Synthesis, Structural Characterization, and Physical Properties of the Type-I Clathrates $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$) and $Cs_8Cd_{18}As_{28}$ Hua He,[†] Alex Zevalkink,[‡] Zachary M. Gibbs,[§] G. Jeffrey Snyder,[‡] and Svilen Bobev^{*,†}[†]Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States[‡]Materials Science and [§]Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, California, 91125, United States

S Supporting Information

ABSTRACT: The first arsenide clathrates $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$) and $Cs_8Cd_{18}As_{28}$ have been synthesized in high yields via a two-step route. These compounds adopt the type-I structure and exhibit structural characteristics different from the recently reported antimonide clathrates $Cs_8Zn_{18}Sb_{28}$ and $Cs_8Cd_{18}Sb_{28}$. In arsenide clathrates, Zn (or Cd) and As atoms are statistically mixed at the three framework sites: 6c, 16i, and 24k; the alkali metals reside inside the cages at the 2a and 6d sites, with the 2a site being only partially filled. Single-crystal X-ray diffraction studies confirm that the Cd atoms preferably occupy the 6c and 24k sites over the 16i site, with more than 80% of Cd found at the former two positions. A unique structural feature is a framework disorder coupled with the partial occupancy of the cage's 2a site. Optical absorption measurements and electronic property measurements reveal a semimetallic-like behavior for $Cs_8Cd_{18}As_{28}$ and semiconductor-like behavior for $A_8Zn_{18}As_{28}$ ($A = Rb, Cs$).

SEM image of $Rb_8Zn_{18}As_{28}$

Type-I clathrate structure

KEYWORDS: arsenides, clathrates, crystal structure, thermoelectrics

■ INTRODUCTION

Clathrates have open-framework structures, where the available “cages” are typically filled by the guest atoms. Such structures are common among the gas hydrates.^{1,2} Since the mid-1960s, it has also been known that certain group 14 elements (e.g., Si, Ge, and Sn) in combination with alkali metals also form clathrates.^{3–5} In the past 20 years, extensive research in this area has shown that a number of elements to the left and the right of group 14 are clathrate-formers if reacted with alkali, alkaline-earth metals.^{6–9} Many of these studies have been instigated following the development of the “phonon glass, electron crystal” (PGEC) concept,¹⁰ which has recognized the potential of such compounds for thermoelectric applications.¹¹ In simplified terms, the small guest atoms inside the oversized clathrate cages are presumed to scatter the heat-carrying phonons, thereby lowering the thermal conductivity. At the same time, the electronic conductivity is retained because of the rigidity of the open-framework, which allows for the facile optimization of the thermoelectric figure of merit ZT ($Z = \alpha^2\sigma/\kappa$, where α is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is the absolute temperature).¹⁰ Since the discovery of promising thermoelectric properties in the type-I clathrate $Sr_8Ga_{16}Ge_{30}$ more than a decade ago,¹² the continued research efforts on this class of materials have shown $ZT \sim 0.8$ at 1050 K for $Ba_8Ga_{16}Ge_{30}$,¹³ $ZT \sim 0.9$ at 680 K for $Ba_8Au_{5.3}Ge_{40.7}$,¹⁴ and even ZT exceeding 1.1 at 1000 K for $Ba_8Ga_{16}Ge_{30}$ doped appropriately with Ni/Zn.¹⁵ Additionally, some type-I clathrates such as $(Na,Ba)_8Si_{46}$ ¹⁶ and Ba_8Si_{46} ¹⁷ have

been reported to be rare examples of superconductors with covalent networks based on sp^3 -Si.

So far, almost exclusively, the intermetallic clathrates that have been synthesized and structurally characterized are based on group 14 elements.^{18–20} The prevalence of Si, Ge, and Sn in such structures is understandable since the framework atoms are all four-bonded. Intermetallic clathrates free of group 14 metals are rarely seen. The two known exceptions include $Ba_8Cu_{16}P_{30}$,²¹ an orthorhombic superstructure of type-I clathrate, and the very recently published antimonide clathrates $Cs_8Zn_{18}Sb_{28}$ and $Cs_8Cd_{18}Sb_{28}$ also with the type-I structure.²² These studies have demonstrated the feasibility of forming clathrate compounds based on group 15 elements. Since our group has had a long-lasting interest in the pnictide-chemistry,^{23–28} our attention was piqued by these discoveries, and we set out to search for new clathrates in related systems. We reasoned that the “stiff” bonds characteristic of arsenide compounds, while beneficial for electronic transport, can also lead to high sound velocity, and thus high lattice thermal conductivity. Arsenide clathrates are expected to have significantly reduced lattice thermal conductivity, while still retaining their desirable strong bonds forming the covalent cages. Reductions in lattice thermal conductivity in clathrate compounds stem from two sources; first, large, complex unit

