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Five Ternary Zintl Phases in the Systems Alkali-Metal–Indium–Bismuth

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Five new compounds of alkali metal, indium, and bismuth were synthesized by direct fusion of the elements. The structures of these compounds, $Na_3In_2Bi_3$ (I) (refined composition $NaIn_{0.61(1)}Bi$, orthorhombic, *Pnma*, $a = 8.062(2)$, $b = 4.8684(8)$, and $c = 9.2455(9)$ Å), Na_3InBi_2 (II) (monoclinic, $P2_1/c$, $a = 18.841(3)$, $b = 9.235(1)$, and $c = 12.661(2)$ Å, $\beta = 98.67(2)°$), $K_7In_4Bi_6$ (III) (refined composition $K_{4.71(3)}In_{2.52(2)}Bi_4$, tetragonal, $P4_3$, $a = 9.703(1)$, and $c = 17.519(4)$ Å), $K_{11}In_6Bi_9$ (IV) (triclinic, $P\bar{1}$, $a = 12.012(7)$, $b = 13.380(4)$, and $c = 13.695(4)$ Å, $\alpha = 76.70(2)$, $\beta = 64.14(3)$, and $\gamma = 75.68(3)°$), and $Rb_7In_4Bi_6$ (V) (tetragonal, $P4_3$, $a = 9.915(2)$ and $c = 17.870(4)$ Å) are built of indium-centered tetrahedra of bismuth that are connected by corner- or/and edge-sharing and form different types of three-dimensional networks. All five compounds are diamagnetic and, therefore, electronically balanced, salt-like Zintl phases. According to EHMO calculations they are wide band-gap semiconductors. © 2002 Elsevier Science (USA)

Key Words: **crystal structures; intermetallic compounds; indium; bismuth; Zintl phases.**

INTRODUCTION

In the past three decades comprehensive research on Zintl phases has led to major discoveries that have immensely broadened our understanding of these systems with, often, complicated electronic structures (1–5). Undoubtedly, the most fascinating compounds among these are the compounds with delocalized bonding that elude description by simple valence rules but obey rather Wade's rules developed for electron counting in deltahedral boranes, $B_nH_n^{2-}$ (6). Typical examples are the numerous isolated or linked deltahedral clusters of group 13 which, due to the only three valence electrons of the elements of this group, usually carry quite high negative charges (5, 7, 8). Similar isolated clusters of group 14 were discovered in the solid state only very recently, although some of them had been known for quite some time in compounds crystallized from ethylenediamine or liquid ammonia solutions (3). Examples of these clusters are *nido*-Ge_9^{4-} in A_4Ge_9 (A = Rb, Cs) (9), *nido*-Pb_9^{4-} in A_4Pb_9 (A = K, Rb, Cs) (10–12), *nido*-Si_9^{4-} in $A_{12}Si_{17}$ (A = K, Rb) (13), and *arachno*-Sn_8^{6-} in $A_4Li_2Sn_8$ (A = K, Rb) (14), all with delocalized bonding. Also in this group is the largest species of group 14, a giant truncated tetrahedron of Ge_{12}^{12-} in $RbLi_7Ge_8$ with localized bonds (15).

With these examples in mind, the next logical step is to look for similar isoelectronic clusters made of elements of two different groups, heteroatomic clusters. Thus, a cluster of four atoms of group 13 (Tr = Triel), five atoms of group 15 (Pn = Pnictide), and a charge of 3 −, i.e., $(Tr_4Pn_5)^{3-}$, will be isoelectronic with Ge_9^{4-}. So will be $(Tr_5Pn_4)^{5-}$, $(Tr_{4.5}Pn_{4.5})^{4-}$, etc. clusters where the formal charge can be varied by simply tuning the ratio between the atoms of Tr and Pn. This gives additional flexibility to the system since the oxidation numbers can be varied without changing the geometry of the cluster, something impossible in simple binary phases. Not just any arbitrary combination of Tr and Pn elements will be appropriate. Some important requirements for the elements are (a) to be distinguishable by X-ray diffraction, i.e., to be sufficiently different in atomic numbers, (b) to be able to form isolated clusters, (c) to have a stable *s* pair of electrons, and of course, (d) to have similar sizes and similar electronegativities. Indium and bismuth satisfy these criteria since they have relatively similar electronegativities (Pauling's), 1.7 vs 1.9, and similar covalent radii, 1.42 vs 1.51 Å (16), respectively. They are also capable of forming clusters on their own, and, as heavy elements, have an inert *s* pair of electrons in the outer shells. Analogously, $[Ga_4Bi_5]^{3-}$ and $[Ga_5Bi_4]^{5-}$ can also be suggested as the electronegativities of Ga and Bi are also relatively close, although the difference in the size is somewhat larger.

Following these ideas we have undertaken exploratory synthesis of the alkali-metal–In–Bi systems, but, so far, no isolated heteroatomic clusters have been found. Instead, the reactions produced a number of Zintl phases with extended structures based on corner- or/and edge-sharing tetrahedra of bismuth centered by indium and with localized bonding.

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Five of these compounds are the subjects of the present paper. The corresponding systems of alkaline-earth–In–Bi and alkali-metal–Ga–Bi were also explored. Until now, all tested reactions proved unsuccessful, yielding compounds of known structure types (below). However, the A–In–Bi phases ($A = \mathrm{Na}$, K, Rb), surprisingly, dissolve in ethylenediamine, and, in the presence of 2,2,2-crypt, compounds with exactly the proposed above deltahedral clusters of $[\mathrm{In_4Bi_5}]^{3-}$ can be crystallized from the solution (17).

We have already reported on the synthesis and structure of a compound in the Cs–In–Bi system, $\mathrm{Cs_7In_4Bi_6}$ (18). Here we report the synthesis and structures of $\mathrm{Na_3In_2Bi_3}$ (**I**), $\mathrm{Na_3InBi_2}$ (**II**), $\mathrm{K_7In_4Bi_6}$ (**III**), $\mathrm{K_{11}In_6Bi_9}$ (**IV**), and $\mathrm{Rb_7In_4Bi_6}$ (**V**).

SYNTHESIS

All manipulations were performed in a glove box with purified N_2 (oxygen and moisture levels below 1 ppm). The elements (all from Alfa-Aesar, 99.9 + % pure) were used as received. The surfaces of Na and K were cleaned with a scalpel immediately before use. Mixtures of the elements scaled to about 500 mg per reaction were loaded in niobium containers which were then closed by arc-welding under argon, and were sealed in fused-silica ampoules under high vacuum. These assemblies were heated at 850°C for 3 days and were then slowly cooled to room temperature at a rate of 5°C/h. Mixtures of elements with compositions of $A_5\mathrm{In_5Bi_4}$ ($A = \mathrm{Na}$, K, Rb) were reacted initially in an attempt to synthesize heteroatomic clusters of $[\mathrm{In_5Bi_4}]^{5-}$ isoelectronic with the known homoatomic *nido*-Tt_9^{4-} ($Tt = \mathrm{Si}$, Ge, Pb) (9–13). Instead, the sodium reaction yielded two coexisting phases identified later as $\mathrm{Na_3In_2Bi_3}$ (**I**) and $\mathrm{Na_3InBi_2}$ (**II**). The potassium analog afforded the simultaneous formation of $\mathrm{K_7In_4Bi_6}$ (**III**) and $\mathrm{K_{11}In_6Bi_9}$ (**IV**), while the rubidium reaction yielded only $\mathrm{Rb_7In_4Bi_6}$ (**V**) and traces of an amorphous phase. All of the products also contained traces of NaBi, $\mathrm{KBi_2}$, or $\mathrm{RbBi_2}$ and, often, unreacted In and/or Bi.

After the structures and compositions of the **I**, **II**, **III**, and **IV** were determined from single-crystal X-ray diffraction, many reactions were loaded with the exact compositions in an attempt to produce each compound as a single phase and with better crystallinity. Also, a variety of temperature profiles were probed including rapid heating to 950°C followed by a rapid quenching to − 196°C (breaking the hot quartz ampoule under liquid N_2), slow heating to moderate temperatures of ca. 550°C, followed by annealing for prolonged periods of ca. 3–4 weeks and then slowly cooling to room temperature. Attempts were also made to synthesize each compound starting from binary precursors such as $\mathrm{KBi_2}$ and $\mathrm{KIn_4}$, for example. In addition, an excess of one of the components was used to presumably serve as possible "flux." Nevertheless, despite all these efforts, the resulting products were always multiphase mixtures. Perhaps, some of the indium is lost as solid solutions with the niobium container (no Nb–In compounds are known).

