The indium subnitrides $\text{Ae}_6\text{In}_4(\text{In}_x\text{Li}_y)\text{N}_{3-z}$ ($\text{Ae} = \text{Sr}$ and $\text{Ba}$)

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The indium nitrides $\text{Sr}_6\text{In}_4(\text{In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}$ have been synthesized from an excess of molten sodium. They crystalize in a stuffed variant of the $\text{Fe}_3\text{Si}$ structure type in the cubic space group $Fd\overline{3}m$ with $Z = 8$. The lattice parameters are $a = 14.3752(4)$ and $15.216(1)\ \text{Å}$, with cell volumes $2970.6(2)$ and $3523.3(6)\ \text{Å}^3$, respectively. In both compounds there are vacancies on some of the indium and nitrogen sites, and in the case of $\text{Sr}_6\text{In}_4(\text{In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$, mixed lithium–indium occupancy of one metal site. It is demonstrated that the partial and mixed occupancies act to carefully tune to electron count to almost fulfill the bonding requirements of the stellar quadrangular subnets of both compounds. Four probe resistivity measurements performed upon a pellet of $\text{Sr}_6\text{In}_4(\text{In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ show it to have a room-temperature resistivity of 6.3 $\text{mΩ-cm}$ with a weak temperature dependence.

Introduction

The binary nitrides of the p-block ($\text{M}_x\text{N}_y$) include boron nitride, silicon nitride, and gallium nitride. The M–N bonds within all three compounds are strong and contain a high degree of covalent character. Furthermore, in bulk form, all three compounds are relatively inert toward oxide formation when heated in air and are very stable in mildly reducing environments; for example, both hexagonal boron nitride and silicon nitride are commercially useful as crucible materials and diffusion barriers, respectively. The intrinsic characteristics of GaN are well suited for the high-power semiconductor industry; GaN is a direct, large band gap semiconductor ($E_g = 3.4\ \text{eV}$) with a small unit cell, moderately strong gallium–nitrogen bonds, and high carrier mobility.

As the p-block metal, M, becomes heavier, the M–N bond strength decreases considerably; for example, indium nitride ($\text{InN}$, $E_g = 0.7\ \text{eV}$) adopts the same wurtzite structure type as gallium nitride but the standard heat of formation of indium nitride is $-28.6\ \text{kJ/mol}$, considerably less than that of gallium nitride, $-156.8\ \text{kJ/mol}$. This difference in strength between the Ga–N and In–N bond results in an interesting schism in the structures and numbers of the alkaline-earth (Ae) containing compounds, $\text{Ae}_6\text{M}_4\text{N}_5$ ($\text{M} = \text{Ga}$ or In). There are almost twice as many reported $\text{Ae}_6\text{Ga}_4\text{N}_5$ compounds than $\text{Ae}_6\text{In}_4\text{N}_5$ compounds, and in the majority of the ternary gallium nitrides, the formal oxidation state of the gallium is either I or III; i.e., it is formally a positive cation.

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In all the reported $\text{Ae}_x\text{In}_y\text{N}_z$ compounds, such as $\text{Ca}_{19}$-$\text{In}_8\text{N}_7$, $\text{Ba}_{10}\text{In}_8\text{N}_9$, there is insufficient nitrogen to fully oxidize the metals; indeed, the formal oxidation state of the indium is negative and indium–indium bonding is apparent. Gallium–gallium bonding occurs only in $\text{Ca}_2\text{Ga}_2\text{N}_4$ and $\text{CaGaN}$, the two $\text{Ae}_x\text{Ga}_y\text{N}_z$ compounds that contain Ga(I), and in the few compounds that contain anionic gallium, $(\text{Ae}_x\text{N})\text{Ga}_3$ $(\text{Ae} = \text{Sr}, \text{Ba})$ and $\text{Ca}_7\text{Ga}_4\text{N}_9$. However, the most significant difference between the ternary indium and gallium nitrides is that none of the $\text{Ae}_x\text{In}_y\text{N}_z$ compounds exhibit direct indium–nitrogen bonds. Direct indium–nitrogen bonding is also absent in all of the known multinary indium nitrides such as $\text{Sr}_6\text{In}_4\text{N}_6$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_2.72$. As will be seen, in both compounds there are considerable vacancies at both an indium and a nitrogen site. Furthermore, in $\text{Sr}_6\text{In}_4\text{N}_6$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_2.72$, the partially occupied indium site is, in fact, statistically occupied by both indium and lithium. Fully occupied positions would equalize the metal ratio and would result in a structure similar to that of NaBa. The partial (and mixed) occupancies of $\text{Sr}_6\text{In}_4\text{N}_6$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_2.72$ are explained with the use of electronic structure calculations, especially COOP analyses of the indium subset.