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cells lead to phonon dispersions dominated by flat, low velocity optical modes, and diminished acoustic branches.²⁹ Second, in clathrate compounds, the contribution from the already small acoustic branch is further reduced by “rattling” of the atoms in the oversized cages, which both scatter and reduce the velocity of the acoustic phonons. In the case of Si, such reductions have been clearly demonstrated—a 100-fold reduction is seen in the type-II Si clathrates relative to the Si with the much simpler diamond structure.³⁰ In addition, arsenide clathrates could potentially serve as a less expensive, more earth abundant replacement for the state-of-art germanium-based clathrate compounds.

In this paper, we report the novel clathrates, $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$) and $Cs_8Cd_{18}As_{28}$, which also adopt the type-I structure, but exhibit their own structural characteristics. These new arsenides expand the chemical range for exploring new intermetallic clathrates, which may lead to the discovery of interesting thermoelectric and/or other physical properties.

EXPERIMENTAL SECTION

Synthesis. All manipulations involving the very reactive alkali metals were done inside an argon-filled glovebox with O_2/H_2O level below 1 ppm or under vacuum. The elemental K, Rb, Cs, Zn, Cd, and As, purchased from either Alfa Aesar or Aldrich with the stated purity above 99.9% wt. were used as received. The first identified arsenide clathrate was $Rb_8Zn_{18}As_{28}$, obtained from a reaction loaded with the corresponding elements in 8:18:28 stoichiometric ratio, following the procedure established for the antimonide-clathrates.²² The reaction mixture, enclosed in a welded Nb-container, which was jacketed in an evacuated fused silica tube, was heated up to 550 °C and maintained at this temperature for 10 days. It was then slowly cooled to room temperature at a rate of 5 °C/h. The reaction product appeared polycrystalline and nearly homogeneous, but under a microscope, we found that majority of the synthesized material was small, plate-shaped crystals with black color, which were identified by single-crystal X-ray diffraction (XRD) as $RbZn_4As_3$.²⁸ Among them, we also observed several dark brown crystals with cubic morphology, which were later identified as $Rb_8Zn_{18}As_{28}$. Similar reactions with K and Cs also produced $K_8Zn_{18}As_{28}$ and $Cs_8Zn_{18}As_{28}$ in low yields, with the majority of the product being KZn_4As_3 and $CsZn_4As_3$.²⁸ Analogous experiments with Cd instead of Zn produced only $Cs_8Cd_{18}As_{28}$ (minor phase) and $CsCd_4As_3$ ²⁸ (major phase); the reaction between Rb, Cd, and As at the same conditions afforded only a mixture of $RbCd_4As_3$ and $CdAs_2$. Further details of these experiments can be found in an earlier publication.²⁸

To obtain the title compounds as single-phase material, adjustments to the reaction conditions were made, including raising the reaction temperatures and changing the cooling rates. They all failed—the AZn_4As_3 and ACd_4As_3 phases ($A = Na, K, Rb, Cs$) were always the major products. Reactions at lower temperature (500 °C or below) produced very inhomogeneous products. To circumvent the formation of AZn_4As_3 and ACd_4As_3 , we reasoned that very different synthetic routes should be employed. The success came from a two-step process, whereby As and Zn (or Cd) were first mixed in alumina crucibles and homogenized at 720 °C for 2 days, which resulted in a mixture of Zn_3As_2 and $ZnAs_2$, or Cd_3As_2 and $CdAs_2$.³¹ Then, these “precursors” were ground into fine powders, and mixed with the alkali metals. The reactions (in welded Nb tubes) were subjected to heat treatment at 550 °C for 3–5 days, and then slowly cooled to room temperature. Such process, although more involved and labor-intensive, yielded $K_8Zn_{18}As_{28}$, $Rb_8Zn_{18}As_{28}$, and $Cs_8Zn_{18}As_{28}$ as nearly phase-pure material. $Cs_8Cd_{18}As_{28}$ was obtained in higher yield by heating the mixtures at lower temperature, 500 °C. The hypothetical $Rb_8Cd_{18}As_{28}$, $Na_8Cd_{18}As_{28}$, and $Na_8Zn_{18}As_{28}$ could not be synthesized by any of the two above-mentioned methods.

