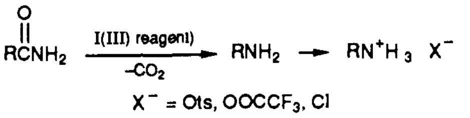
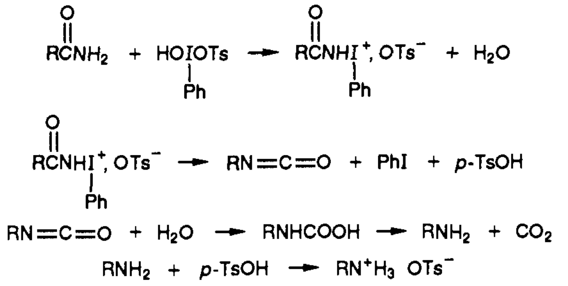
ment. A mechanism for the reaction with PhI(OH)(OTs),



$$\mathrm{RC(=O)NH_2} \xrightarrow[-\mathrm{CO_2}]{\mathrm{I(III)\ reagent)}} \mathrm{RNH_2} \rightarrow \mathrm{RN^+H_3\ X^-} \qquad (17)$$

$$\mathrm{X^- = OTs,\ OOCCF_3,\ Cl}$$

analogous to the Hofmann rearrangement, was proposed by Koser and co-workers.[28a]



$$\mathrm{RC(=O)NH_2 + HOI(Ph)OTs \rightarrow RC(=O)NHI^+(Ph),OTs^- + H_2O}$$

$$\mathrm{RC(=O)NHI^+(Ph),OTs^- \rightarrow RN{=}C{=}O + PhI + \mathit{p}\text{-}TsOH}$$

$$\mathrm{RN{=}C{=}O + H_2O \rightarrow RNHCOOH \rightarrow RNH_2 + CO_2}$$

$$\mathrm{RNH_2 + \mathit{p}\text{-}TsOH \rightarrow RN^+H_3\ OTs^-} \qquad (18)$$

We have found that iodosylbenzene reacts with neat formamide immediately, releasing gas as the iodosylbenzene becomes solubilized. The reaction of iodosylbenzene with acetamide in acetonitrile resulted in slow release of gas and uptake of iodosylbenzene into the solution.

Conclusions

We have found new iron complexes, $(Et_3HN)Fe^{III}(bpb)X_2$ (X = Cl, OTf), capable of catalyzing the olefin epoxidation by iodosylbenzene. Although the yields of epoxide are not high due to iodosylbenzene-consuming competition reaction that also occurs in the absence of substrate, epoxides are found to be the predominant products. The epoxidation reaction occurs with stereochemical retention. We have also found that a nonredox metal salt, $Al(OTf)_3$, can catalyze the same reaction, suggesting strongly that high-valent metal oxo intermediates are not involved. In addition to epoxide, other products have also been observed in all of the reactions. The presence of these products suggests that the mechanisms of these reactions are related to those occurring between olefins and soluble iodine(III) compounds, and this leads us to propose a new mechanism. Iodine(III) species are found to be capable of isomerizing *cis*-stilbene in the absence of metal catalyst, which can explain *cis*-stilbene isomerization and loss of stereochemistry in some metal-catalyzed reactions by iodosylbenzene. All of our observations are consistent with a mechanism that does not require changes in oxidation state of the metal ion and that involves electrophilic attack of I^{III} at the olefin.

Acknowledgment. We thank Dr. Saeed I. Khan for assistance in solving the crystal structures. Financial support from the National Science Foundation (J.S.V.) and the Office of Naval Research (F.D.) is gratefully acknowledged.