PHASE AND ELEMENTAL ANALYSIS

Phase analysis of the products was carried out by powder X-ray diffraction on an Enraf-Nonius Guinier camera (under vacuum) with $\mathrm{Cu}K\alpha_1$ radiation. For that matter a representative portion of the finely ground sample is isolated between two pieces of cellophane tape together with NBS (NIST) silicon as an internal standard. The tape protects the specimen from contact with oxygen and moisture during transfer from the glove box to the camera.

Qualitative microprobe analysis was performed on single crystals from all samples and confirmed the presence of alkali metal, In, and Bi only.

STRUCTURE DETERMINATION

Single-Crystal X-Ray Diffraction

Several crystals from each sample were picked in the glove box and sealed in thin-walled glass capillaries. Overall, all phases were very poorly diffracting, and many crystals had to be checked in order to select relatively good ones for data collection. Data were collected for **I** through **IV** on an Enraf-Nonius CAD4 single-crystal diffractometer with monochromated Mo $K\alpha$ radiation at room temperature (ω–2θ scans, $2\theta_{\max} = 50°$). Compound **V** is isostructural with **III** and only the lattice parameters were determined. The data sets were corrected for Lorentz and polarization effects, and for absorption with the aid of 6ψ-scans for **I**, and 3ψ-scans for **II**, **III**, and **IV**. Subsequently, the data were further treated for absorption using the Xabs (DIFABS) software but some problems with absorption persisted, and this is reflected in some of the R-factors (19). The unit cell parameters for all compounds were confirmed by axial photographs. The structures were solved by direct methods and were refined on F^2 with the aid of the SHELXTL-V5.1 software package (20). Details of the data collection and structure refinements are given in Table 1, while positional along with equivalent isotropic displacement parameters, anisotropic displacement parameters, and important distances are listed in Tables 2, 3, and 4, respectively.

$\mathrm{Na_3In_2Bi_3}$. A full sphere of data was collected on a dark-to-black, irregularly shaped single crystal of **I** ($0.25 \times 0.15 \times 0.10$ mm). Axial photographs along the orthorhombic axes confirmed *mmm* Laue class which, together with the observed systematic absences, indicated two possible space groups, *Pnma* and *Pna*2$_1$. The intensity statistics suggested the centrosymmetric space group, and the structure was successfully solved and refined in *Pnma* ($R_1 = 4.14$,

TABLE 1
Selected Data Collection and Refinement Parameters for $Na_3In_2Bi_3$ (I), Na_3InBi_2 (II), $K_7In_4Bi_6$ (III),[a] and $K_{11}In_6Bi_9$ (IV)

	I	**II**	**III**	**IV**
Empirical formula	$NaIn_{0.67}Bi$	$Na_9In_3Bi_6$	$K_{4.67}In_{2.67}Bi_4$	$K_{11}In_6Bi_9$
Formula weight	308.61	1805.25	1324.70	2999.84
Temperature (K)	293(2)			
Wavelength (Å), Mo$K\alpha$	0.71073			
Crystal system	Orthorhombic	Monoclinic	Tetragonal	Triclinic
Space group, No.	$Pnma$, 62	$P2_1/c$, 14	$P4_3$, 78	$P\bar{1}$, 2
Unit cell dimensions (Å)	$a = 8.062(2)$	$a = 18.841(3)$	$a = 9.703(1)$	$a = 12.012(7)$
	$b = 4.8684(8)$	$b = 9.235(1)$		$b = 13.380(4)$
	$c = 9.2455(9)$	$c = 12.661(2)$	$c = 17.519(4)$	$c = 13.695(4)$
				$\alpha = 76.70(2)°$
		$\beta = 98.67(2)°$		$\beta = 64.14(3)°$
				$\gamma = 75.68(3)°$
Volume (Å^3), Z	362.9(1), 4	2177.8(5), 4	1649.4(4), 4	1900.2(9), 2
$\rho_{\text{calculated}}$ (g/cm^3)	5.649	5.506	5.335	5.243
μ (cm^{-1})	525.52	515.63	473.18	462.62
Absorption correction	ψ-scan and Xabs			
Theta range (deg)	3.35 to 24.95	2.19 to 24.92	2.10 to 24.95	2.14 to 25.02
Reflections collected	2544	4206	3268	9496
Data/restraints/parameters	359/0/20	3796/0/164	2881/1/120	5845/0/239
Goodness-of-fit on F^2	1.379	1.001	1.029	1.025
Final R^b indices [$I > 2\sigma_I$] (%)	$R_1 = 4.14$	$R_1 = 6.83$	$R_1 = 7.82$	$R_1 = 7.35$
	$wR_2 = 10.21$	$wR_2 = 14.16$	$wR_2 = 15.34$	$wR_2 = 14.75$
Largest diff. peak (e/Å^3)	1.41	3.23	2.80	7.59
hole (e/Å^3)	−2.51	−3.26	−2.29	−8.35

[a] The lattice parameters of the isostructural $Rb_7In_4Bi_6$ are $a = 9.915(2)$ and $c = 17.870(4)$ Å. [b] $R_1 = [\sum \| F_o| - |F_c\|]/\sum |F_o|$; $wR_2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$.

$wR_2 = 10.21\%$ for 339 reflections with $I > 2\sigma_I$ and 20 parameters). One position for Bi and one for In were located from the direct methods while one sodium was found from the difference Fourier map. All three positions are at special four-fold sites of Wyckoff type 4*c* (Table 2) and, therefore, the ideal composition of **I** would be NaInBi if all positions are fully occupied. However, the thermal parameter of the In was anomalously large, and when the site occupancy was freed to vary it refined 61(1)% occupied (refined composition $NaIn_{0.61(1)}Bi$). This occupancy of nearly $\frac{2}{3}$ provides an electronically balanced compound which is in agreement with the observed diamagnetism and the results from the EHMO calculations (below). The final refinement was carried out for a composition of $NaIn_{0.67}Bi$, which can be formulated as $Na_3In_2Bi_3$ for simplicity.

Na_3InBi_2. The crystals of this compound appear the same as those of **I** and could not be separated in a rational manner. Many crystals were checked for singularity, and a quarter of a sphere of data was collected on the best one (0.22 × 0.16 × 0.16 mm). The axial photographs showed Laue symmetry 2/*m*, and the systematic absences suggested only $P2_1/c$. The structure was subsequently solved and refined in that space group ($R_1 = 6.83$, $wR_2 = 14.16\%$ for 1879 reflections with $I > 2\sigma_I$ and 164 parameters). Most of the atoms in the asymmetric unit were easily located from the structure solution while the remaining ones were found from difference Fourier maps. There are 6 bismuth, 3 indium, and 9 sodium positions (Table 2). All positions are general and this accounts for the formula $Na_9In_3Bi_6$, simplified as Na_3InBi_2. This stoichiometry represents an electronically balanced compound consistent with the observed diamagnetic behavior and the EHMO calculations.

$K_7In_4Bi_6$ and $Rb_7In_4Bi_6$. A quarter of a sphere of data was collected on a dark, irregularly shaped crystal of $K_7In_4Bi_6$ (0.18 × 0.12 × 0.08 mm). The 4/*m* Laue symmetry and the correct unit cell axes were confirmed from axial photography. The only extinction condition of 00*l* ($l = 4n$) readily indicated two possible space groups, the chiral enantiomorphs $P4_1$ and $P4_3$. The structure was solved and refined in the latter with final *R*-factors of $R_1 = 7.82$ and $wR_2 = 15.34\%$ for 1805 reflections ($I > 2\sigma_I$) and 120 parameters. There are 4 bismuth, 4 indium, and 5 potassium positions (Table 2) of four-fold symmetry which would give a formula of $K_5In_4Bi_4$. However, the unreasonably short distances of less than 2 Å from K5 to In3 and In4 suggested

TABLE 2

Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Na_3In_2Bi_3$ (I), Na_3InBi_2 (II), $K_7In_4Bi_6$ (III), and $K_{11}In_6Bi_9$ (IV)