X-ray Powder Diffraction. X-ray powder diffraction patterns were taken at room temperature using a Rigaku MiniFlex powder

diffractometer with filtered Cu K α radiation. The data were analyzed with the JADE 6.5 package with the purpose of estimating the phase purity of the reaction products. On the basis of that, the patterns from samples synthesized by the two-step route indicated very high yield of the clathrate phases that matched very well with the simulated patterns from single-crystal data (Figure 1).

Figure 1. Powder XRD patterns of $Cs_8Cd_{18}As_{28}$ (top) and $Rb_8Zn_{18}As_{28}$ (bottom), in comparison with the simulated patterns from the single-crystal diffraction data.

According to their X-ray powder diffraction patterns taken immediately after the completion of the reactions and after 2 weeks in open air, the title compounds are stable to air and moisture over this period of time.

Single Crystal XRD. Single crystal XRD was carried out on a Bruker SMART CCD-based diffractometer. Full spheres of data were collected in four batch runs, with frame width of 0.4° in ω and θ , controlled by the SMART program.³² Data integration and semi-empirical absorption correction were done employing the SAINT-plus³³ and SADABS codes.³⁴ The structures were solved by direct methods and refined by full matrix least-squares on F^2 using the SHELXL package.³⁵ Before the last refinement cycles, the atomic coordinates were set to conform with the literature,³¹ even though standardization will require origin shift by $1/2 \ 1/2 \ 1/2$. Noteworthy details of the structure refinements follow.

The gathered intensity data were readily sorted by XPREP, confirming the cubic symmetry and the systematic absence conditions for the cubic space group $Pm\bar{3}n$ (No. 223), adopted by almost all clathrates with the type-I structure (Figure 2).³¹ Indeed, the solution by the direct method in the chosen space group proceeded smoothly, and a few refinement cycles of a model type-I clathrate structure with Zn/Cd/As occupying the framework sites and the alkali metals located at the centers of the cages confirmed its validity. Since Zn and As have similar atomic scattering form factors, unambiguous refinement of the Zn/As occupancies was not possible. Instead, we refined the $Cs_8Cd_{18}As_{28}$ structure to convergence and used the final Cd/As ratios to constrain the refinements of $K_8Zn_{18}As_{28}$, $Rb_8Zn_{18}As_{28}$, and $Cs_8Zn_{18}As_{28}$.

Figure 2. (a) “Average” crystal structure of type-I clathrate with the cubic space group $Pm\bar{3}n$; (b) Thermal ellipsoid presentation (95% probability level) of two types of cages—the 20-atom pentagonal dodecahedra [5^{12}] and the 24-atom tetrakaidehedra [$5^{12}6^2$]—data from the refinements of $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$.

In all cases, however, there were several indications of a potential discrepancy between the established atomic coordinates for the clathrates with the type-I structure and our structural data. Using $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ as an example, the Cd/As mixed occupation was refined at each of the three framework sites, first individually and then collectively (assuming no vacancies on the framework sites exist). These trial refinements resulted in about 50% Cd occupancy at both 6c and 24k sites, respectively, and about 20% Cd at the 16i site (Figure 2).

Refinements of all positions with anisotropic displacement parameters showed that a significant electron density, about $5\text{--}7\text{ e}^-/\text{\AA}^3$, remained in the difference Fourier map. This residual density was located within the smaller cages, $\sim 0.4\text{ \AA}$ away from the 16i site. Such a short distance is unphysical, even for a light atom like N or O; attributing this to a possible “rattling” of the alkali metal atom inside the cage also does not seem plausible because (1) the location of the residual density was too close to the framework atom, and (2) the alkali metals in the bigger cages did not show propensity for being displaced from the geometric center of the oversized 24-atom polyhedron. Thus, the residual density was attributed to the disorder (dislodgment) of the framework-atoms at the known 16i site. Therefore, this position was modeled as split between two nearby sites with the same multiplicity and Wyckoff letter—in a ratio 9:1. To reduce the number of the refined variables, the Cd/As occupations at both 16i sites were not varied, but constrained to be the same as in the model without the split, that is, close to 1:4. For additional details, we refer to the CIFs in the Supporting Information, which are also deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers: CSD-424862 for $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$, CSD-424860 for $\text{K}_8\text{Zn}_{18}\text{As}_{28}$, CSD-424763 for $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$, and CSD-424861 for $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$.