Registry No. 1, 135270-98-3; **2**, 135225-28-4; **3**, 135225-27-3; $(Et_3HN)Fe^{III}(bpb)Cl_2$, 135225-30-8; $(Et_3HN)Fe^{III}(bpb)Cl_2$, 135271-00-0; $Al(OTf)_3$, 74974-61-1; $Fe(OTf)_2$, 59163-91-6; $Fe(OTf)_3$, 63295-48-7; $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, 135225-31-9; $O[IPh(OTf)]_2$, 88016-29-9; Li(OTf), 33454-82-9; iodosylbenzene, 536-80-1; cyclohexene, 110-83-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; styrene, 100-42-5; *trans*-β-methylstyrene, 873-66-5; norbornene, 498-66-8; 1-octene, 111-66-0; cyclohexene oxide, 286-20-4; *trans*-2,3-diphenyloxirane, 1439-07-2; *cis*-2,3-diphenyloxirane, 1689-71-0; phenyloxirane, 96-09-3; *trans*-2-methyl-3-phenyloxirane, 23355-97-7; *exo*-1,2-epoxynorbornane, 3146-39-2; 1,2-epoxyoctane, 2984-50-1; 4-methoxystyrene, 637-69-4; 4-methylstyrene, 622-97-9; 4-chlorostyrene, 1073-67-2; 3-chlorostyrene, 2039-85-2; 3-acetamidocyclohexene, 39819-72-2; bicyclo[2.2.1]-5-heptene-2-carboxylic acid, 67999-50-2; iodobenzene diacetate, 3240-34-4; norbornene, 498-66-8; 1,4-diiodobenzene, 624-38-4; iodobenzene, 591-50-4; *cis*-1,2-cyclohexanediol ditriflate, 91146-10-0.

Supplementary Material Available: Tables of the fractional coordinates, bond distances, bond angles, and isotropic and anisotropic temperature factors for $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, **1** and **3** (19 pages); listing of calculated and observed structure factors for $(Et_3HN)Fe^{III}(bpb)Cl_2{\cdot}CH_3CN$, **1** and **3** (33 pages). Ordering information is given on any current masthead page.

$Ca_{14}GaAs_{11}$: A New Compound Containing Discrete $GaAs_4$ Tetrahedra and a Hypervalent As_3 Polyatomic Unit

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Abstract: In the course of investigating the synthesis and properties of several ternary Ga–As Zintl compounds, a new Zintl compound has been prepared: $Ca_{14}GaAs_{11}$. This compound has been prepared in high yield from the stoichiometric combination of the elements in a sealed Nb tube, sealed in an evacuated quartz ampule, at 1100 °C for 4 days. It crystallizes in the tetragonal space group $I4_1/acd$ with lattice parameters a = 15.642 (2) Å and c = 21.175 (4) Å (room temperature). Single-crystal X-ray diffraction data were collected at 130 K ($I4_1/acd$, Z = 8, a = 15.620 (3) Å, and c = 21.138 (4) Å). Its structure is composed of isolated $GaAs_4$ tetrahedra that are separated by As_3 linear units, As and Ca. The As_3 units are situated between the tetrahedra and alternate by 90° down the c axis. Although the As–As distance in the As_3 unit is rather long (2.956 (2) Å), it is consistent with the long I–I distance observed in the isoelectronic, hypervalent I_3^- anion and therefore is considered to be formally an As_3^{7-} anion. Optical data are consistent with a semiconducting compound, indicating an optical band gap of about 1.49 eV, slightly higher in energy than that observed for GaAs. The synthesis, structure, and bonding in this compound will be discussed.

Introduction

Basic research on crystalline semiconductors has played a key role in the development of solid-state devices.[1] GaAs and III/V semiconductors[2] are important for electronic and optoelectronic applications such as quantum devices,[1b] high-speed computers,[1c] and photovoltaics.[1d] A large group of materials that may have unique semiconductor properties are the so called ternary Zintl phases.[3] This class of materials contains ternary I–III–V and

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(1) See for example: (a) *Crystalline Semiconducting Materials and Devices*; Butcher, P. N., March, N. H., Tosi, M. P., Eds.; Plenum Press: New York 1986. (b) Bate, R. T. *Sci. Am.* **1988**, *258*, 96. (c) Seitz, C. L.; Matisoo, J. *Phys. Today* **1984**, 38. (d) Hamakawa, Y. *Sci. Am.* **1987**, *256*, 87.

