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$Eu_4Ga_8Ge_{16}$: A New Four-Coordinate Clathrate Network

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We report a new clathrate phase composed of europium atoms occupying cage voids in a gallium/germanium tetrahedral cage network. $Eu_4Ga_8Ge_{16}$ crystallizes in orthorhombic space group *Cmcm* with $a = 4.1349(6)$, $b = 11.2842(15)$, and $c = 13.2408(18)$. The compound is believed to satisfy the Zintl−Klemm concept of bonding to form a network solid with a unique one-dimensional line of Eu atoms aligned along the crystallographic *a*-axis, charge balancing an electron-deficient Ga/Ge framework. The compound was observed to melt incongruently at 684(1) °C by differential thermal analysis (DTA). Single-crystal electrical conductivity measurements gave 130 S/cm at room temperature with a metallic temperature dependence. The room-temperature thermopower (Seebeck coefficient) was measured to be 40 μV/K.

Alkaline earth clathrate compounds such as $M_8Tt_{16}Tr_{30}$ (M = Sr, Ba; Tr = Al, Ga, In; Tr = Si, Ge, Sn) are receiving substantial attention as potential thermoelectric energy-conversion devices.[1−3] Their high mobility and low thermal conductivity create a unique situation similar to the hypothetical “Phonon-Glass Electron-Crystal” [4] (PGEC). A PGEC conducts electrons like a crystal but scatters heat-carrying phonons like disordered glass, providing the ideal situation for an efficient thermoelectric device. The factors governing performance are summed up by a thermoelectric figure of merit Z ($=S^2\sigma/\lambda$; S = Seebeck coefficient, σ = electrical conductivity, and λ = thermal conductivity) multiplied by temperature to give a unitless figure of merit.

ZT can be optimized by tuning the transport parameters involved. A particularly effective way to tune the thermal conductivity is by inclusion of a guest heavy atom that will “rattle” and scatter acoustic phonons responsible for heat transport.[5,6] Zintl phases of the late main group elements are often small band gap semiconductors or semimetals that form large unit cells.[7] Such a large unit cell allows for a complex band structure at the fermi level, often providing a large Seebeck coefficient. Heavy atoms included within the cage will reduce the existence range for acoustic phonons,[8] consequently reducing the thermal conductivity. For these reasons cage structures containing rare earth guests are of considerable interest.

Recent advances in flux growth of transition metal silicides[9,10] and alkaline earth metal group XIV pnictogens[11] has led to a variety of new phases. Synthetic flux methods afford the solid-state chemist a situation closer to that of aqueous solution crystal growth, allowing rapid transport to and from growing crystal faces.[12] Our exploration of gallium as a flux for the growth of known clathrate compounds has met with a large degree of success. Large stoichiometric crystals of $M_8Ga_{16}T_{30}$ (M = Ba, Sr) (T = Ge, Si) can be grown from gallium fluxes,[13,14] yielding a favorable situation for thermoelectric property measurements, thus avoiding the inherent problems of pressed powders.

Europium is known to behave similarly to barium and strontium with an accessible formal dipositive state, even in aqueous environments.[15] It is then not surprising to expect Eu to form a clathrate $Eu_8Ga_{16}Ge_{30}$. Indeed, Nolas et al. synthesized and explored the

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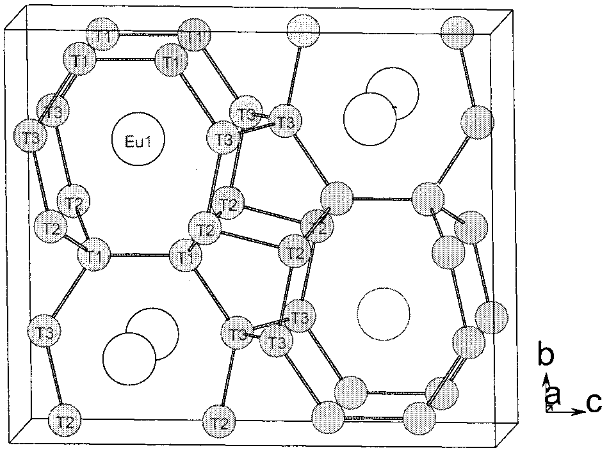