The nature of this peculiar framework behavior of the structures of the arsenide-clathrates remained nebulous until it was realized that the alkali metals atoms in the small dodecahedral cage are not occupying it 100% of the time. For $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$, the 6d site occupation factor did not deviate from unity when freed to vary, while the 2a site was found to be about 2/3 occupied. This means that when the Cs atom at the 2a site is missing, the framework-atoms move toward the center of the cage, as shown in Figure 3, to compensate for the created “empty” space. The final refined stoichiometry using this structural model is $\text{Cs}_{7.26(1)}\text{Cd}_{17.9(2)}\text{As}_{28.1(2)}$. For the sake of simplicity, the idealized formula $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ is used throughout this manuscript.

EDX Analysis. The compositions of the arsenide clathrates were also independently determined by means of energy dispersive X-ray spectroscopy (EDX). The crystals were mounted on an aluminum stub using carbon tape, and then placed in a JEOL JSM-7400F scanning electron microscope equipped with an INCA-Oxford energy-dispersive spectrometer. Multiple crystals were analyzed, and the results were

Figure 3. Schematic representation of the dislodgment of the framework 16i site (M2). When the dodecahedral cage is vacant, that is, when the Cs atom is missing 1/3 of the time, the Cd/As atoms at the 16i site move toward the center of the cage (M2' site) to compensate for the created empty space.

then averaged. The determined compositions were consistent (within the error of the analysis) with the refined formulas.

Thermal Analysis. Differential scanning calorimetry-thermogravimetric (DSC-TG) analysis was carried out on $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$, $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$, and $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ using a SDT Q600 from TA Instruments. Samples were ground into powders and loaded into alumina pans. Temperature was ramped at a rate of $10\text{ }^\circ\text{C}/\text{min}$; the process was monitored under a constant flow ($100\text{ mL}/\text{min}$) of high purity argon to prevent oxidation at elevated temperatures. According to the tests, all tested clathrates' samples decompose without melting. $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ and $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$ were stable up to $600\text{ }^\circ\text{C}$, showing significant weight-loss upon being heated to higher temperature; $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ was less stable, starting to decompose at about $550\text{ }^\circ\text{C}$. This finding corroborates the observation that $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ had to be synthesized at lower temperature ($500\text{ }^\circ\text{C}$) than the Zn-analogue $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$.

Optical Absorption Measurement. The polycrystalline powders of $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$, $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$, and $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ were washed by dilute HCl solution to remove the small amount of impurities before the measurements. Optical absorption measurements were conducted at room temperature using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Spectra were obtained with a Nicolet 6700 FTIR spectrophotometer (Thermo Scientific) equipped with a Praying Mantis Diffuse Reflection accessory (Harrick) and DTGS detector and KBr beam splitter. Spectra were analyzed by first referencing the raw intensity to that obtained from measuring a mirror, then calculating the Kubelka–Munk function $F(R) = k/s = (1 - R_\infty)^2/2R_\infty$, where k is the absorption coefficient, s is the scattering coefficient, and R_∞ is the diffuse reflectance from an optically thick layer. Direct gaps were obtained by plotting $(F(R)h\nu)^2$ vs $h\nu$, and extrapolating $(F(R)h\nu)^2$ to 0; indirect gaps were obtained by plotting $(F(R)h\nu)^{1/2}$ vs $h\nu$, and extrapolating $(F(R)h\nu)^{1/2}$ to 0, where $h\nu$ is the incident photon energy. The O–H stretching band, which was also seen in the spectra of $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$, was most likely due to the surface oxidation in the mineral acid solutions, used to remove a Cs_3As_7 impurity. This minor phase is air-sensitive and hydrolyzes quickly in air, complicating all measurements.

Measurements of the Seebeck Coefficient and Electrical Resistivity. Polycrystalline $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$, $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$, and $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ were hot pressed in high-density graphite dies (POCO) using 1/2 ton of force on a 12 mm diameter surface (43 MPa of pressure). $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ was first hot pressed at $450\text{ }^\circ\text{C}$. However, powder XRD after hot pressing showed significant amount of ZnAs_2 impurity, which was most likely due to the decomposition of the sample. Thus, lower temperatures had to be applied. $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ was then pressed at $400\text{ }^\circ\text{C}$ for 1 h, and the so-obtained pellet had a density of $3.9\text{ g}/\text{cm}^3$, which was 75% of theoretical density. $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ and $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$ were hot pressed at $350\text{ }^\circ\text{C}$ for 1 h, and the densities of the resultant pellets were about 73% and 71% of their respective theoretical densities. Small amount of arsenic was present in all samples after hot pressing. Further lowering the hot pressing temperature resulted in only loose powder. Electrical

resistivity was determined using the Van der Pauw technique; and details of the Seebeck coefficient measurements can be found in ref 36.