Figure 1. Stella quadrangula formed from capping every tetrahedral face of an inner tetrahedron.

transition-metal nitrides such as $\text{Co}_8\text{Mo}_6\text{N}_7$ and $\text{Fe}_2\text{W}_2\text{N}_5$, in which the nitrogen atoms occupy the octahedral 16c sites.

The crystal orbital overlap population (COOP) and the very closely related crystal orbital Hamilton population (COHP) analyses are very useful electronic structure tools. Both analyses yield information about the bonding or antibonding nature of pairwise interactions in solids. They thus allow the local bonding interactions of an extended solid to be isolated and analyzed. Just as in molecules, these interactions can be bonding or antibonding and, as noted by Dronskowski, nature always attempts to maximize the filling of bonding states and to minimize the filling of antibonding states. This can be achieved in various ways, and it often leads to unusual structural features or physical properties. For example, the ferromagnetism of itinerant electrons in iron, cobalt, and nickel can be explained via spin-polarized COHP analysis. In another study, COOP analysis makes apparent the source of the decreasing lattice parameter in the series of compounds $\text{Ti}_x\text{TB}_2$ $(T = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni})$, a decrease larger than that expected from the change of size of the T atom. The COOP analysis revealed that although the Ti–Bi interactions remain strong throughout the series, the T–T bonding increases as the extra electrons funnel into the d–d bonding of these elements. Hence the contraction of the lattice parameter has a physical and an electronic root.

In this paper we introduce the isosctructural compounds $\text{Sr}_6\text{In}_4\text{Li}_{1.32}\text{N}_2.49$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_2.72$. As will be seen, in both compounds there are considerable vacancies at both an indium and a nitrogen site. Furthermore, in $\text{Sr}_6\text{In}_4\text{Li}_{1.32}\text{N}_2.49$, the partially occupied indium site is, in fact, statistically occupied by both indium and lithium. Fully occupied positions would equalize the metal ratio and would result in a structure similar to that of NaBa. The partial (and mixed) occupancies of $\text{Sr}_6\text{In}_4\text{Li}_{1.32}\text{N}_2.49$ and $\text{Ba}_6\text{In}_{1.78}\text{N}_2.72$ are explained with the use of electronic structure calculations, especially COOP analyses of the indium subset.

Experimental Section

Due to the reactivity of both the reagents and products with water vapor and oxygen, all manipulations for both compounds were carried out in an argon-filled glovebox unless otherwise stated.

\[ \text{SrIn}_2\text{In}_{1.92}\text{Li}_{0.92}\text{N}_2\text{N}_{2.49} \]

Two initial reactions were performed. In both cases Na (Aldrich, ACS reagent grade), 200 mg, Sr (filed from rod), 88 mg, In (99.9%), 70 mg, and NaN\(_3\) (99.9%), 70 mg (atomic ratios of Na:Sr:In\(_2\):N\(_2\) = 16.0:1.6:1:0.6) were loaded into a niobium tube (internal volume \(\approx 5.4 \times 10^{-6}\) m\(^3\)). A 3.5 mg amount of Li (99.9%) (atomic ratio In:Li = 1:0.8) was also added to the first tube. The niobium containers were sealed under 0.1 MPa of argon in a Centorr Associates arc furnace and then were themselves sealed under vacuum in fused silica tubes, to protect the niobium from oxidation during heating. These starting materials were heated to 800 °C in 15 h, they remained at that temperature for 24 h, and they were linearly cooled to 200 °C over 200 h, at which point the furnace was shut off and allowed to cool naturally. Upon completion of the reactions, unreacted sodium was removed by sublimation from the products by heating the niobium tubes to 350 °C under a pressure of approximately \(10^{-1}\) Pa for 8 h.