Figure 1. $Eu_4Ga_8Ge_{16}$ unit cell, T = Ga/Ge mixed site.

thermoelectric properties of this compound.[2,16]

By using the Ga flux approach, we have found a new clathrate with composition form $Eu_4Ga_8Ge_{16}$ and structure shown in (Figure 1). The structure is similar in spirit to the zeolite family of compounds; however, a search of the zeolite database revealed no known natural or synthetic zeolitic analogs. This compound is a new inorganic clathrate, which we will call type IV after the historical types I & II gas hydrate[17] clathrates and the synthetic $Ba_6In_4Ge_{21}$[18] or K_8Sn_{25}[19] type III.

Experimental Section

Synthesis. The compound was initially discovered as a minority phase in a reaction intended to synthesize $Eu_8Ga_{16}Ge_{30}$. The product isolated from the gallium flux contained a heterogeneous mix of $Eu_4Ga_8Ge_{16}$ and Ge crystals. The synthesis was performed using a large excess of gallium metal intended as a solvent for the reaction. In an argon-filled drybox europium metal (99.9%, Cerac) and germanium (99.999%, Cerac) were mixed in stoichiometric portions along with excess gallium (99.999% Cerac; typically 75% by weight) and placed in a corundum crucible, set inside a stainless steel bomb. Europium metal is known to be toxic so care should be taken when working with it. The reaction was heated to 1100 °C and cooled to room temperature. The crystals were isolated from the reaction flux by sonication in warm water. The warm water will form a molten gallium/water suspension that can be decanted off. Several wash cycles are required to remove all the gallium. A quicker alternative isolation procedure involves dissolution of the gallium flux in concentrated hydrochloric acid.

Phase Separation. The isolated material from the flux contained only the products $Eu_4Ga_8Ge_{16}$ and Ge. In the isolated products, the separated Ge phase impurity was determined by weight to be 65.7 ± 0.7% and the $Eu_4Ga_8Ge_{16}$ to be 34.1 ± 0.7%. A mass balance for the reaction accounts for the entire amount of Ge in either $Eu_4Ga_8Ge_{16}$ or Ge phases, but accounts for only 15.5% by weight of the total Eu starting materials that were used to form the clathrate. The remainder of the Eu forms Eu_xGa_y phases that were dissolved during the isolation steps along with the excess gallium flux and were therefore not recovered. Because of their similarity in solubility and density, the Ge phase was separated from the $Eu_4Ga_8Ge_{16}$ phase by a three-step procedure using a series of sieves, gravity separation, and a final visual inspection step. The isolated batch of crystals was size fractionated by sifting through a series of wire mesh sieves of decreasing size (typically 50-μm steps from 400 to 125 μm, Gilson Inc., Worthington, OH). Ge crystals were separated from the $Eu_4Ga_8Ge_{16}$ crystals in the size fractions by utilization of the fact that the Ge crystals, which typically grew into octahedral shapes, have less surface area susceptible to friction when resting on a plane and will roll down an incline plane (typically 45° or less) while the thick needlelike clathrate crystals will not. The Ge crystals were collected at the bottom of the plane in a collecting bin, leaving the clathrate phase still on the incline. Several incline plane steps are sufficient for sorting the majority of the Ge phase from the clathrate phase. Each size-sorted batch of separated clathrate phase was checked by powder diffraction to verify phase purity before combining with the other phase fractions.

Crystallographic Studies. A Siemen's SMART CCD diffractometer utilizing Mo Kα radiation and a graphite monochromator was used to collect a full sphere of data in reciprocal space. Data were obtained for $-5 < h < 5$, $-14 < k < 14$, and $-16 < k < 16$. No decay was observed over the length of the data collection as determined by a comparison of a final set of 50 data frames to the initial 50 frames. The program SMART[20] was used to collect the raw data and index the unit cell, determined to be $a = 4.1349(6)$, $b = 11.2842(15)$, and $c = 13.2408(18)$. SAINT[20]was used for data reduction and XPREP[20] used for space group selection.