Atom	Site	*x*	*y*	*z*	U_{eq}
$Na_3In_2Bi_3$ (**I**)					
Bi	4*c*	0.2360(1)	$\frac{1}{4}$	0.3868(1)	0.0365(5)
In[a]	4*c*	0.3664(5)	$\frac{1}{4}$	0.0704(3)	0.0391(9)
Na	4*c*	0.976(2)	$\frac{1}{4}$	0.8205(1)	0.046(3)
Na_3InBi_2 (**II**)					
Bi1	4*e*	0.29604(9)	0.6218(2)	0.8463(2)	0.0171(5)
Bi2	4*e*	0.2076(1)	0.0995(2)	0.6885(2)	0.0193(4)
Bi3	4*e*	0.95754(9)	0.8975(2)	0.6445(2)	0.0192(5)
Bi4	4*e*	0.5304(1)	0.3680(2)	0.8290(2)	0.0205(4)
Bi5	4*e*	0.1243(1)	0.8718(2)	0.0028(2)	0.0179(4)
Bi6	4*e*	0.3661(1)	0.0951(2)	0.0143(2)	0.0191(5)
In1	4*e*	0.2518(2)	0.9231(3)	0.8863(3)	0.0181(7)
In2	4*e*	0.0935(2)	0.9338(4)	0.5506(3)	0.0187(7)
In3	4*e*	0.4174(2)	0.5653(4)	0.7164(3)	0.0236(8)
Na1	4*e*	0.0697(9)	0.074(2)	0.808(2)	0.026(4)
Na2	4*e*	0.2378(9)	0.431(2)	0.649(2)	0.023(4)
Na3	4*e*	0.409(1)	0.428(3)	0.979(2)	0.038(5)
Na4	4*e*	0.286(1)	0.682(2)	0.111(2)	0.033(5)
Na5	4*e*	0.2184(9)	0.327(2)	0.925(2)	0.031(5)
Na6	4*e*	0.950(1)	0.810(2)	0.914(2)	0.036(5)
Na7	4*e*	0.880(1)	0.187(2)	0.734(2)	0.037(6)
Na8	4*e*	0.388(1)	0.154(3)	0.758(2)	0.049(6)
Na9	4*e*	0.448(1)	0.821(2)	0.928(2)	0.031(5)
$K_7In_4Bi_6$ (**III**)					
Bi1	4*a*	0.8040(2)	0.5928(2)	0.8633(1)	0.0287(6)
Bi2	4*a*	0.2676(2)	0.3836(2)	0.9309(1)	0.0293(6)
Bi3	4*a*	0.4137(2)	0.8830(3)	0.9094(1)	0.0314(6)
Bi4	4*a*	0.9391(2)	0.0930(3)	0.8457(1)	0.0285(6)
In1	4*a*	0.1949(5)	0.0884(5)	0.9359(2)	0.036(1)
In2	4*a*	0.0277(6)	0.4025(5)	0.8236(2)	0.037(1)
In3[b]	4*a*	0.513(2)	0.199(2)	0.9451(8)	0.046(4)
In4[b]	4*a*	0.701(2)	0.303(2)	0.8343(8)	0.040(3)
K1	4*a*	0.092(2)	0.780(2)	0.7584(8)	0.042(4)
K2	4*a*	0.666(1)	0.903(1)	0.7649(7)	0.030(3)
K3	4*a*	0.297(2)	0.125(2)	0.7408(9)	0.053(4)
K4	4*a*	0.552(1)	0.565(1)	0.0249(8)	0.036(3)
K5[a]	4*a*	0.597(2)	0.230(2)	0.896(1)	0.028(4)
$K_{11}In_6Bi_9$ (**IV**)					
Bi1	2*i*	0.7349(1)	0.7164(1)	0.0020(1)	0.0235(4)
Bi2	2*i*	0.5435(1)	0.7476(1)	0.7871(1)	0.0256(4)
Bi3	2*i*	0.7603(2)	0.9171(1)	0.2703(1)	0.0232(4)
Bi4	2*i*	0.1552(2)	0.7238(1)	0.9983(1)	0.0253(4)
Bi5	2*i*	0.9337(2)	0.7711(1)	0.5747(1)	0.0220(4)
Bi6	2*i*	0.3067(2)	0.5890(1)	0.3462(1)	0.0216(4)
Bi7	2*i*	0.3649(2)	0.7720(1)	0.5805(1)	0.0248(4)
Bi8	2*i*	0.8391(2)	0.5535(1)	0.2805(1)	0.0259(4)
Bi9	2*i*	0.7272(2)	0.0718(1)	0.7620(1)	0.0273(4)
In1	2*i*	0.7360(3)	0.8471(2)	0.7922(3)	0.0262(7)
In2	2*i*	0.8795(3)	0.7534(2)	0.1150(3)	0.0235(7)
In3	2*i*	0.2924(3)	0.8555(2)	0.7924(3)	0.0245(7)
In4	2*i*	0.0695(3)	0.5493(2)	0.5384(3)	0.0286(7)
In5	2*i*	0.2123(3)	0.7804(2)	0.4541(3)	0.0289(7)
In6	2*i*	0.383(2)	0.548(1)	0.537(1)	0.12(2)
K1	2*i*	0.624(1)	0.4527(8)	0.1906(9)	0.039(3)
K2	2*i*	0.796(1)	0.5430(8)	0.8069(9)	0.037(2)
K3	1*c*	0	$\frac{1}{2}$	0	0.028(3)
K4	2*i*	0.0427(9)	0.7416(8)	0.2860(9)	0.035(2)
K5	2*i*	0.0606(9)	0.7142(7)	0.7788(8)	0.028(2)
K6	2*i*	0.5500(9)	0.7464(8)	0.2895(8)	0.032(2)
K7	2*i*	0.4102(9)	0.7179(8)	0.0702(8)	0.032(2)
K8	2*i*	0.700(1)	0.6926(8)	0.5149(9)	0.035(2)
K9	2*i*	0.608(1)	0.9910(8)	0.073(1)	0.049(3)
K10	2*i*	0.064(1)	0.9878(8)	0.616(1)	0.056(4)
K11	2*i*	0.595(1)	0.9784(8)	0.589(1)	0.042(3)
K12	1*a*	0	0	0	0.17(1)

[a] Occupancy of $\frac{2}{3}$. [b] Occupancy of $\frac{1}{3}$.

fractional occupancy. Moreover, the thermal parameters of the three atoms were much larger than the rest, and therefore they were freed to vary. As a result of this, In3 and In4 refined very close to $\frac{1}{3}$ (within 8σ) and K5 refined close to $\frac{2}{3}$ (within 2σ) occupancies. The fact that only the distances between K5 and the two In positions are too short, while the In3–In4 distance is "normal" (Table 4), means that when K5 is occupied both In3 and In4 are missing, and vice versa. Furthermore, the resulting composition of $K_{4.71(3)}In_{2.52(2)}Bi_4$, simplified as $K_{4.67}In_{2.67}Bi_4$ or rather as $K_7In_4Bi_6$, corresponds to an electronically balanced compound in agreement with the observed diamagnetism and results from EHMO calculations. The final refinement for **III** was carried out with fixed occupancies for the three atoms. The unit cell parameters determined for a single crystal of **V**, $a = 9.915(2)$ and $c = 17.870(4)$ Å, indicated that the compound is isostructural with **III**, and data were not collected.

$K_{11}In_6Bi_9$. The crystals of this compound were very small and anisotropic which made it very difficult to work with them. Many crystals were tried before a relatively good one ($0.10 \times 0.08 \times 0.06$ mm) could be found. A hemisphere of data was collected after finding a triclinic cell. The structure was solved and refined in the centrosymmetric space group $P\bar{1}$ with $R_1 = 7.35$, $wR_2 = 14.75\%$ for 3010 reflections ($I > 2\sigma_I$) and 239 parameters. There are 9 bismuth, 6 indium, and 12 potassium positions (Table 2). Two atoms, In6 and K12, have unusually large anisotropic displacement parameters (Table 3). This suggested partial occupancy but when freed to vary and/or refined as split positions the overall refinement did not improve. The fact that K12 is at an inversion center suggested that the noncentrosymmetric space group $P1$ might be a better choice. However, the problem persisted even when refined in that space group. Thus, the final refinement was in $P\bar{1}$ with all positions fully occupied. This accounts for the formula $K_{11}In_6Bi_9$ which corresponds to an electronically balanced compound in