(2) According to the recent IUPAC convention, groups III and V are groups 13 and 15, respectively; groups I and II are groups 1 and 2, respectively.

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II–III–V compounds[2] whose structures can be interpreted according to the Zintl–Klemm–Busmann rules.[3] In all these compounds, the electropositive atoms donate their electrons to the more electronegative main group atoms, which in turn form the correct number of hetero- and homoatomic bonds such that each element has a complete octet. Generally, these Zintl phases are distinct from either the insulators or the typical intermetallic phases because the structures can be described by simple valence rules and they are normally semiconductors. This electron-counting scheme, the Zintl concept, shows that classical descriptions of bonding are still valid in the field of metal–main group compounds. There has been recent interest in the use of these ternary main group Zintl compounds as precursors to the synthesis of thin-film III–V type semiconductors.[4,5]

The variety of structures obtained with ternary main group Zintl compounds[3] provides incentive to study structure–property relationships of these materials. There are three alkali or alkaline earth gallium arsenide compounds[5-7] whose structures have been determined to date. These three compounds are related to GaAs in that each compound consists of $GaAs_4$ tetrahedra that are linked together in a polymeric framework. Ca_3GaAs_3 is made up of $GaAs_4$ tetrahedra that are linked through common corners to form an infinite chain denoted by $[GaAs_2As_{2/2}]^{6-}_{\infty}$. In $Ca_5Ga_2As_6$, two of these chains are linked together by As–As bonds to form a double chain of $GaAs_4$ tetrahedra denoted by $[(GaAsAs_{2/2}(As_2)_{1/2})_2]^{0-}_{\infty}$. $K_3Ga_3As_4$ is made up of distorted $GaAs_4$ tetrahedra which share a common edge to form covalently bonded sheets of $[(GaAs_{4/3})_3]^{3-}_{\infty}$. In the course of investigating the synthesis and properties of the two known ternary Ca–Ga–As compounds (Ca_3GaAs_3[6] and $Ca_5Ga_2As_6$[7]), we have synthesized a new compound: $Ca_{14}GaAs_{11}$. This is the first example of a solid-state compound containing a $GaAs_4$ tetrahedron that is not part of a one-, two-, or three-dimensional $GaAs_4$ network. In addition, this structure contains a novel As_3 linear polyatomic unit. Although the structure can be describe as consisting of isolated polyanions, the optical data are indicative of semiconducting behavior. Herein, we describe the synthesis, structure, and properties of $Ca_{14}GaAs_{11}$.

Experimental Section

Synthesis. $Ca_{14}GaAs_{11}$ was initially synthesized by reacting the elements Ca (Anderson Physics Lab, 99.99%), Ga (J. Matthey, 99.99%), and As (J. Matthey, 99.99%) in a 4:1:3 ratio. The reactants and products were handled in nitrogen-filled dry boxes with typical water levels less than 1 ppm. The reactants were pressed into a pellet, placed in an alumina boat, and sealed in a silica ampule under $^1/_5$ atm of purified Ar. The reaction vessel was placed into a furnace and heated to 1350 °C (60 deg/h). It was allowed to remain at that temperature for 1 h and then cooled to 1000 °C (30 deg/h) and subsequently cooled (~200 deg/h) to room temperature. The air-sensitive product was primarily a microcrystalline powder of Ca_3GaAs_3 and black, hexagonal plates. The composition of the latter was determined by microprobe analysis and single-crystal X-ray diffraction data.

Once the composition of the crystals was determined, $Ca_{14}GaAs_{11}$ could be synthesized in high yields by reacting stoichiometric combinations of the elements or by reacting stoichiometric combinations of Ca_3As_2, GaAs (J. Matthey, 99.9999%), and As or Ca_3As_2, Ga, and As sealed in a Nb tube with $\sim ^1/_5$ atm of purified argon within the outer SiO_2 jacket. The reaction was air quenched after 4 days at 1100 °C. The air-sensitive product from the reaction primarily consisted of some well-formed hexagonal plates together with microcrystalline material which could be identified as $Ca_{14}GaAs_{11}$. A very small amount of unidentified impurity was also present in the powder mixture.