Systematic absences allowed two possible space groups *Cmcm* and $Cmc2_1$. In the absence of piezoelectric measurements, which would verify a noncentrosymmetric space group, refinements were carried out in both the noncentrosymmetric $Cmc2_1$ and centrosymmetric *Cmcm*. Empirical absorption corrections were made using SADABS.[21] The refinements were performed using SHELXTL[20] software incorporating a full matrix least-squares technique. Refining on $F_0{}^2$ in *Cmcm* with 434 unique reflections, 24 parameters, and no restraints gave wR2 = 0.1191 and the conventional R1 = 0.0465. Refining on $F_0{}^2$ in $Cmc2_1$ on 809 unique reflections, 44 parameters, and no restraints gave wR2 = 0.1142 and the conventional R1 = 0.0443.

When the number of parameters is considered for each scenario, no significant statistical improvement was achieved by refinement in the lower symmetry $Cmc2_1$ space group verified by application of the *R*-factor ratio test[22] at the 99.5% confidence level. In addition, refinements in the $Cmc2_1$ space group showed large correlation coefficients (±0.8) in the positional parameters for pairs of framework atoms. Such large coefficients are expected for atoms related by a center of inversion when improperly refined in a noncentrosymmetric space group.[23] For these reasons the *Cmcm* space group was chosen as correct.

Table 1 contains selected crystallographic parameters. Because of similar X-ray scattering cross sections of gallium versus germanium, ~7% difference, we were unable to refine framework site preferences for these two atoms. A ratio of 33% gallium and 67% germanium, consistent with the stoichiometry determined by elemental analysis, was fixed for each site shown along with the positional parameters in Table 2. Atomic displacement parameters (ADPs) were allowed to refine anisotropically for all sites. Framework Ga and Ge atoms showed small deviations from isotropic behavior, while the guest Eu atoms deviate significantly from isotropic behavior, as shown in Figure 2 and given in Table 3. Additional crystallographic information is available in the Supporting Information.

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Table 1. Selected Crystallographic Structure Refinement Data for $Eu_4Ga_8Ge_{16}$

empirical formula	$Eu_4Ga_8Ge_{16}$
formula weight	2327.4
a	4.1349(6)
b	11.2842(15)
c	13.2408(18)
volume	617.80(15)
Z	1
temperature	293 K
crystal size	0.1 × 0.53 × 0.04 mm
F(000)	10.12
density	6.255
absorption coefficient (mm^{-1})	37.63
extinction coefficient	0.0178(15)
reflections collected	3093
reflections refined	427
least-squares goodness of fit	1.332
no. of parameters/no. of restraints	24/0
wR2	0.1191
R1	0.0465
largest peak and valley (e/Å^3)	3.328, −4.487

Table 2. Unit Cell Contents, Site Occupancy Factor (s.o.f.), and Isotropic Displacement Parameters, U_{eq} (Å^2 × 10^3), for $Eu_4Ga_8Ge_{16}$

atom	x	y	z	(s.o.f.)	U_{eq}
Eu(1)	0	0.2079(7)	0.25	1	20.5(4)
Ga/Ge(1)	0	−0.06997(8)	0.34388(6)	0.3333/0.6667	12.1(4)
Ga/Ge(2)	−0.5	0.2687(8)	0.40823(7)	0.3333/0.6667	14.6(4)
Ga/Ge(3)	−0.5	0.24418(9)	0.44810(8)	0.3333/0.6667	15.0(4)

Table 3. Anisotropic Displacement Parameters (Å^2 × 10^3) for $Eu_4Ga_8Ge_{16}$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Eu(1)	18.0(6)	15.3(6)	28.0(6)	0	0	0
Ga/Ge(1)	16.3(6)	6.4(6)	13.7(6)	1.3(4)	0	0
Ga/Ge(2)	16.4(6)	9.7(6)	17.6(7)	−3.5(4)	0	0
Ga/Ge(3)	18.0(6)	7.1(6)	19.8(7)	2.7(3)	0	0