TABLE 3
Anisotropic Displacement Parameters for $Na_3In_2Bi_3$ (I), Na_3InBi_2 (II), $K_7In_4Bi_6$ (III), and $K_{11}In_6Bi_9$ (IV)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Na_3In_2Bi_3$ (**I**)						
Bi	0.0313(7)	0.0418(7)	0.0366(7)	0.000	-0.0039(5)	0.000
In	0.052(2)	0.039(2)	0.027(1)	0.000	0.0015(1)	0.000
Na	0.042(7)	0.049(7)	0.048(7)	0.000	0.011(6)	0.000
Na_3InBi_2 (**II**)						
Bi1	0.0174(9)	0.0169(9)	0.017(1)	-0.0004(7)	0.0033(7)	0.0016(7)
Bi2	0.0207(9)	0.0179(8)	0.019(1)	0.0023(8)	0.0022(7)	-0.0028(7)
Bi3	0.0190(9)	0.0213(9)	0.0174(9)	0.0026(7)	0.0034(7)	-0.0008(7)
Bi4	0.0187(9)	0.0213(9)	0.021(1)	-0.0008(8)	0.0018(7)	0.0024(8)
Bi5	0.0186(9)	0.0178(9)	0.0174(9)	0.0005(7)	0.0029(6)	-0.0006(7)
Bi6	0.0190(9)	0.0179(9)	0.021(1)	0.0016(7)	0.0041(7)	-0.0020(7)
In1	0.019(2)	0.019(1)	0.016(2)	-0.0001(1)	0.0003(1)	-0.0009(1)
In2	0.020(2)	0.019(2)	0.017 (2)	0.0012(1)	0.0024(1)	0.0014(1)
In3	0.023(2)	0.025(2)	0.023(2)	-0.0001(1)	0.0039(1)	0.0008(2)
Na1	0.019(9)	0.028(9)	0.029(9)	0.006(9)	-0.007(8)	0.009(8)
Na2	0.024(9)	0.009(8)	0.036(9)	0.013(8)	-0.001(8)	0.004(7)
Na3	0.03(1)	0.05(1)	0.03(1)	-0.027(9)	0.003(9)	0.016(8)
Na4	0.04(1)	0.04(1)	0.03(1)	0.008(9)	0.017(9)	-0.008(9)
Na5	0.02(1)	0.03(1)	0.05(1)	0.004(8)	0.012(9)	0.003(8)
Na6	0.04(1)	0.04(1)	0.03(1)	-0.002(9)	-0.003(9)	0.009(9)
Na7	0.02(1)	0.05(1)	0.04(1)	-0.015(9)	-0.012(9)	0.002(9)
Na8	0.06(2)	0.05(1)	0.04(1)	-0.01(1)	0.01(1)	-0.01(1)
Na9	0.02(1)	0.03(1)	0.04(1)	0.005(9)	0.002(9)	-0.001(8)
$K_7In_4Bi_6$ (**III**)						
Bi1	0.028(1)	0.035(1)	0.023(1)	0.008(1)	-0.001(1)	0.004(1)
Bi2	0.028(1)	0.028(1)	0.031(1)	0.003(1)	-0.008(1)	-0.002(1)
Bi3	0.031(1)	0.039(1)	0.024(1)	0.009(1)	0.004(1)	0.001(1)
Bi4	0.027(1)	0.032(1)	0.027(1)	-0.005(1)	-0.001(1)	-0.004(1)
In1	0.043(3)	0.034(3)	0.031(2)	0.004(2)	-0.012(2)	0.001(2)
In2	0.045(3)	0.034(3)	0.031(2)	-0.009(2)	-0.004(2)	0.002(2)
In3	0.051(9)	0.059(9)	0.029(7)	0.006(7)	0.001(7)	-0.018(8)
In4	0.048(9)	0.039(8)	0.033(7)	0.001(7)	-0.009(7)	0.005(7)
K1	0.048(9)	0.035(8)	0.043(8)	0.006(7)	0.011(7)	0.002(8)
K2	0.045(8)	0.031(7)	0.015(6)	-0.007(5)	0.001(6)	-0.004(7)
K3	0.046(9)	0.076(9)	0.039(8)	0.013(8)	0.013(7)	0.014(9)
K4	0.030(8)	0.037(8)	0.041(8)	0.001(7)	0.012(7)	0.000(7)
K5	0.030(9)	0.038(9)	0.016(8)	0.003(7)	-0.004(9)	0.016(8)
$K_{11}In_6Bi_9$ (**IV**)						
Bi1	0.0243(9)	0.0293(9)	0.0193(9)	-0.0037(6)	-0.0103(7)	-0.0056(7)
Bi2	0.0227(8)	0.0237(8)	0.033(1)	-0.0025(7)	-0.0144(7)	-0.0042(6)
Bi3	0.0247(9)	0.0207(8)	0.0257(9)	-0.0051(6)	-0.0126(7)	-0.0003(6)
Bi4	0.0200(8)	0.0342(9)	0.0207(9)	-0.0049(7)	-0.0082(7)	-0.0019(7)
Bi5	0.0231(9)	0.0254(8)	0.0198(9)	-0.0049(6)	-0.0098(7)	-0.0045(6)
Bi6	0.0227(8)	0.0229(8)	0.0199(9)	-0.0037(6)	-0.0087(7)	-0.0043(6)
Bi7	0.0259(9)	0.0266(9)	0.0197(9)	-0.0054(7)	-0.0073(7)	-0.0020(7)
Bi8	0.035(1)	0.0243(8)	0.0202(9)	-0.0021(6)	-0.0113(7)	-0.0085(7)
Bi9	0.034(1)	0.0213(8)	0.0286(9)	-0.0035(7)	-0.0138(8)	-0.0048(7)
In1	0.031(2)	0.021(2)	0.034(2)	-0.004(1)	-0.021(1)	-0.004(1)
In2	0.021(2)	0.024(1)	0.028(2)	-0.006(1)	-0.011(1)	-0.003(1)
In3	0.022(2)	0.022(1)	0.030(2)	-0.008(1)	-0.009(1)	-0.004(1)
In4	0.037(2)	0.024(2)	0.021(2)	-0.003(1)	-0.007(1)	-0.008(1)
In5	0.029(2)	0.034(2)	0.027(2)	-0.011(1)	-0.008(1)	-0.009(1)
In6	0.61(4)	0.25(2)	0.21(2)	0.06(1)	-0.18(3)	-0.28(2)
K1	0.035(6)	0.043(6)	0.041(7)	-0.011(5)	-0.014(5)	-0.008(5)
K2	0.038(6)	0.038(6)	0.043(7)	-0.008(5)	-0.023(5)	-0.004(5)
K3	0.028(7)	0.031(7)	0.019(7)	-0.007(5)	-0.008(6)	0.008(6)
K4	0.023(5)	0.041(6)	0.041(6)	-0.010(5)	-0.016(5)	0.003(4)

TABLE 3—*Continued*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K5	0.028(5)	0.037(5)	0.026(5)	− 0.001(4)	− 0.018(4)	− 0.007(4)
K6	0.028(5)	0.045(6)	0.027(6)	− 0.003(4)	− 0.012(4)	− 0.013(4)
K7	0.026(5)	0.038(6)	0.028(6)	0.004(4)	− 0.006(4)	− 0.014(4)
K8	0.036(6)	0.042(6)	0.027(6)	− 0.018(4)	− 0.007(5)	− 0.003(5)
K9	0.077(9)	0.035(6)	0.054(8)	− 0.005(5)	− 0.045(8)	− 0.011(6)
K10	0.055(8)	0.028(6)	0.109(9)	− 0.020(6)	− 0.049(9)	− 0.005(5)
K11	0.053(7)	0.037(6)	0.041(7)	0.000(5)	− 0.025(6)	− 0.008(5)
K12	0.47(9)	0.03(2)	0.6(1)	0.01(4)	0.5(1)	0.02(4)

agreement with the observed diamagnetism and results form band calculations.

PROPERTY MEASUREMENTS

Magnetizations were measured on a Quantum Design MPMS-SQUID magnetometer at a field of 3 T in the temperature range of 10–300 K. The samples were contained in a special holder designed for air-sensitive compounds described elsewhere (18). The raw data were corrected for the paramagnetic contribution of the fused-silica container. However, the molar susceptibilities could not be calculated because the samples were not pure phases. Nevertheless, the magnetizations are negative and temperature independent, within the ranges of $(-5.17$ to $-5.21) \times 10^{-4}$ emu for 17 mg of a mixture of **I** and **II** and $(-1.83$ to $-1.79) \times 10^{-4}$ emu for 20 mg of a mixture of **III** and **IV**. These data, negative even after eventual corrections for the ion-core diamagnetism of A^{+}, In^{3+}, and Bi^{5+}, indicate diamagnetic compounds. Furthermore, the magnetization of a 21 mg sample of **V** containing only traces of the Laves phase $RbBi_2$ is negative (and temperature independent) after all corrections, and the molar susceptibility falls within the range of $(-9.77$ to $-9.79) \times 10^{-4}$ emu/mol.

BAND CALCULATIONS

Extended Hückel band calculations for **I**, **II**, **III**, and **IV** were carried out within the tight binding approximation (21). Density of states and crystal orbital overlap populations were calculated on the basis of 144 k-points for **I**, 156 k-points for **II**, 64 k-points for **III**, and 272 k-points for **IV**, respectively. Only the In and Bi atoms from the anionic sublattice were taken into account. The default atomic orbital parameters H_{ii} and ζ_1 were employed. For Bi: 6*s* -15.19 eV and 2.56, 6*p* -7.79 eV and 2.07. For In: 5*s* -12.60 eV and 1.90, 5*p* -6.19 eV and 1.68. The cations were not included in the calculations, although addition of alkali-metal states would certainly bias the results. Nevertheless, these approximate results help in the understanding of the bonding in these intermetallic Zintl phases.