X-ray Powder Diffraction. Characterization was carried out by X-ray powder techniques (Guinier) at room temperature. The sample was mounted between pieces of tape with NBS silicon included as an internal standard. X-ray powder data were obtained with a focusing Guinier camera (Enraf-Nonius) equipped with a silica monochromator to give Cu Kα_1 radiation. The powder patterns were indexed according to information obtained from the single-crystal structural refinement. The corresponding lattice constants (a = 15.642 (2) Å, c = 21.175 (4) Å) were determined by standard least-squares refinement.

Table I. Crystallographic Data for $Ca_{14}GaAs_{11}$

fw	1454.98
space group	$I4_1/acd$ (no. 142, origin choice 2)
crystal size, mm	0.175 × 0.275 × 0.05
a, Å	15.620 (3)
c, Å	21.138 (4)
V, Å^3	5157 (2)
T, K	130
Z	8
ρ_{calcd}, g cm^{-3}	3.75
radiation, Å	Mo Kα (λ = 0.71069)
μ(Mo Kα), cm^{-1}	173.68
transmission factors, %	8.1–51.3
no. of parameters refined	61
R^a	0.033
$R_w{}^a$	0.029 [$w = 1/\sigma^2(F_o)$]

[a] $R = \sum||F_o| - |F_c||/|F_c|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$.

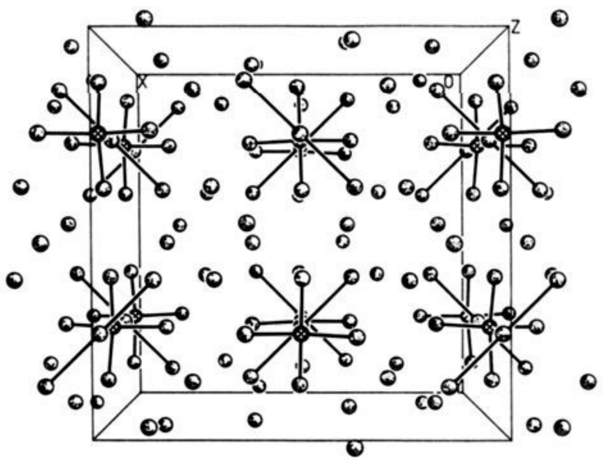

Figure 1. A perspective view down the c axis showing the relative orientation of the $GaAs_4$ tetrahedra, the As_3 units, and the As^{3-} anions in the cell. The As atoms are indicated by circles with a random dot pattern and the Ga atoms are indicated by cross-hatched circles.

Single-Crystal X-ray Study. The reaction container was opened in a dry box equipped with a microscope. Several suitable crystals of $Ca_{14}GaAs_{11}$ were coated with a hydrocarbon oil to minimize exposure to air. The crystal selected for data collection (dimensions: 0.175 × 0.275 × 0.05 mm^3) was mounted on a fiber and transferred to the diffractometer where it was placed in a cold stream of nitrogen.[8] Unit cell parameters were obtained from a least-squares refinement of 24 reflections with 15° < 2θ < 30°. The crystal lattice was determined to be tetragonal I by the automatic indexing routine of the diffractometer software. This was verified from axial photographs and systematic extinctions. Diffraction data in the positive octant to a maximum 2θ of 55° were collected at 130 K on a Syntex P2_1 diffractometer equipped with a modified LT-1 low-temperature apparatus. No decomposition of the crystal was observed (inferred from the intensity of two check reflections). The data were corrected for Lorentz and polarization effects. Of the 1004 unique data, a total of 855 reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The space group determination was unambiguous. The structure was solved by direct and difference Fourier methods and was refined with SHELXTL, Version 5.1, installed on a Data General Eclipse computer. A correction for absorption was applied.[9] Neutral atom scattering factors were those of Cromer and Waber.[10] The