The products of the reactions were analyzed with powder X-ray diffraction (XRD) using a Scintag theta-theta diffractometer with copper K\(\alpha\) radiation. The samples were prepared for analysis in an argon filled glovebox and covered with Mylar film to prevent aerial oxidation. As analyzed by powder X-ray diffraction (XRD), the products of the two tubes were different, q.v. Results and Discussion. The contents of the lithium-containing tube warranted further analysis; therefore, a sample was removed for single-crystal XRD analysis. Single-crystal X-ray data were collected with Mo K\(\alpha\) radiation on a Bruker SMART CCD equipped with a graphite monochromator. The Bruker software package SAINT\(^{33}\) was used to integrate the data, an empirical absorption correction\(^{34}\) was applied, and the files for SHELX\(^{35}\) were prepared by XPREP.\(^{36}\) The indium and strontium atoms were found by direct methods, and the nitrogen sites were subsequently found from the Fourier difference map. It was not possible to locate any lithium atoms. The suite of programs within WinGX\(^{37}\) was also used for further refinement and analysis.

The elemental composition of the crystals was elucidated by electron microprobe analysis using a JEOL 8900 electron microprobe. To prevent decomposition or oxygen contamination of the samples, they were transferred from an argon-filled glovebox to the microprobe in a specially designed portable antechamber that avoids any air exposure during transfilling.\(^{38}\)

Multiple sealed tube reactions between 7\(\text{Na}:1.4\text{Sr}:\text{In}_2:0.4\text{Li}:1.6\text{N}_2\) provided a bulk sample of \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\) for neutron diffraction and transport measurements. The Sr:In ratio in these reactions was fixed to be the same as observed in the microprobe analysis of the single crystals. A small amount of lithium was also included in these reactions because although lithium had not been observed within the single-crystal X-ray solution, it was an essential reagent for the formation of \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\). An example reaction mixture was Na (Aldrich, ACS reagent grade), 266 mg, Sr (filed from rod), 234 mg, In (99.9%), 217 mg, Li (99.9%), 5 mg, and NaN\(_3\) (99.9%), 130 mg, which were loaded into a niobium tube (internal volume \(\approx 8.1 \times 10^{-6}\) m\(^3\)), sealed, and heated in a manner identical with the initial reactions outlined above, except that the slow cooling step was eliminated; i.e., after 24 h at temperature, the furnace was shut off and allowed to cool naturally. Following the reaction, the sodium was removed as described above. The powder XRD pattern from each reaction was identical, and therefore, the products were combined into one bulk sample which was thoroughly mixed. All but three peaks in the powder XRD pattern of this bulk sample could be indexed upon the unit cell of \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\). The intensity of each of the three impurity peaks is \(\approx 5\%\) of the most intense \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\) peak. One peak can be assigned to indium, but both of the other two can be assigned to either SrO or \(\text{SrIn}_2\); the impurity peaks are too broad to be unambiguously assigned.

When using gaseous reagents in sealed environments, it is prudent to perform simple ideal gas law calculations to ascertain the pressures involved in the reactions. A 130 mg amount of NaN\(_3\) provides approximately 3 mmol of N\(_2\), which, at 800 °C and in a volume of \(8.1 \times 10^{-6}\) m\(^3\), corresponds to a dinitrogen pressure of 3.2 MPa; at temperatures less than 900 °C, it is reasonable to assume that very little nitrogen reacts with the niobium tube.\(^{39}\) If all the strontium and indium present in the tubes formed \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\), the remaining dinitrogen in the tube would correspond to a pressure of approximately 2.2 MPa at 800 °C; in general, it is found that the niobium tubes can withstand approximately 3–3.5 MPa at temperatures <1000 °C, without bursting or leaking.

Neutron diffraction was performed upon a 2.05 g sample of \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\) which had been loaded into a vanadium container (length 50 mm, inner diameter 9.2 mm) inside a dry helium-filled glovebox and sealed with an indium gasket. The sample holder was sealed in a vacuum cryostat, and a closed-cycle helium refrigerator was used for temperature control. Neutron powder diffraction data were collected at 173 K (the same temperature as the single-crystal data collection) using the BT-1 32 detector neutron powder diffractometer at the NCNR, NBSR. A Cu(311) monochromator with a 90° takeoff angle, λ = 1.5402- (2) Å, and in-pile collimation of 15 min of arc were used. Data were collected over the range of 9–148° in 2θ with a step size of 0.05° in 2θ. The instrument is described in the NCNR WWW site (http://www.ncnr.nist.gov/). Following data collection, a full profile Rietveld analysis of the data was carried out with the programs GSAS\(^{40}\) and EXPUG\(^{41}\) and the single crystal-derived unit cell and atomic coordinates were used as the starting model, including the placement of N1 on the 32e site with 5% occupancy.