Elemental Analysis. Inductively coupled plasma emission spectroscopy (ICP) was performed on a Thermo Jarrel Ash Iris CID spectrometer. Calibration was made with known elemental standards (High Purity Standards Inc). All samples were prepared by dissolution in concentrated nitric acid via sonication and dilution to give the proper molarity range for analysis. Seven samples taken from the isolated pure fractions were analyzed to give 26.38 ± 0.35% Eu, 24.89 ± 0.75% Ga, and 48.43 ± 1.07% Ge by weight taken at the 95% confidence interval. Conversion to molar ratios, normalization by the number of moles of Eu, and multiplication by 4 yields a stoichiometry of $Eu_{4.00\pm0.07}Ga_{8.23\pm0.34}Ge_{15.38\pm0.46}$. The confidence interval shown for all of the components falls within the 5% error expected with the ICP technique.[24]

Electrical Transport and Thermopower. Indium solder was used to attach electrical leads under a microscope onto a single crystal (0.9 × 0.455 × 3.3 mm) of the material. Ohmic contacts were verified by current vs voltage measurements (not shown). Measurements were made using low-frequency ac (100 Hz) techniques utilizing a lock-in amplifier to give an overall pseudo-dc measurement. A liquid-nitrogen cryostat was used to achieve the low-temperature measurements. Thermopower measurements were made on a pressed pellet made from the pure isolated fraction of $Eu_8Ga_8Ge_{16}$. The thermopower was measured using a home-built apparatus that monitors the open circuit voltage across the sample in a temperature gradient (<8 °C).

Thermal Analysis. Differential thermal analysis (DTA) was carried out on a Netzsch 409STA apparatus under an argon atmosphere purified in situ through a Ti-sponge Gettering furnace. A 43.2-mg sample was ramped at a rate of 3 K/min in both the heating and the cooling steps.

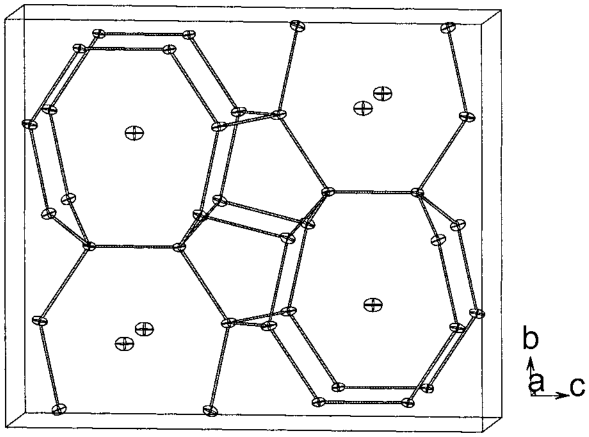

Figure 2. ORTEP diagram viewed down the a-axis with 50% thermal ellipsoids.

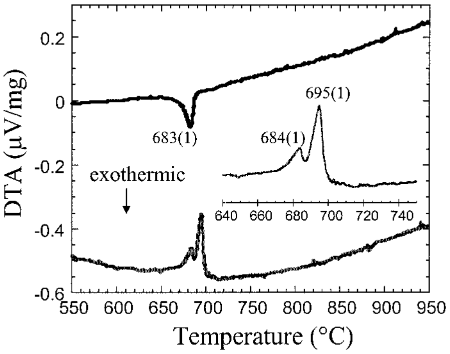

Figure 3. DTA scan showing the heating (lower) and cooling (upper) curves for $Eu_4Ga_8Ge_{16}$.