RESULTS

$Na_3In_2Bi_3$

The simplest among all four structures is the structure of this compound (Fig. 1). It crystallizes with relatively high symmetry, orthorhombic, and fairly small unit cell (Table 1). There are only three crystallographically unique atoms, one of each kind (Table 2). The indium atoms center bismuth tetrahedra that share edges and corners, and form a three-dimensional network with channels (Fig. 1). The channels, made of eight-member rings of alternating indium and bismuth atoms (Fig. 1a), make it very reminiscent of the zeolite structures or of the body-centered orthorhombic $BaIn_2$ with the $CeCu_2$ (or KHg_2) structure type (22). They run along the *b*-axis and are occupied by the sodium cations. The structure can be viewed also as made of chains of edge-sharing tetrahedra running along *b*. The chains are then connected to each other by sharing the remaining vertices (Figs. 1b and 2). Shared in each tetrahedron are two edges in the *cis* position within the chain (Fig. 1b) and a vertex with a neighboring chain. Similar chains are observed in the recently reported $Cs_7In_4Bi_6$ (18).

The $InBi_4$ tetrahedra are mildly distorted with angles between 102.17(7) and 115.35(7)° and distances within the range 3.006(4)–3.108(3) Å (Table 4). The sodium atoms are well positioned in the channels with Na–In and Na–Bi distances in the ranges 3.590(9)–3.90(1) and 3.33(1)–3.538(9) Å, respectively. A fully occupied indium position would make equimolar the indium-to-bismuth ratio. This would mean that the framework is neutral since the 1:1 composition, i.e., a so-called III-V compound, is electronically balanced and isoelectronic to silicon. If this was the case, the available sodium cations would be extra and would make the compound metallic, in disagreement with the measured diamagnetism. However, removal of an indium atom causes a shortage of three electrons, which can be balanced by three sodium countercations. This will lead to a general formula of $Na_{3x}In_{1-x}Bi$ which, for $x = \frac{1}{3}$, transforms into $Na_3In_2Bi_3$. This is exactly the refined formula of the compound for occupancy of $\frac{2}{3}$ of the indium site. EHMO calculations carried out on a superstructure cell in order to model the partially occupied indium site indicated that the

TABLE 4

Important Distances (Å) in $Na_3In_2Bi_3$ (I), Na_3InBi_2, (II), $K_7In_4Bi_6$ (III), and $K_{11}In_6Bi_9$ (IV)

	$Na_3In_2Bi_3$ (**I**)	
Bi–	In	3.006(4)
	2 × In	3.080(2)
	In	3.108(3)
In–	Bi	3.006(4)
	2 × Bi	3.080(2)
	Bi	3.108(3)
Na–	Bi	3.33(1)
	2 × Bi	3.419(9)
	2 × Bi	3.539(9)
	2 × In	3.590(9)
	In	3.72(1)
	2 × In	3.82(1)
	In	3.90(1)
	2 × Na	4.13(2)
	2 × Na	4.237(8)
	Na_3InBi_2 (**II**)	
In1–	Bi1	2.970(4)
	Bi2	2.998(4)
	Bi5	3.039(4)
	Bi6	2.956(4)
In2–	Bi2	2.980(4)
	Bi3	2.956(4)
	Bi3	3.001(4)
	Bi5	2.962(4)
In3–	Bi1	3.056(4)
	Bi4	2.995(4)
	Bi4	3.047(4)
	Bi6	2.988(4)
Bi1–	In1	2.970(4)
	In3	3.056(4)
Bi2–	In1	2.998(4)
	In2	2.980(4)
Bi3–	In2	2.956(4)
	In2	3.001(4)
Bi4–	In3	2.995(4)
	In3	3.047(4)
Bi5–	In1	3.039(4)
	In2	2.962(4)
Bi6–	In1	2.956(4)
	In3	2.988(4)
	$K_7In_4Bi_6$ (**III**)	
In1–	Bi2	2.951(5)
	Bi3	2.948(5)
	Bi4	2.943(5)
	Bi4	2.982(5)
In2–	Bi1	2.934(5)
	Bi2	2.999(5)
	Bi3	3.006(5)
	Bi4	3.148(5)
In3–	In4	2.85(2)
	Bi1	3.05(1)
	Bi2	2.99(2)
	Bi3	3.27(2)
In4–	In3	2.85(2)
	Bi1	3.03(1)
	Bi2	2.83(1)
	Bi4	3.09(2)

TABLE 4—*Continued*

Bi1–	In2	2.934(5)
	In3	3.05(1)
	In4	3.03(1)
Bi2–	In1	2.951(5)
	In2	2.999(5)
	In3	2.99(2)
	In4	2.83(1)
Bi3–	In1	2.948(5)
	In2	3.006(5)
	In3	3.27(2)
Bi4–	In1	2.943(5)
	In1	2.982(5)
	In2	3.148(5)
	In4	3.09(2)
	$K_{11}In_6Bi_9$ (**IV**)	
In1–	Bi1	2.996(4)
	Bi2	2.971(4)
	Bi5	3.093(4)
	Bi9	2.921(3)
In2–	Bi1	2.962(3)
	Bi3	3.051(3)
	Bi4	2.950(4)
	Bi8	3.069(4)
In3–	Bi2	2.982(4)
	Bi3	2.952(3)
	Bi4	2.978(4)
	Bi7	3.038(4)
In4–	In4	2.982(6)
	Bi5	2.991(4)
	Bi6	2.982(4)
	Bi8	3.052(4)
In5–	Bi5	3.038(4)
	Bi6	2.978(4)
	Bi7	2.991(4)
	Bi9	3.057(4)
In6–	In6	2.63(5)
	Bi6	3.02(1)
	Bi7	3.13(1)
	Bi8	3.10(2)
Bi1–	In1	2.996(4)
	In2	2.962(3)
Bi2–	In1	2.971(4)
	In3	2.982(4)
Bi3–	In2	3.051(3)
	In3	2.952(3)
Bi4–	In2	2.950(4)
	In3	2.978(4)
Bi5–	In1	3.093(4)
	In4	3.049(3)
	In5	3.038(4)
Bi6–	In4	2.982(4)
	In5	2.978(4)
	In6	3.02(1)
Bi7–	In3	3.038(4)
	In5	2.991(4)
	In6	3.13(1)
Bi8–	In2	3.069(4)
	In4	3.052(4)
	In6	3.10(2)
Bi9–	In1	2.921(3)
	In5	3.057(4)

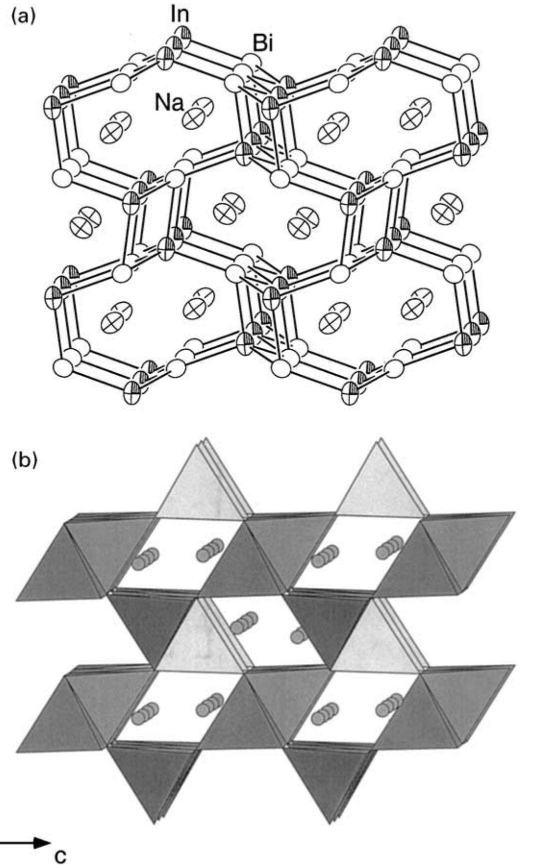

FIG. 1. ORTEP (a) and polyhedral (b) views of the orthorhombic structure of $Na_3In_2Bi_3$ along the *b* axis. (a) In, Bi, and Na are shown as full, open, and crossed ellipsoids, respectively (80% probability level). (b) The tetrahedra are Bi_4 centered by In. Chains of edge-sharing tetrahedra run along the *b* axis.

compound is an insulator with an approximate band gap of about 4 eV. The formula $Na_3In_2Bi_3$ indicates also that there are no four-bonded bismuth atoms in the structure (as it may look from Fig. 1). A four-bonded bismuth atom generates a formal charge of 1 + , which, together with the formal charge of 1- for a four-bonded indium atom, would make impossible the stoichiometry $Na_3In_2Bi_3$. Three- and two-bonded bismuth atoms, on the other hand, generate 0 and 1- formal charges, respectively, and therefore the formula can be rationalized as Na_3(4-bonded In^-)$_2$(3-bonded Bi^0)$_2$(2-bonded Bi^-).