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Table II. Distances and Angles for $Ca_{14}GaAs_{11}$

As(1)–Ca(1)	3.019 (2)	As(2)–Ca(1)	3.071 (2)
As(1)–Ca(2)	3.040 (2)	As(2)–Ca(1′)	3.051 (2)
As(1)–Ca(3)	3.209 (1)	As(2)–Ca(2)	2.953 (2)
As(1)–Ca(4)	2.998 (2)	As(2)–Ca(2′)	3.512 (2)
As(1)–As(4)	2.956 (2)	As(2)–Ca(3)	3.124 (2)
As(4)–Ca(2)	3.220 (2)	As(2)–Ca(4)	2.979 (2)
As(4)–Ca(1)	3.005 (2)	As(2)–Ca(4′)	3.230 (2)
As(3)–Ca(1)	3.035 (2)	As(3)–Ca(4)	3.085 (2)
As(3)–Ca(1′)	3.003 (2)	As(3)–Ca(4′)	3.068 (2)
As(3)–Ca(2)	2.958 (2)	As(3)–Ca(4″)	3.565 (2)
As(3)–Ca(2′)	3.052 (2)	Ga–As(2)	2.546 (1)
As(3)–Ca(3)	2.913 (2)	Ga–Ca(2)	3.446 (2)
As(2)–Ga–As(2)	113.0 (1)	As(2)–Ga–As(2′)	107.8 (1)

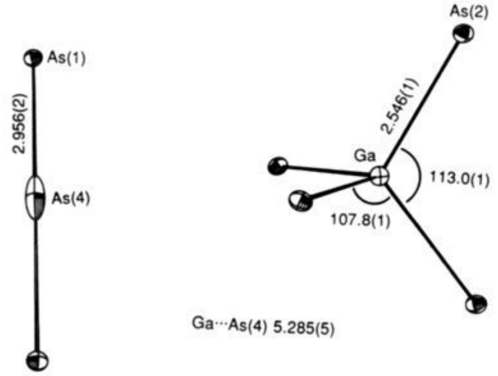

Figure 2. A perspective view showing the relative orientation of the $GaAs_4$ tetrahedron and the As_3 polyatomic unit. Important bond lengths (Å) and angles (deg) are shown. Thermal ellipsoids are drawn at 70%.

compound is isostructural to the Zintl compound, $Ca_{14}AlSb_{11}$.[11] The final difference Fourier map was flat to ±0.8 e/Å^3. Table I summarizes crystal data and some of the data collection and refinement parameters. Atomic positional parameters, anisotropic thermal parameters, and structure factor tables are available as supplemental material.

Spectroscopy: Near-IR and optical transmission spectroscopy was performed on a Hitachi U-2000 spectrophotometer. The samples were ground into mulls in a drybox and placed between optical plates.

Results and Discussion

In the framework of the Zintl–Klemm–Busmann rules,[3] the structure of this compound can be understood as consisting of 14 Ca^{2+} cations, 4 As^{3-} anions, a $GaAs_4^{9-}$ tetrahedron, and a linear As_3^{7-} unit. A perspective view of the structure showing the unit cell with the Ca cations omitted for the sake of clarity is shown in Figure 1. Important bond distances and angles are listed in Table II. The $GaAs_4$ tetrahedra have $\bar{4}$ point symmetry and are translated by $^1/_2$ along the *c* axis while the As_3 anions have 222 point symmetry and are staggered by 90° with respect to each other as shown in Figure 1. The $GaAs_4$ tetrahedron is shown in Figure 2 and is slightly distorted with As–Ga–As angles of 113.0 (1)° and 107.8 (1)°. This distortion of the tetrahedra to $\bar{4}2m$ symmetry is attributed to packing constraints and to anion–anion repulsion. The Ga–As(2) bond length of 2.532 (1) Å is typical for these ternary Ca–Ga–As compounds[6,7] (2.476–2.695 Å). It is, however, longer than that observed in the binary compound, GaAs (2.448 Å).[12] There are eight Ca–As(2) distances in the range 2.953–3.230 Å. While somewhat shorter than the sum of the ionic radii for Ca^{2+} and As^{3-} (3.22 Å),[13] they are typical for Zintl compounds and for Ca–As binary compounds.[14]