A four-probe resistivity measurement was carried out on a 400 mg pellet of \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\). This pellet was prepared by pressing the powder and heating at 600 °C for 150 h in a niobium tube (internal volume \(\approx 22.1 \times 10^{-6}\) m\(^3\)). A 65 mg amount of sodium azide was also added to provide a dinitrogen atmosphere of approximately 0.5 MPa at the reaction temperature. The sodium was subsequently removed via sublimation by heating to 350 °C under a pressure of ca. \(10^{-1}\) Pa for 8 h. \(\text{SrIn}_2(\text{In}_{3.2}\text{Li}_{0.92})\text{N}_2\text{N}_{2.49}\) is extremely air and moisture sensitive, and because of this, the cylindrical pellet was not cut into a rectangular shape before loading into a home-built, airtight sample holder that provides four contacts


\(^{(34)}\) Sheldrick, G. M. SADABS; Institute for Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1999.

\(^{(35)}\) Sheldrick, G. M. SHELX; Institute for Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1999.


to the sample via four gold pressure pins, as previously described. The resistance of the pellet was measured from 5 to 299 K in 2 K increments. To convert the measured resistance to resistivity, a geometrical factor is required. This was obtained by measuring the room-temperature resistance of an aluminum slug of the same dimensions as the Sr$_4$In$_2$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ pellet and comparing it to 2.74 $\mu\Omega$cm, the literature value at 295 K. The pellet of Sr$_4$In$_2$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ was returned to the glovebox after the resistivity measurements, ground up, and analyzed with powder XRD in a manner identical with that described above.

Ba$_4$In$_{78}N_{72}$, Ba (99.99%), In (99.999%), and Na (99.95%), in a Ba:In:Na atomic ratio of 2:1:6, were weighed and loaded in a BN crucible (inside diameter 7 mm, height 37.5 mm, 99.5%). The crucible was placed into a stainless steel container (1/2 in. outer diameter) and sealed under argon gas, and the whole assembly was connected to a nitrogen gas feed line. A schematic illustration of the stainless steel container was shown in a previous paper. After heating the sample to 750 °C in an electric furnace, nitrogen gas (>99.9999%) was introduced into the container and the pressure was maintained at 7 MPa with a pressure regulator. The sample was heated at this temperature for 1 h and then cooled to 550 °C at a rate of 2 °C/h under 7 MPa of nitrogen gas. Below 550 °C, the sample was cooled to room temperature in the furnace by shutting off the furnace power. The products in the crucible were washed in liquid ammonia (99.999%) to dissolve away the sodium flux. The details of the sodium extraction procedure were described previously.

To verify the elemental composition of Ba$_4$In$_{78}N_{72}$, a hand-picked sample of Ba$_4$In$_{78}N_{72}$ crystals was dissolved in 1.3 mol/L of HNO$_3$ solution and the Ba and In ratio was measured by ICP emission spectroscopy (Perkin-Elmer OPTIMA3300).

**Electronic Structure Calculations.** The electronic structures of both title compounds were investigated with the program YAeHMOP. The unit cell dimensions of Ba$_4$In$_{78}N_{72}$ (i.e. $a = 10.7597$ Å, $\alpha = 60^\circ$) and orbital energies and exponents from ref 47 were used to calculate the COOP curve shown in Figure 5b. All other calculations (including those in the Supporting Information) were performed using the atomic coordinates and unit cell dimensions of Sr$_4$In$_2$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ (i.e. $a = 10.152$ Å, $\alpha = 60^\circ$) using Slater type orbitals with the default settings of the energies and exponents. Average property calculations were carried out with a set of 60 k points, and band structures were calculated with 40 points between special positions. All the energies and exponents are listed in the Supporting Information, Table S1.

**Results and Discussion**

**Sr$_4$In$_2$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$.** The two initial reactions that differed only in the presence or absence of lithium had important consequences because the powder XRD patterns of their products were completely different. Following the removal of sodium via sublimation, the lithium-free mixture yielded a gray, crystalline product whose powder XRD pattern consisted of many peaks, most of which could be assigned to Sr$_4$In$_2$N and SrIn$_2$ and none of which could be indexed to Sr$_4$In$_2$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$. The removal of sodium from the lithium-containing reaction mixture by sublimation yielded a mass of highly crystalline, silvery-yellow bodies and the peaks in the powder XRD pattern could not be matched to any known phase, but all could be indexed upon a cubic cell of $a = 14.4026(2)$ Å. A unit cell of this dimension could not be found in any of our databases, and therefore, some of these silvery-yellow crystals were placed into polybutene oil for optical inspection and single crystal selection.