Na_3InBi_2

The structure of Na_3InBi_2 is fairly complicated (Fig. 3). It is again built of indium-centered tetrahedra of bismuth. The structure can be rationalized as assembled of hexamers of such tetrahedra (outlined in Fig. 3). The middle two tetrahedra of the hexamer share an edge (an inversion center) while the rest share corners. The hexamers are then interconnected as building bricks by sharing with each other all remaining corners.

The $InBi_4$ tetrahedra are somewhat more distorted compared to **I** with angles in the range 100.4(1)–117.6(1)° and distances from 2.956(4) to 3.056(4) Å (Na–Bi distances are in the range 3.08(2)–3.53(2) Å). All bismuth atoms are 2-bonded in this structure, and this translates into a formal charge of 1- per bismuth atom. All indium atoms are 4-bonded which means also a formal charge of 1- per indium atom. Therefore, $[InBi_2]$ carries a charge of 3-, which is balanced by the three sodium cations in the formula Na_3InBi_2. The rationalization of the stoichiometry can be approached also as for compound **I**. Starting from neutral InBi (same as In_2Bi_2) removal of one indium atom generates a charge of 3-, and this is compensated by the three sodium cations. Therefore, the compound is electronically balanced, salt-like, and this is confirmed by the observed temperature-independent negative magnetization. It is in agreement with the results from EHMO calculations, which give an approximate band of more than 5 eV.

$K_7In_6Bi_4$

This is the first A–Tr–Pn compound that crystallizes in this very rare chiral tetragonal space group $P4_3$ (Fig. 4). Actually, tetragonal symmetry itself is very uncommon for these ternary systems for which the vast majority of structures are of lower symmetry. The formula of the compound, $K_7In_4Bi_6$ (more appropriately $K_{4.67}In_{2.67}Bi_4$), reflects the nearly 1/3 occupancy of the In3 (occupied 26(2)%) and In4 (occupied 26(1)%) sites and nearly $\frac{2}{3}$ occupancy of the K5 site (occupied 71(3)%). Although this formula is the same as

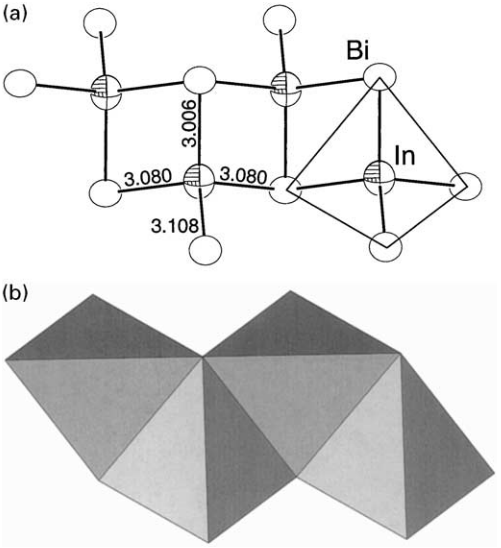

FIG. 2. ORTEP (a) and polyhedral (b) views of the chains of edge-sharing tetrahedra of $InBi_4$ in $Na_3In_2Bi_3$ (thermal ellipsoids at 80% probability, *b* is horizontal). Each tetrahedron shares two *cis* edges.

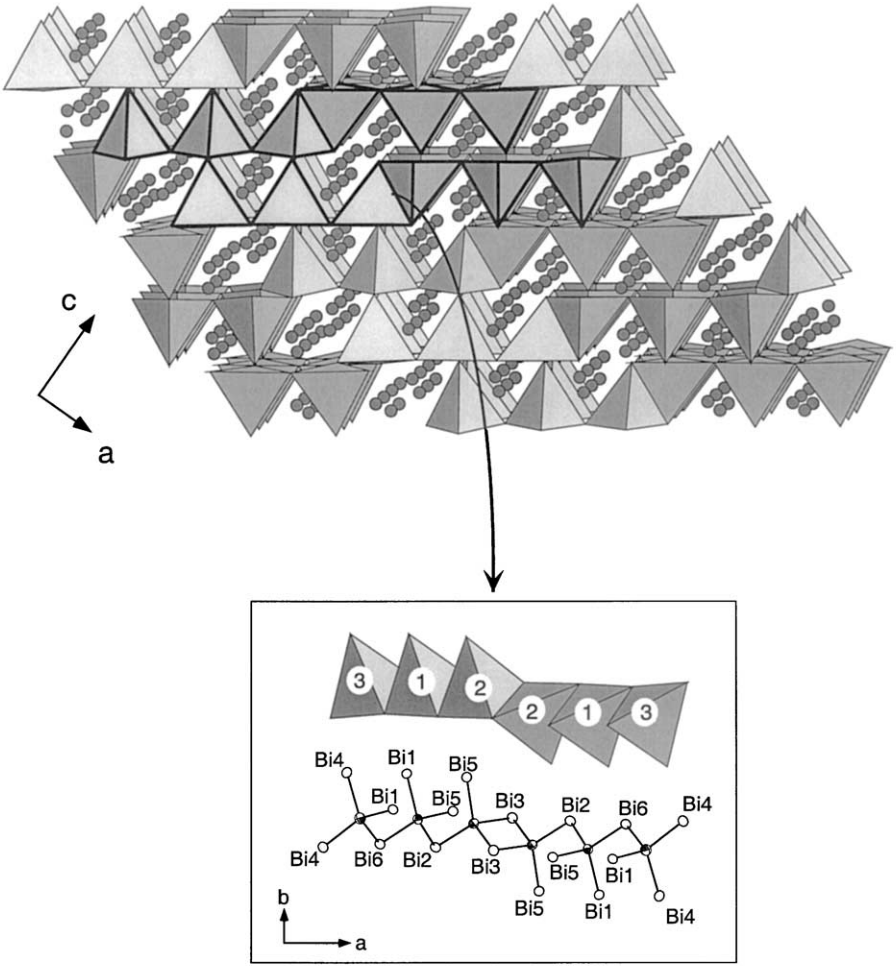

FIG. 3. Polyhedral view of the monoclinic structure of Na_3InBi_2 down the *b* axis. It is built of hexamers (outlined) of $InBi_4$ tetrahedra. The middle two tetrahedra of the hexamer share an edge (an inversion center) while the others share corners. The hexamers are interconnected by sharing all remaining corners. The detailed section (boxed) shows the numbering of the indium atoms in the polyhedral view, and of the bismuth atoms in the ORTEP view (thermal ellipsoids at the 90% level).

the previously reported triclinic $Cs_7In_4Bi_6$, the two compounds are not isostructural (18). However, there are many common features in the two structures. Thus, both structures contain chains of edge-sharing $InBi_4$ tetrahedra. However, the sequences of shared *trans* and *cis* edges are different for the two structures. The repeating unit of the chains in **III** is shown in Fig. 5a and the sequence here is simply alternating *cis* and *trans* modes, i.e., CTCTCTCT. This particular sequence makes the chains helical, spiral-like (Fig. 4b), as might be expected for a $P4_3$ space group. The *trans* mode provides the translation along the chain axis while the *cis* mode provides the turns, and when combined they form a helix. The chains in $Cs_7In_4Bi_6$, on the other hand, are not helical, and the repeating sequence there is different, TCTTCTCCTTCC (18).

Two of the four unique indium atoms, In1 and In2, are tetrahedrally coordinated by four bismuth atoms and center the tetrahedra that make the chains (Fig. 5a). The other two sites, the $\frac{1}{3}$ occupied In3 and In4, are outer indium atoms, In_o, since they are positioned outside the chains and are coordinated tetrahedrally by three bismuth atoms and one other outer indium atom from a neighboring chain (Fig. 5b). Hence, the chains become linked by these external In_o–In_o bonds with a distance of 2.85(2) Å (Table 4), and form a three-dimensional structure in a very similar manner as in $Cs_7In_4Bi_6$ (18). These external In_o atoms "pinch" the corresponding pairs of tetrahedra which fold more around the hinge, the shared edge, and get much closer to each other, as is clearly visible from the polyhedral drawings (Fig. 5b). This is expressed in the dihedral angle between the faces of such neighboring tetrahedra which is much smaller than the ideal 109.5°. This also causes greater distortion in the tetrahedra themselves expressed in the much wider ranges of angles, 94.37(1)–122.2(2)°, and distances, 2.934(5)–3.148(5) Å.