Discussion

Thermal Analysis. The melting point and recrystallization temperatures were determined by DTA shown in Figure 3. Two distinct peaks are seen on the heating curve occurring at 684(1) and 695(1) °C, corresponding to an incongruently melting compound $Eu_4Ga_8Ge_{16}$ at a peritectic temperature followed by the melting of remaining crystalline phases into the liquid. The pre-DTA analyzed sample was determined to be pure by powder diffraction, while the post-DTA analyzed sample showed peaks corresponding to $Eu_4Ga_8Ge_{16}$, Ge, and an unknown Eu_xGa_y phase not corresponding to any of the know Eu−Ga phases. Recrystallization occurred at 683(1) °C, exhibiting very little supercooling.

Structure and Bonding. The gallium flux synthetic technique has proven successful for the discovery of a new phase of rare earth group 13/14 Zintl phase. The four-coordinate bonding network determined by X-ray structural refinements along with the composition results would suggest that a two-electron transfer from the Eu atoms to the electron-deficient Ga−Ge bonds is taking place to compensate for the lack of one electron per every four-framework bonds, similar to the type I clathrate bonding scheme.[25] This illustrates a classic Zintl phase scenario.

The covalent framework bonds in $Eu_4Ga_8Ge_{16}$ are not as strong as the bonds of the similar structure

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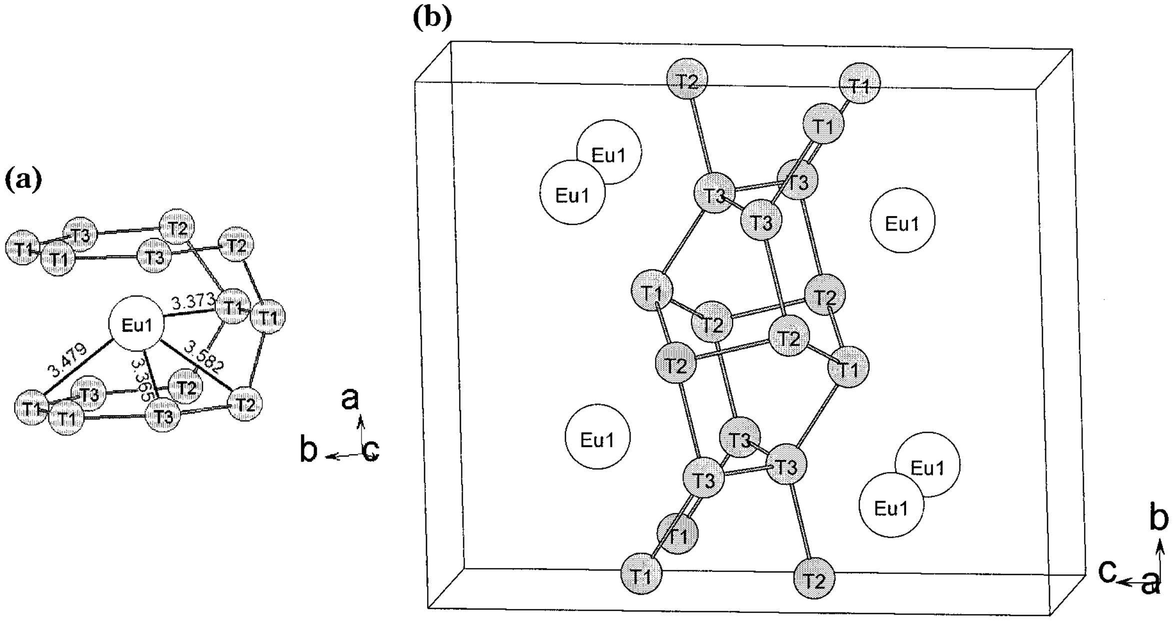