RESULTS AND DISCUSSION

Synthesis. The high yield synthesis of the new compounds proved to be a tedious task. Although the antimonide clathrates can be successfully synthesized by direct fusion of the corresponding elements,²² this synthetic route resulted in less than 30% yields of the arsenide clathrates. This adverseness might be due to the distinctly different physical properties of the starting materials. The existence of KZn_4As_3 , RbZn_4As_3 , CsZn_4As_3 , and CsCd_4As_3 ,²⁸ which are compositionally not very different from the clathrates, also hampered the prospects toward qualitative reaction yields. This obstacle could be overcome by a two-step synthetic route, which involved reacting the As and Zn (or Cd) and grinding the fused binary mixture into a fine powder. Following that, almost phase-pure arsenide clathrates could be obtained by reacting the precursors with stoichiometric amounts of the alkali metals at moderate temperatures for relatively short periods of time. The morphology of the crystals is consistent with the cubic symmetry; a representative image of the product from a reaction of Rb with “ $\text{Zn}_9\text{As}_{14}$ ” precursor, acquired with the aid of an electron microscope (1000-fold magnification) is provided in Figure 4.

Figure 4. Image of the cube-shaped crystals of $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$, taken in a JEOL scanning electron microscope, using accelerating voltage of 3 kV and magnification of 1000.

Structural Characterization. As mentioned already, the structures of the title compounds are isotypic with the cubic type-I clathrate structure. This structure has been considered in

detail elsewhere,⁹ and will not be discussed at length here. Relevant crystallographic information from the single-crystal refinements is tabulated in Table 1. We only point out that of the 3 unique crystallographic sites on the open framework, 6c, 16i, and 24k, only the 16i site shows preferred occupation by As; the remaining two sites are refined as nearly equiatomic mixtures of Cd (or Zn) and As (Table 2). Similar Zn/Sb

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq}^a) of $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$

atom	site	x	y	z	U_{eq} ($\text{\AA}^2$)
Cs1 ^b	2a	0	0	0	0.013(1)
Cs2	6d	1/4	1/2	0	0.029(1)
M1 ^c	6c	1/4	0	1/2	0.013(1)
M2 ^c	16i	0.1852(1)	x	x	0.021(1)
M2' ^c	16i	0.1535(7)	x	x	0.021(1)
M3 ^c	24k	0	0.3079(1)	0.1211(1)	0.019(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^bOccupancy 0.63(1). ^cM denotes mixed Cd/As with occupancies 0.48(1)/0.52, 0.20(1)/0.80, and 0.49(1)/0.51, respectively. M2 and M2' are two adjacent sites—0.879(4):0.121.

distribution is also noted in $\text{Cs}_8\text{Zn}_{18}\text{Sb}_{28}$ (6c site: Zn/Sb = 44/56; 16i site: Zn/Sb = 20/80; 24k site: Zn/Sb = 50/50).²² This means that homoatomic As–As and particularly Cd–Cd (or Zn–Zn) bonds are largely avoided, and that the framework is based on predominantly heteroatomic interactions. Earlier density functional calculations have confirmed that the Zn–Zn bonds will be disadvantageous to the stability of $\text{Cs}_8\text{Zn}_{18}\text{Sb}_{28}$,³⁷ which must also be true for the arsenide clathrates, considering that the Cd–As and Zn–As bonds are even stronger than the Cd–Sb and Zn–Sb ones.

The site preferences (aka the “coloring”) among the three framework positions in the pnictogen-based clathrates and those in the tetrel-based clathrates deserve further discussion. In the tetrel-based clathrates with a general formula $\text{A}_8\text{M}_x\text{Tt}_{46-x}$ (A = alkali metal or alkaline earth metal; M = element from group 12, 13; Tt = Si, Ge, Sn), the substituents M are known to have a marked preference for the 6c site.^{38–41} Computational analysis of the type-I clathrate structure reveals that the 6c site has the lowest Mulliken population and thereby should be mostly taken by the element(s) with the lowest electronegativity.⁴² These findings are supported by another study on

Table 1. Selected Crystallographic Data for the Type-I Arsenide Clathrates (Cubic Space Group $Pm\bar{3}n$ (No. 223); $Z = 1$)