The electron count in $K_7In_4Bi_6$ can be rationalized in the same way as for compounds **I** and **II**. Since the equimolar

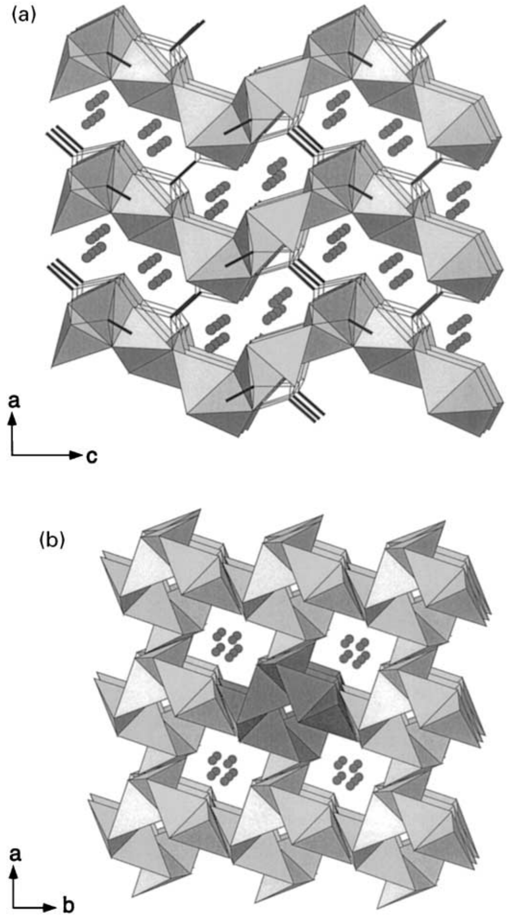

FIG. 4. Polyhedral views of the tetragonal structure of $K_7In_4Bi_6$ along the *b* axis (a) and the *c* axis (b). The structure is made of chains of edge-sharing tetrahedra of $InBi_4$. The chains are interconnected by outer In_o–In_o bonds shown with thicker black lines in (a). These bonds are omitted in (b) for clarity. The helical nature of the chains is clearly visible in (b).

InBi is a neutral compound, it does not need countercations. Removal of an indium atom creates a formal charge of 3-, and therefore, removal of six indium atoms from $In_{12}Bi_{12}$ gives $[In_6Bi_{12}]^{18-}$. Next, the addition of a pair of indium atoms that are bonded to each other, i.e., In_o–In_o, reduces the negative charges by four, since two of the additional six electrons are used for the In_o–In_o bond. This brings the formula to $[In_8Bi_{12}]^{14-}$ and defines the overall stoichiometry of the compound as $K_{14}In_8Bi_{12}$ (same as $K_7In_4Bi_6$). The final result is an electronically balanced, diamagnetic compound which is in agreement with the temperature-independent and negative magnetization data. The EHMO calculations indicated an approximate band gap of about 5 eV.

$K_{11}In_6Bi_9$

The structure of $K_{11}In_6Bi_9$ is undoubtedly the most complicated, a result of the low triclinic symmetry and the complicated connectivity between the $InBi_4$ tetrahedra. There are 6 indium, 9 bismuth, and 12 potassium positions in the asymmetric unit. Four of the six indium atoms are tetrahedrally coordinated by four bismuth atoms, while the other two, In4 and In6 (outer indium, In_o), are also tetrahedrally coordinated but by three bismuth atoms and one other outer indium atom. The structure can be viewed as made of bilayers of corner-sharing tetrahedra that are parallel to the *ac* plane (Fig. 6). Neighboring layers are related to each other by inversion. They are linked to each other via two sets of external In_o–In_o bonds that are nearly perpendicular to each other and with distances of 2.982(6) and 2.63(5) Å for In4–In4 and In6–In6, respectively (Figs. 6, 7). The latter is unusually short for an In–In distance mainly due to the very diffuse thermal ellipsoids and, correspondingly, the "uncertain location" of the two In atoms. Both In4 and In6 are bonded to two bismuth atoms from one layer and a third one from the neighboring layer (Fig. 7). The very poorly diffracting crystals of $K_{11}In_6Bi_9$, the very low symmetry (triclinic) and relatively large cell at the same time, and the exceptionally strong and anisotropic absorption due to the

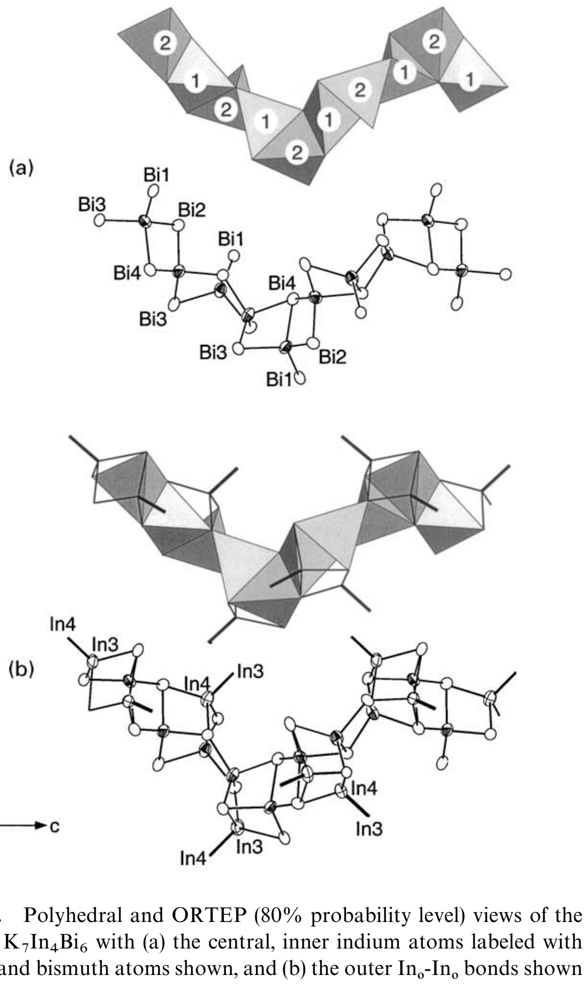

FIG. 5. Polyhedral and ORTEP (80% probability level) views of the chains in $K_7In_4Bi_6$ with (a) the central, inner indium atoms labeled with numbers and bismuth atoms shown, and (b) the outer In_o-In_o bonds shown (thicker black lines) and the outer indium atoms labeled.

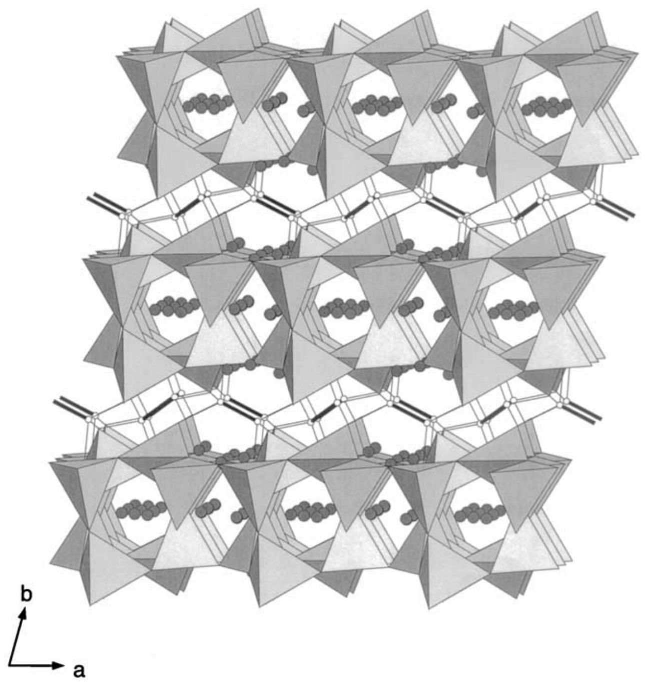

FIG. 6. Polyhedral view of the triclinic structure of $K_{11}In_6Bi_9$ along the *c* axis. The structure is made of double layers of corner-sharing $InBi_4$ tetrahedra. The bilayers are connected to each other by outer In_o–In_o bonds shown as thicker black lines. Each outer indium is also bonded to two bismuth atoms from one layer and another one from the neighboring layer.

very heavy elements are the most likely reasons for the poor quality of the structure determination. This is expressed in relatively large uncertainties in the structure refinement as well as large peaks in the final difference Fourier map.