Figure 4. (a) Cage showing coordination of Eu ions and Eu−T distances. (b) Framework structure connecting adjacent cages.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Eu_4Ga_8Ge_{16}$

atoms	distances (A)	atoms	angles (deg)
Eu1−T1 (×2)	3.3731(12)	T1−T1−T2 (×2)	110.02(3)
Eu1−T1 (×4)	3.4788(10)	T2−T1−T2	112.32(5)
Eu1−T2 (×4)	3.5827(9)	T1−T1−T3	123.36(3)
Eu1−T3 (×4)	3.3653(9)	T2−T1−T3 (×2)	100.29(3)
T1−T1	2.4862(17)	T1−T2−T1	112.32(5)
T1−T2 (×2)	2.4891(7)	T1−T2−T2 (×2)	103.05(4)
T1−T3 (×2)	2.5104(13)	T1−T2−T3 (×2)	120.10(3)
T2−T1 (×3)	2.4891(7)	T2−T2−T3	91.86(5)
T2−T2	2.5045(19)	T3−T3−T3	112.57(8)
T2−T3	2.5083(13)	T3−T3−T2 (×2)	99.68(5)
T3−T1	2.5104(13)	T3−T3−T1 (×2)	105.05(5)
T3−T3	2.4854(12)	T2−T3−T1	134.48(5)

($M_8Ga_{16}Ge_{30}$; M = Sr, Ba) as evidenced by the melting points of 684(1) °C versus 764 °C and 957 °C, respectively.[26] This decreased structural stability in $Eu_4Ga_8Ge_{16}$ is most likely a result of the distortion of the tetrahedral framework bonds from the ideal 109.4° (bond lengths and angles given Table 4). The *Cmcm* structure is comprised of two main features, a cage composed of two fused puckered eight atom rings sharing two atoms (Figure 4a) and a five- and six-membered ring section resulting from the joining of adjacent cages (Figure 4b). The eight-ring cage window bond angles of 120.11°−134.4° are the main destabilizing factors of this structure versus the less strained $Sr_8Ga_{16}Ge_{30}$ or isostructural $Eu_8Ga_{16}Ge_{30}$ with six-ring window bond angles of 124.8°.

It is important to note that the Eu atoms occupying cage voids are at most weakly coupled through the eight-membered rings. The Eu−Eu distance is 4.135 Å in $Eu_4Ga_8Ge_{16}$ versus 3.989 Å for the Eu^0−Eu^0 distance in the metal[27] and 5.352 Å for $Eu_8Ga_{16}Ge_{30}$.[16] The ionic radius of Eu^{2+} (1.35 Å) is also too small to allow direct bonding of the Eu−Eu through the cage window. Anisotropy in the ADPs is found for the Eu atoms parallel to the eight-ring windows and perpendicular to the one-dimensional Eu chain, confirming their weekly bound nature, as shown in Table 3.

This rattling behavior in an oversized cage is important for reducing the thermal conductivity in the material by scattering acoustic phonons[8] and hence increasing the figure of merit, *Z*, for the thermoelectric material. If the isolated Eu^{2+} ions are treated as Einstein rattlers weakly coupled to the lattice, Sales and co-workers[5] showed with remarkable accuracy that the ADPs can be used to predict the Debye temperature, velocity of sound, and the lattice thermal conductivity for clathrate-type structures. In the absence of thermal conductivity measurements, the ADP parameters in Table 3, and the formulas found in ref 5, the Debye temperature was determined to be $\Theta_D = 185(18)$ K and the velocity of sound $v_s = 1930(130)$ m/s (numbers in parentheses indicate standard deviation). If the rattlers are considered to be localized or Einstein oscillators, the phonon mean free path is then taken as the distance between oscillators or the Eu−Eu 4.135 Å distance. This gives a lattice thermal conductivity of 0.40(0.04) W m^{-1} K^{-1}, a factor one-third that of fused silica.[27] While this is only an approximation, Sales and co-workers showed an excellent fit to experimental thermal conductivity for the Tl rattlers in the skutterdite $Tl_xCo_4Sb_{12-y}Sn$ as well as a close comparison of the predicted to the experimental thermal conductivity of the $Ba_8Ga_{16}Ge_{30}$ clathrate.

