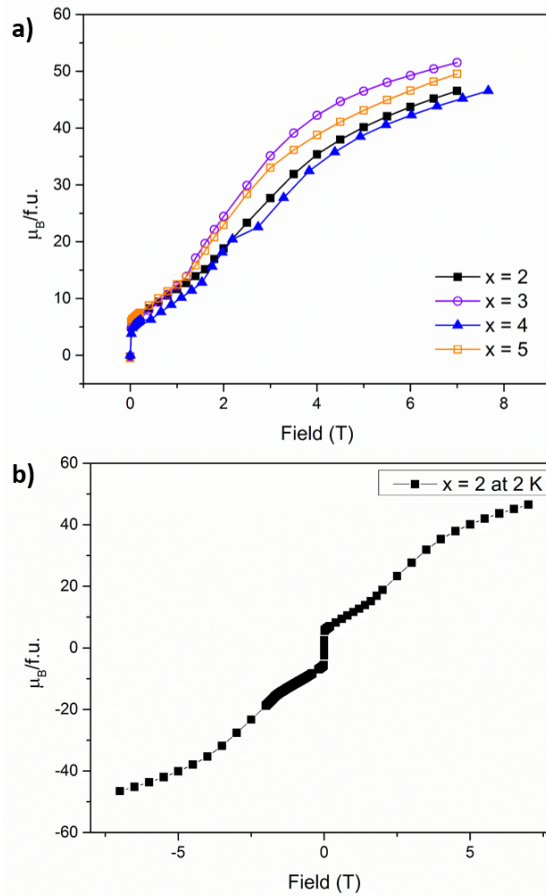


Figure 13: (a) Field-dependent magnetization of each sample from 0T to 7T at 2 K. (b) Field dependent magnetization of sample $x = 2$ from -7T to 7T at 2 K.

Figure 13a shows field-dependent magnetization of each sample from 0 to 7 T at 2 K. The samples all follow very similar ordering patterns, however none show saturation at $\sim 55 \mu_B/f.u.$ as would be expected for samples with 7 Eu^{2+} cations/formula unit. Figure 13b shows a full loop M vs H measurement for sample $x = 2$. This confirms that there are complex magnetic interactions taking place, attributable to the complex Eu network in the compound. Very close to 0T, there is a ferromagnetic ordering taking place, and as the magnetic field increases, the magnetic coupling changes. At higher fields, this coupling changes yet again and the magnetization appears to slightly turn over as if there is a possibility of saturation.

Conclusions. A new quaternary compound $\text{Eu}_7\text{Cd}_4\text{Sb}_{8-x}\text{As}_x$ was successfully synthesized using the Sn flux method and characterized by single crystal x-ray diffraction and electron microprobe analysis. It exists as a limited solid solution, owing to the fact that the size of the Sb/As pseudoatom in this limited range is ideal to preserve this structure. The site preference of the As atoms can be roughly explained by simple size effects, and theoretical calculations further

elucidate reasons for As site preference. Magnetic susceptibility is suggestive of all Eu as Eu^{2+} cations, which is consistent with Zintl-Klemm electron counting rule. Electrical resistivity with increasing temperature indicative of metallic/semimetallic behavior. These compounds, especially the Sb-rich species, have relatively low resistivity between 50 and 300 K, ranging from ~ 0.57 to $\sim 26 \text{ m}\Omega\cdot\text{cm}$, and resistivity increases as expected with As content. Although reactions intended to synthesize either $\text{Eu}_7\text{Cd}_4\text{Sb}_8$ or $\text{Eu}_7\text{Cd}_4\text{As}_8$ failed, the low resistivity coupled with the large unit cell, complex structure, and heavy atom incorporation that may yield low thermal conductivity show that the mixed occupancy species has potential to be a good thermoelectric material at low temperatures.

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Supporting Information Available: X-ray crystallographic files in CIF format, images of elemental X-ray mapping of Sn, density of states plots of eight models of $\text{Eu}_7\text{Cd}_4\text{Sb}_7\text{As}$, and additional magnetism data.

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A new Zintl phase structure type, $\text{Eu}_7\text{Cd}_4\text{Pn}_8$, has been synthesized and characterized. The compound only exists as a mixed-occupancy solid solution, with Sb and As occupying Pn sites and acting as a pseudoatom appropriately sized for $2 \leq x \leq 5$.