There are no edge-sharing tetrahedra in the structure of $K_{11}In_6Bi_9$, and all bismuth atoms are 2- or 3-bonded to indium (Table 4). Similar to compound **III** the presence of outer indium atoms causes substantial distortions in the tetrahedra. Thus, the corresponding distances and angles are quite dispersed within the ranges 2.921(3)–3.13(1) Å and 87.3(1)–129.1(1)°, respectively (K–Bi distances from 3.59(1) to 3.96(1) Å).

Following the methodology for electron counting, already discussed above, we get $[In_8Bi_{18}]^{30-}$ when 10 indium atoms are removed from the neutral $In_{18}Bi_{18}$. Adding two pairs of indium atoms that are bonded to each other, In4–In4 and In6–In6, provides four electrons per pair. This brings the stoichiometry and the formal charge to $[In_{12}Bi_{18}]^{22-}$ where the 22 extra electrons are provided by 22 potassium cations in the formula $K_{22}In_{12}Bi_{18}$ (same as $K_{11}In_6Bi_9$), and the compound is electronically balanced. Again, this is in agreement with the measured temperature-independent diamagnetism and the results from extended Hückel calculations of the anionic part of the structure estimate the band gap to be more than 5 eV.

DISCUSSION

We can compare the structures of the four compounds reported here with the structure of other known compounds in the general systems of alkali metal and elements of groups 13 (*Tr*) and 15 (*Pn*). These systems are apparently quite rich on such ternary compounds, many of them with similar or equivalent atomic ratios but with quite different structures because of different elements. Good examples are the structures of $Cs_7In_4Bi_6$ (18), and the isostructural $K_7In_4Bi_6$ and $Rb_7In_4Bi_6$. Apparently, the different sizes of the alkali metals cause different packing in the structures which translates into differences in the chains of $InBi_4$ tetrahedra. Although quite similar, the sequences of *cis* and *trans* sharing in the chains are not exactly the same, and as a result of this, the connections between them are also different. It should also be pointed out that these three compounds are the only pnictide-rich compounds for all combinations of *A*, *Tr*, and *Pn* with *Tr*–*Tr* bonds but without *Pn*–*Pn* bonding.

Ternary compounds with the same overall stoichiometry of A_3TrPn_2 as in compound **II** are also known but their structures differ markedly. Thus, the structure of $[K_2Na]$ $TrPn_2$ where Tr = Ga, In and Pn = P, As consists of isolated chains of edge-shared tetrahedra (isosteric with SiS_2)

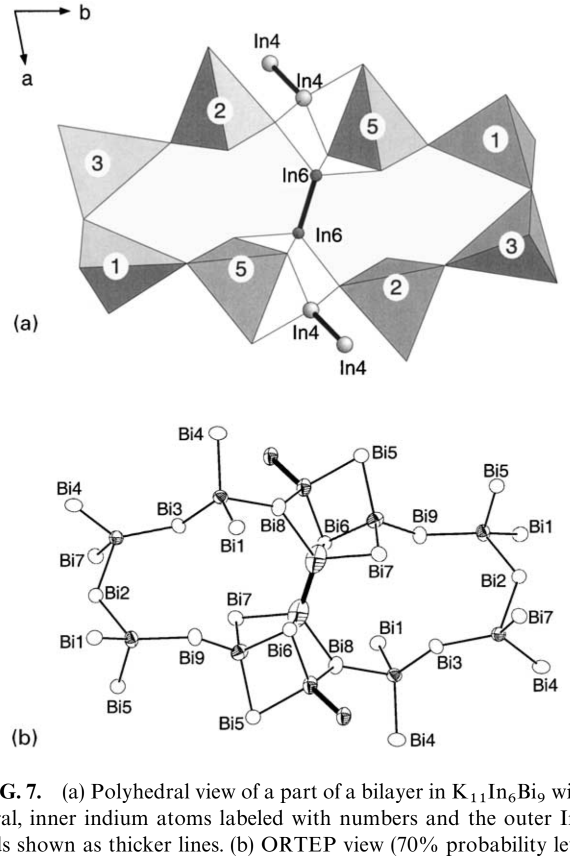

FIG. 7. (a) Polyhedral view of a part of a bilayer in $K_{11}In_6Bi_9$ with the central, inner indium atoms labeled with numbers and the outer In_o–In_o bonds shown as thicker lines. (b) ORTEP view (70% probability level) of the same part of the bilayer as in (a) with all bismuth atoms shown and labeled.

TABLE 5
Lattice Parameters (from Single-Crystal Diffraction Work) for Other Zintl Compounds in the *A*–Ga–Bi, and *AE*–In–Bi Systems (*A* = K, Rb; *AE* = Ca, Sr, Ba)

Compound	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	Structure type	Ref.
$K_{20}Ga_6Bi_{12.66}$	$P6_3/m$	18.1447(7)		5.495(1)	1566.9(3)	$K_{20}Ga_6As_{12.66}$	(32)
$Rb_{20}Ga_6Bi_{12.66}$	$P6_3/m$	18.6257(7)		5.723(1)	1719.5(3)	$K_{20}Ga_6As_{12.66}$	(32)
$Ca_{11}In_xBi_{10-x}$	$I4/mmm$	12.214(2)		17.485(4)	2608.2(7)	$Ca_{11}Bi_{10}$	(33)
$Sr_{11}InBi_9$	$Iba2$	12.598(1)	13.342(1)	17.838(1)	2998.4(4)	$Ca_{11}InBi_9$	(34)
$Ba_{14}InBi_{11}$	$I4_1/acd$	18.620(1)		24.616(2)	8534.5(6)	$Ca_{14}AlSb_{11}$	(35)

(23), and the structure of $[K_2Na]InSb_2$ is made of two-dimensional layers made of corner- and edge-shared tetrahedra (24). None of these even resembles the structure of Na_3InBi_2. Perhaps the most closely related to **I** and **II** is Na_3InSb_2, which is built of corner-sharing tetrahedra (25). They form eight-membered rings like in both **I** and **II** and also, the predominant connectivity in compound **II** is via corner-sharing and only a small fraction is by edge-sharing. Generally the Na–In–Bi compounds do not exhibit In–In bonding in contrast with the K, Rb, and Cs analogs.

Some of the known *A–Tr–Pn* compounds exhibit *Pn–Pn* bonds although their stoichiometries are quite close to some of the compounds reported here. For example, $K_{10}In_5Sb_9$ is very close in composition to $K_{11}In_6Bi_9$ but its structure is made of chains of edge-shared $InSb_4$ tetrahedra that are then connected by external Sb–Sb bonds (26). $Ba_7Ga_4Sb_9$ has chains of corner-shared $GaSb_4$ tetrahedra that are also linked similarly by Sb–Sb bonds (27). There is also a series of isostructural compounds $A_2Tr_2Pn_3$ for A = Na, K, Rb, and Cs, Tr = Al, Ga, and In, and Pn = As and Sb (28). This composition is quite close to compounds **I** and **II**, $Na_3In_2Bi_3$ and Na_3InBi_2, respectively, but feature completely different building units. The structure contains layers of $[Tr_2Pn_3]^{2-}$ made of corner- and edge-shared $TrPn_4$ tetrahedra (28), and the layers are then connected to each other by short *Pn–Pn* bonds. Similar structures with Bi are not known, most likely because of the larger size of the bismuth and its quite inert *s* pair. All *A*–In–Bi phases seem to exhibit quite different structures from the known *A–Tr–Pn* compounds of the lighter pnictides.

From this brief examination it seems that the inherently complicated structure and stoichiometry of any of these compounds cannot be uniformly explained, and each case should be considered and rationalized by its own. The structural motifs are rich in variation of the way the common tetrahedral units are connected. Evidently, this diversity arises from the fact that different number of bonds, and consequently, different charges are possible, especially for the atoms of the *Pn* element. The structures of the five new compounds are all based on In-centered tetrahedra of bismuth with different connectivity modes and all are electronically balanced, salt-like Zintl phases according to the magnetic measurements and EHMO calculations.

Besides the purely scientific interest of understanding the relationship between structure and bonding in these phases, there are also some practical aspects through their use as precursors for solution chemistry (17). Furthermore, ternary and quaternary phases built of heavy atoms and with complicated structures are worth exploring for thermoelectric applications (29). Unfortunately, the reactivity and the air and moisture sensitivity of the title compounds are evidently obstacles for finding such utilization. Surprising recent reports, however, have indicated that similar compounds of indium and antimony but with alkaline- or rare-earth cations instead of alkali metal are air stable and relatively inert toward nonoxidizing acids and bases (30, 31). We have carried out similar syntheses in the systems (*AE*)–In–Bi for *AE* = Ca, Sr, and Ba as well as *A*–Ga–Bi, but all found compounds are isostructural with known ones (Table 5). The next step is to take a closer look at the rare-earth In–Bi systems or possibly systems with mixed cations.

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