Electrical Transport Measurements. The room-temperature Seebeck coefficient was measured to be 40 μV/K. The positive sign indicates the carriers are primarily holes. Figure 5 shows the temperature-dependent electrical conductivity increasing with decreasing temperature, indicating metallic-like electrical transport. However, this interpretation does not agree with a Zintl description of bonding in this compound where all valence framework Ga/Ge bands are thought

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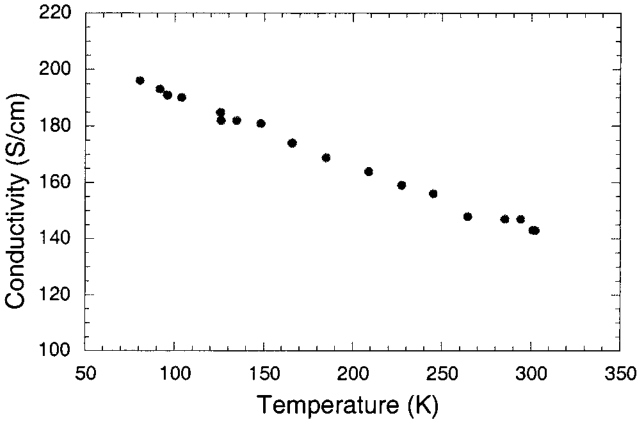

Figure 5. Temperature-dependent electrical conductivity for a single crystal of $Eu_4Ga_8Ge_{16}$.

to be filled through the donation from the guest Eu atoms.

If the Ga/Ge ratio is not the perfect 1:2 and is 1:1.999, for instance, then 1 in 1000 unit cells contains 1 extra gallium, then the dopant concentration is 2.5×10^{19}, a carrier concentration well above the critical concentration for metallic behavior of phosphorus doped in silicon.[28] Corbett noted that the predicted semiconducting behavior has been found in relatively few of the known "closed shell" Zintl compounds.[7] It is difficult to assign whether incomplete charge transfer from the guest or slight nonstoichiometry are responsible for the deviation from semiconducting behavior. The precision as well as accuracy of the ICP technique is not sufficient to answer this question.

The composition confidence interval alone spans a vast doping regime that could easily encompass doping concentrations leading to semiconducting or metallic properties. Magnetic measurements offer little insight into the conduction electrons due to masking of the small Pauli paramagnetic signal by the several orders of magnitude larger paramagnetic signal from the Eu ions. Ultrapure stoichiometric samples need to be prepared to ascertain the true semiconducting or metallic nature of this compound.

Composition. The composition analysis would appear to overcount Ga and undercount Ge in the formula $Eu_{4.00\pm0.07}Ga_{8.23\pm0.34}Ge_{15.38\pm0.46}$. It is difficult to rule out the possibility of mixed valency in the form of Eu^{2+}/Eu^{3+} necessitating more gallium in the Ga/Ge framework for charge-balancing reasons. Such a scenario is under current investigation through magnetic susceptibility measurements and Mössbauer spectroscopy.[29] Summing the framework atoms gives 23.61 ± 0.47 four-coordinate atoms, suggesting the possibility of structural vacancies or defects in the framework. Systematic structural refinements with fixed defects on framework sites showed poorer refinement statistics than the nondefect model, indicating a defect-free structure is correct.

Summary. We report the synthesis, structure, compositional, and preliminary electrical transport measurements of a new clathrate structure. This structure shows a unique one-dimensional nonbonded line of Eu atoms aligned along the *a*-axis occupying voids in eight-membered ring cages. The compound is thermodynamically less stable than the other alkaline earth germanium type I clathrates because of strain created by a greater distortion of the four-coordinate lattice from the ideal tetrahedral angle. From a thermoelectric standpoint, the compound shows an insufficient Seebeck coefficient to be currently considered as a viable thermoelectric candidate. However, previous work on the $Sr_8Ga_{16}Ge_{30}$ showed that the Seebeck coefficient in these clathrate materials vary widely with variations in composition.[1] The low predicted thermal conductivity in $Eu_4Ga_8Ge_{16}$ warrants further investigation into the stoichiometric effects on the Seebeck coefficient.

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Supporting Information Available: Additional crystallographic data on $Eu_4Ga_8Ge_{16}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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