	$\text{K}_{7.22(2)}\text{Zn}_{18.1}\text{As}_{27.9}$	$\text{Rb}_{7.17(2)}\text{Zn}_{18.1}\text{As}_{27.9}$	$\text{Cs}_{6.36(1)}\text{Zn}_{18.1}\text{As}_{27.9}$	$\text{Cs}_{7.26(1)}\text{Cd}_{17.9(2)}\text{As}_{28.1(2)}$
formula weight	3554.8	3885.3	4117.8	5083.6
temperature (K)			200(2)	
radiation			Mo K α , $\lambda = 0.71073$ Å	
a (Å)	10.7173(6)	10.7413(6)	10.7731(8)	11.3281(5)
V (Å ³)	1230.99(12)	1239.28(12)	1250.32(16)	1453.69(11)
ρ_{cal} (g cm ^{−3})	4.80	5.21	5.47	5.81
μ (cm ^{−1})	278.4	340.5	313.7	267.4
data/restraints/parameters	310/0/18	305/0/18	310/0/18	350/0/20
GOF on F^2	1.011	1.050	1.062	1.066
R_1 ($I > 2\sigma_I$) ^a	0.0145	0.0198	0.0147	0.0212
wR_2 ($I > 2\sigma_I$) ^a	0.0300	0.0356	0.0336	0.0519
largest diff. peak/hole (e [−] Å ^{−3})	0.381/−0.384	0.743/−0.907	0.790/−0.503	1.126/−0.935
weight coefficients, A/B	0.0148/0.7775	0.0130/2.2420	0.0207/1.2548	0.0294/6.9309

^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 $w = 1/[\sigma^2 F_o^2 + (AP)^2 + BP]$, and $P = (F_o^2 + 2F_c^2)/3$, A/B = weight coefficients.

Table 3. Selected Interatomic Distances (Å) in $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$) and $Cs_8Cd_{18}As_{28}$ ^a

		$K_8Zn_{18}As_{28}$	$Rb_8Zn_{18}As_{28}$	$Cs_8Zn_{18}As_{28}$	$Cs_8Cd_{18}As_{28}$
M1–	M3 (×4)	2.4712(4)	2.4777(6)	2.4930(4)	2.6206(6)
M2–	M2 ^b	2.471(2)	2.479(3)	2.469(2)	2.542(4)
	M3 (×3)	2.4944(4)	2.4953(6)	2.4940(5)	2.6193(7)
M3–	M1	2.4712(4)	2.4777(6)	2.4930(4)	2.6206(6)
	M3	2.5304(7)	2.548(1)	2.5734(8)	2.744(1)
	M2 ^b (×2)	2.4944(4)	2.4953(6)	2.4940(5)	2.6193(7)

^aM denotes mixed occupied Zn/As or Cd/As. ^bFor simplicity, we only quote the distances between the established positions (dislodged M2' is not included), so that the coordination of each M-position is 4-fold.

the Ga distribution in $A_8Ga_{16}Tt_{30}$ ($A = Sr, Ba, Tt = Si, Ge$),⁴³ which also indicates that the 6c site is almost exclusively occupied by Ga. However, in the cases of $Cs_8Zn_{18}Sb_{28}$ and $Cs_8Cd_{18}As_{28}$, this is not the case. In $Cs_8Cd_{18}As_{28}$ (Table 2), we can only note an apparent preference of As for the 16i site, in about 4:1 ratio. $Cs_8Zn_{18}Sb_{28}$ structure exhibits the same occupation at this site, which suggests that the differences between the atomic sizes of Zn/Sb and Cd/As (they are exactly the opposite in the two cases) cannot be the reason for this particularity. The disparity between the “coloring” of the framework positions in the tetrel- and the pnictogen-based clathrates must then be attributed to the greater electronegativity differential between the framework-building elements themselves, as well as the more ionic interactions between the alkali metals and pnictogens compared to the tetrel elements.

The interatomic distances within the Cd/As framework in $Cs_8Cd_{18}As_{28}$ are in the range 2.542(4)–2.744(1) Å, with the shortest distance 2.542(4) Å found between neighboring 16i sites (Table 3). Considering that the Pauling radius of As is significantly smaller than that of Cd ($r_{As} = 1.210$ Å, $r_{Cd} = 1.382$ Å),⁴⁴ and that the 16i position is almost 80% As, this observation is not difficult to understand. The Cd–As distances match those reported for other cadmium-arsenides such as $KCdAs$ (2.725 Å),⁴⁵ $Ba_2Cd_2As_3$ (2.715–2.909 Å),²⁶ and $RbCd_4As_3$ (2.638–3.195 Å).²⁸ The corresponding distances in $A_8Zn_{18}As_{28}$ are justifiably shorter (2.469(2)–2.5734(8) Å), which is due to the similar Zn and As radii, ($r_{Zn} = 1.213$ Å).⁴⁴ The Zn–As are comparable with the Zn–As distances reported in $NaZnAs$ (2.537 Å),⁴⁵ Ba_2ZnAs_2 (2.592 Å),⁴⁶ among others.