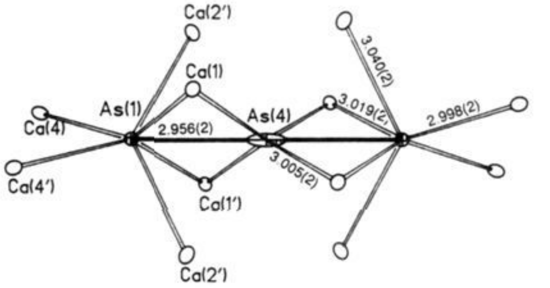

Figure 3. A view showing the important bond lengths (Å) for the As_3 unit. Thermal ellipsoids are drawn at 70%.

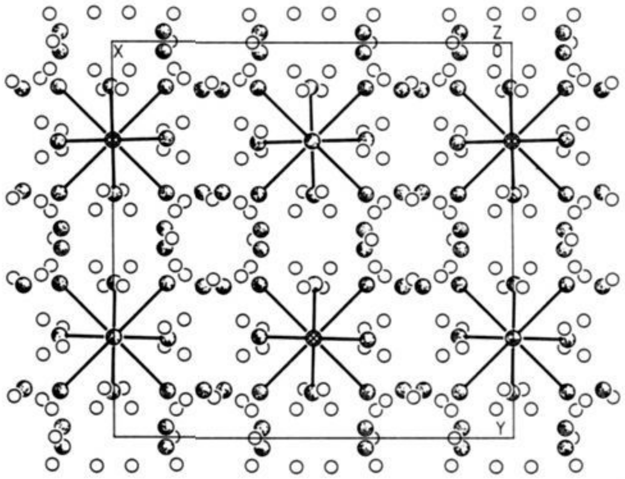

Figure 4. [001] projection of the structure of $Ca_{14}GaAs_{11}$. The Ca and Ga atoms are indicated by open and cross-hatched circles, respectively. The As atoms are indicated by circles with a random dot pattern.

The As_3 linear unit, shown in Figure 2, is symmetric about the central As(4); the bond length for As(1)···As(4) is 2.956 (2) Å. The anisotropic thermal parameter on the central As is elongated along the bond for reasons that are not well understood, but this may be due to some positional disorder that would make the two As–As distances inequivalent. The distance of 2.956 Å is considerably longer than a normal As–As single bond (2.4 Å),[10,15] but it is consistent with the longer distances observed in the analogous Sb_3 (3.196 (2) Å) and Bi_3 (3.336 (2) Å) units observed in $Ca_{14}AlSb_{11}$[11] and $Ca_{14}MnBi_{11}$.[12] All other As–As distances are considerably longer (≥3.904 Å) and are not considered to be homoatomically bonded. By analogy to the I_3^- anion, which has an I–I bond distance in the range 2.90–3.10 Å compared to I_2 which has an I–I bond distance of 2.67 Å,[16] the As_3 unit is given a formal charge of 7–. Therefore, As_3^{7-} is isoelectronic to I_3^-. This is a modification of the Zintl rules in that we have allowed the central As of the As_3 unit to expand its octet to accept ten electrons (5 electron pairs, dsp^3 hybridization). Theoretical calculations[17] indicate that it is more nearly correct to view the As_3^{7-} unit as a 3-center 4-electron hypervalent bond[18] rather than

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(10) Neutral atom scattering factors and corrections for anomalous dispersion are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