The alkali metal atoms, as previously stated, are located at the centers of the pentagonal dodecahedra and the tetrakaidecahedra, the 2a and 6d sites, respectively (Figure 2). Unlike $Cs_8Zn_{18}Sb_{28}$ and $Cs_8Cd_{18}Sb_{28}$ in which both 2a and 6d sites are fully occupied,²² the 2a sites in the arsenide clathrates show partial occupancy. This intricacy of the structure is coupled to the displacement of the atom at the M2 site (88%) to the M2' site (12%). Apparently, by this, nature compensates for the empty pentagonal dodecahedra by significantly distorting the cage. We attribute the dislodgement of the 16i site to a vacancy of the alkali metal atom site, although other interpretations have also been considered. For example, splitting at the 16i site has also been reported in $K_7B_7Si_{39}$,⁴⁷ and explained by the significant size difference between B and Si; however in our case, had the alkali metal at the 2a site not been vacant, the atom at the M2' site would come at an unphysically short distance to it, rendering such hypothesis invalid. Other cases involving defect and disorder at neighboring positions are known, such as the inverse type-I clathrate $Sn_{24}P_{19.3}I_8$.⁴⁸ In the latter structure, the P atoms at the 6c site are not with full occupancy, which leads to the splitting of the neighboring 24k site, occupied by the Sn atoms.

An interesting observation also worth noting with regard to the under-occupied 2a sites in $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$)—the refined occupancies decrease from 61% ($K_8Zn_{18}As_{28}$) to 58% ($Rb_8Zn_{18}As_{28}$) to 18% ($Cs_8Zn_{18}As_{28}$), suggesting a size-dependence. A possible explanation for this is the realization that the dodecahedral cage is not large enough for Cs, therefore the Cs atoms are a poor match for this polyhedron. We reasoned that if a smaller alkali metal, such as Na, is introduced, one might be able to synthesize $Cs_8Na_2Zn_{18}As_{28}$, where the large Cs atoms are occupying the larger 24-atom tetrakaidecahedral cages and the Na atoms are fully occupying the 20-atom pentagonal dodecahedral cages. We attempted such reactions and indeed obtained clathrates, as evidenced by the X-ray powder patterns. However, poor crystal quality made unequivocal structural determination difficult; whether the 2a site is fully occupied by Na or partially occupied by Cs (or Cs/Na) is not confirmed yet. Nonetheless, the above argument can be applied to explain the Cs 100% occupancy in the (Zn/Sb)₂₀ dodecahedra in $Cs_8Zn_{18}Sb_{28}$ and the nearly 2/3 occupancy in the (Cd/As)₂₀ dodecahedra in $Cs_8Cd_{18}As_{28}$ —in those cases, because of the larger Sb and Cd atoms, the same atomic arrangement is a better match for the atomic size of Cs. Notice that the Zn/As framework is rigid, as evidenced from the Zn–As distances that show little or almost-no-dependence on the size of the alkali metal atoms, confirming the notion that the framework is rigid and cannot be expanded to provide the necessary space for the guest. Such subtle differences in the structures should alter the electronic structure and the transport properties, as discussed in the following section.

Properties. The arsenide clathrates with general formulas $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$) and $Cs_8Cd_{18}As_{28}$ are expected to be semiconductors, since they can be rationalized as electron-precise Zintl phases.^{42,49} Correspondingly, the electron balance will be disrupted because of the observed alkali metal vacancies at the 2a site. We can therefore argue that instead of the idealized $A_8M_{18}As_{28}$ formulas, this system can still fulfill Zintl valence requirements with the stoichiometry $A_{8-x}M_yAs_{46-y}$, where $y = 18 - x/3$. Hence, to retain the electroneutrality, $Cs_8Zn_{18}As_{28}$ (most vacancies) will be slightly As-rich relative to $K_8Zn_{18}As_{28}$ (least vacancies), even though we could not refine the Zn/As ratios from the X-ray data. Like clathrates, the stable composition of the filler atoms in skutterudites is strongly influenced by the overall electron count.⁴⁹ The optical absorption and electronic transport property measurements, below, lend support to this hypothesis and corroborate the elucidated structural models. However, it is also possible for clathrate compounds to deviate significantly from the Zintl condition,⁵⁰ allowing for increased carrier concentration and optimization of the thermoelectric properties.