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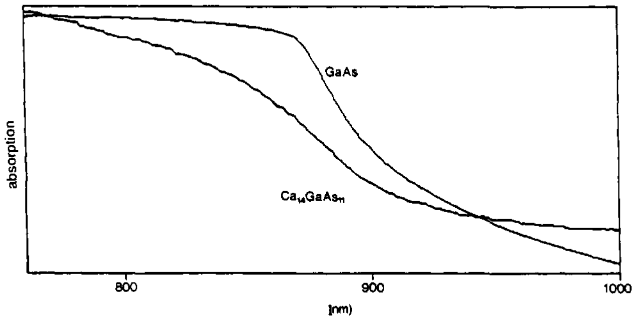

Figure 5. Optical absorption spectra of GaAs and $Ca_{14}GaAs_{11}$ mulls. Intensity is in arbitrary units.

one with dsp^3 hybridization for the central As. The large anionic charge is stabilized by six Ca–As(1) and four Ca–As(4) interactions of ~3.0 Å as shown in Figure 3.

In addition to As atoms in the polyatomic units, there are also isolated As atoms, As(3). These atoms are located between the $GaAs_4$ tetrahedra and the As_3 linear units and form a spiral along a screw axis coincident with the *c* axis. The outline of this circle can be clearly seen in the [001] projection of the structure (Figure 4). The closest As ion to As(3) is another As(3) anion in the spiral at 3.92 Å; all other As(3)···As distances are ≥4.2 Å. These anions are surrounded by eight Ca cations with seven shorter Ca–As(3) distances corresponding to 3.085 (2) and 3.068 (2) Å for Ca(4), 3.035 (2) and 3.003 (2) Å for Ca(1), 3.052 (2) and 2.958 (2) Å for Ca(2), and 2.913 (2) Å for Ca(3) and one long Ca(4)···As(3) distance of 3.562 (2) Å. This coordination is similar to that observed in the Zintl compound Ca_2As_3.[14a]

The structure and bonding in $Ca_{14}CaAs_{11}$ can be described according to the Zintl rules as consisting of polyatomic anions as well as isolated anions associated by electrostatic bonding. One might expect this material to be an insulator, although there are materials that have crystal structures in full accordance with the Zintl–Klemm–Busmann concept but with "wrong physical properties".[3] $Ca_{14}GaAs_{11}$ forms opaque, black crystals that have a high luster, similar in appearance to GaAs, which leads one to speculate that they will have semiconducting behavior. We have been unable to obtain temperature-dependent resistivity data so far due to the small size and air sensitivity of the $Ca_{14}GaAs_{11}$ crystals. In order to obtain some information on the electronic properties of $Ca_{14}GaAs_{11}$ and to compare its properties to GaAs, near-IR and optical absorption spectra were taken at room temperature (Figure 5). The absorption edge observed in these spectra is indicative of semiconducting behavior.[19] The measured spectrum for GaAs, shown in Figure 5, has a maximum in the absorption edge at ~874 nm or 1.42 eV which is attributed to the band gap in agreement with the published spectrum.[20] The absorption edge for $Ca_{14}GaAs_{11}$ is at slightly lower wavelength (~834 nm), and the band gap is about 1.49 eV, slightly higher in energy than that observed for GaAs. It is also broader and less well defined compared to GaAs. This may be due to an indirect absorption process or the presence of other absorption processes; however, further interpretation of the optical data is not possible without single-crystal and temperature-dependent studies.

The $Ca_{14}GaAs_{11}$ structure can be understood by applying a modified Zintl–Klemm–Busmann concept. It is the first example of a discrete $GaAs_4$ tetrahedron and a linear As_3 anion. We have been able to prepare the compounds $A_{14}GaX_{11}$ (A = Ca, Sr; X = As, Sb).[21] and property measurements on this series of compounds are in progress. Although temperature-dependent resistivity data have not yet been obtained for $Ca_{14}GaAs_{11}$, the near-IR and optical spectra are indicative of semiconducting and not insulating behavior.

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Supplementary Material Available: Tables of atomic positional parameters and anisotropic thermal parameters (2 pages); listing of structure factors (3 pages). Ordering information is given on any current masthead page.

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