The Kubelka–Munk functions $F(R)$ vs $h\nu$ obtained from the optical absorption measurements are plotted in Figure 5. The

Figure 5. Plots of the Kubelka–Munk functions $F(R)$ vs $h\nu$, obtained from the optical absorption measurements.

spectra of $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ have no clear feature, only peaks that are related to optical phonons and impurities, that is, the O–H absorption (~ 0.4 eV) are noticeable, indicating metallic behavior of this compound. On the other hand, both spectra of $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$ and $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ indicate band gaps, suggesting semiconductor character of these two compounds. The spectra of $\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$ show a slow rise in absorption, suggesting an indirect band gap. Extrapolating $(F(R)h\nu)^{1/2}$ to 0, the size of band gap could be derived, which measures about 0.2 eV. The general shape of the absorption spectra of $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ resembles a direct gap, which is about 0.1 eV extracted directly from the $(F(R)h\nu)^2$ function (see Supporting Information).

As shown in Figure 6, polycrystalline $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ exhibits very low Seebeck coefficients, starting from positive 11 $\mu\text{V}/\text{K}$ at

Figure 6. Temperature dependence of the Seebeck coefficient of $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$.

300 K, increasing to 12 $\mu\text{V}/\text{K}$ at 375 K, and then slowly decreasing to 8 $\mu\text{V}/\text{K}$ at 525 K, which indicates that $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ may be a semimetal with a small number of both electrons and holes and a band gap of less than zero, in contrast to the Ge clathrates such as $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ that show simple semiconductor behavior with thermoelectric properties that can be modeled with a single band.⁵⁰ This is consistent with its relatively flat resistivity with temperature, as well as the metallic behavior indicated by its optical absorption. The resistivity of $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ at room temperature is high, about 1.1 $\Omega\cdot\text{cm}$, and it decreases quickly with temperature (Figure 7), suggesting semiconductor behavior of this sample, which is also consistent with its optical absorption. The size of the band gap derived from the logarithmic plot of resistivity vs $1/T$ is about

Figure 7. Temperature dependence of the resistivity of pressed-pellets of polycrystalline $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ (a) and $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ (b).

0.11 eV, comparable with that obtained from the absorption measurement (~ 0.1 eV). For comparison, $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$, a compound with a variant of the type-I structure,²¹ shows metallic conduction and positive Seebeck coefficient;⁵¹ the clathrate-like compound $\text{Rb}_{16}\text{Cd}_{25}\text{Sb}_{36}$ is reported to be a *p*-type semiconductor.⁵² A parallel could also be drawn with the filled skutterudites, such as $\text{RFe}_4\text{Sb}_{12}$ ($R = \text{Ca}, \text{Sr}, \text{Ba}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Eu}, \text{and Yb}$),⁵³ where the filling fraction is very high (close to 1) and a *p*-type semiconducting behavior is observed. In contrast, most *n*-type skutterudites typically have less than 50% filling fraction.⁵⁴

$\text{Cs}_8\text{Zn}_{18}\text{As}_{28}$ shows resistance that it is out of the measurable range of the instrument. Of course, this could be due to the porous pellet instead of its intrinsic behavior. The Seebeck measurements on the same specimen show a negative Seebeck coefficient, which decreases as the temperature increases (see Supporting Information), suggesting intrinsic carrier activation, which is in consistent with the absorption measurement. The Seebeck measurements on $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ were not reproducible. It might be possible that the $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$ samples are intrinsic semiconductors with nearly equal number of holes and electrons, which leads to very low voltage reading on the Seebeck system, and thus to substantial error in the measurement.

CONCLUSIONS

The first arsenide clathrate compounds $\text{A}_8\text{Zn}_{18}\text{As}_{28}$ ($A = \text{K}, \text{Rb}, \text{Cs}$) and $\text{Cs}_8\text{Cd}_{18}\text{As}_{28}$ have been synthesized and characterized. These compounds adopt the type-I structure with Zn/As or Cd/As forming the clathrate framework and alkali metals occupying the cages. The optical absorption and electronic property measurements have confirmed them as semiconductor/semimetal. With the vast majority of the tetrel-based clathrates known to be *n*-type semiconductors, the pnictide

clathrates may offer a different area for exploring new *p*-type thermoelectric materials. Currently, we are conducting more exploratory work for pnictide-based clathrates and related compounds with interesting physical properties.

■ ASSOCIATED CONTENT

■ Supporting Information

Tables of atomic coordinates and equivalent isotropic displacement parameters for $A_8Zn_{18}As_{28}$ ($A = K, Rb, Cs$), figures of the optical absorption plots, and Seebeck coefficient of $Cs_8Zn_{18}As_{28}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (302) 831-6335. E-mail: bobev@udel.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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