Optical inspection of the sample in oil showed it to consist of opaque, black polyhedral crystals and black plate crystals. Several of both types of crystal were loaded onto the goniometer head so that a stream of cold nitrogen froze the polybutene oil and held the crystals stationary and protected from the air. The black, platelike crystals gave unit cells that were very similar to that of Li$_4$SrN$_2$, but this compound must have been present in concentrations less than a few percent as its peaks were not readily visible in the powder XRD pattern of the bulk sample. The single-crystal diffraction peaks of the opaque, black, polyhedral crystals collected at 173 K could be indexed by a face centered cubic cell with $a = 14.3572(7)$ Å, which is, as expected, slightly smaller than the cell found from the analysis of the room-temperature powder XRD data. A suitable multifaceted, almost spherical crystal of this type was found $[0.1 \times 0.1 \times 0.1]$ mm$^3$, and following data collection, the crystal structure was obtained in the cubic space group $Fd\bar{3}m$ (No. 227, origin at $3m$). In the initial solution the 16d site ($1/2$, $1/2$, $1/2$) was occupied by sodium to give a Sr:In:Na ratio of 6:4:2. This ratio was not supported by the microprobe analysis (vide infra) which, instead, suggested a Sr:In:Na ratio of 6:4.3:0. Placing indium on the 16d site and allowing the 16d site occupancy to vary led to an occupancy of approximately 16% and a Sr:In ratio of 6:4.3, in good agreement with the microprobe data.

The anisotropic displacement parameters of the nitrogen atom occupying the 16c site (0,0,0) were found to be large in the direction of the body diagonal of the unit cell. The magnitude of the isotropic displacement parameter, however, was not unusually large and hence did not indicate any partial occupancy. Therefore, a split site model was used in which the nitrogen atom was moved slightly away from the 16c site to a more general 32e site ($x$, $x$, $x$; $x = 0.01$) but with a fixed occupancy of 50%. The displacement parameter of the nitrogen atom sitting on the 8a site (1/8, 1/8, 1/8) was also unusually large. The site occupancy for this atom was also allowed to vary, and it refined smoothly and reproducing...
ibly to 46%. These details lead to the stoichiometry Sr6-In4.32N2.47 with R1 = 0.040 and wR2 = 0.075 for all data. The program ADDSYM was used to check for higher symmetry, but none was found and, at this point, the atomic coordinates found were standardized with STRUCTURE TIDY and used as the starting model for the subsequent Rietveld refinement of the neutron diffraction pattern. Details of the X-ray crystal structure refinement, atomic coordinates, and the anisotropic displacement parameters of this partial model are shown in the Supporting Information, Tables S2–S4, respectively. An ORTEP representation is also shown in Figure S1 of the Supporting Information.

Semiquantitative electron microprobe spectroscopy was used to ascertain the Sr:In ratio. The average of nine readings taken from the flat faces of suitable crystals showed only the presence of strontium and indium in the ratio of Sr:In = 1.37 ± 0.17, in good agreement with that expected from the X-ray single-crystal structure (Sr:In = 1.39). No sodium peaks were observed either in energy dispersive or in wavelength dispersive mode. In addition, wavelength dispersive analysis revealed the presence of nitrogen, but a small signal was also observed for oxygen. The magnitude of the oxygen peak was typical of a small amount of surface oxidation of the highly air and moisture sensitive Sr6In4(In0.32-Li0.92)N2.49 crystals.

Despite the good agreement between the single-crystal X-ray data and electron microprobe analysis, there were still two questions that needed answering. The first is the partial occupancies of the indium 16d site, the nitrogen 32e/16c site, and the nitrogen 8a site (as noted in Table S3). Partial occupancies or unusual displacement parameters can be indicative of poor absorption corrections. Sr6In4(In0.32-Li0.92)-N2.49 has a large absorption coefficient of \( \mu = 28 \text{ mm}^{-1} \) for Mo K\( \alpha \) radiation. The program SADABS was used to correct for absorption (\( R_{\text{int}} = 0.0556 \)), and because of the almost-spherical shape of the crystal, it is expected that it will be well modeled. An analytical face-indexed absorption correction is superior to this, but due to the highly faceted nature of the crystal, this was not attempted in this case. It is very unusual or perhaps suspicious for three of the five atoms to have such peculiarities with their displacement parameters/occupancies, but these exact same features were reproduced in Ba6In4.78N2.72 (vide infra) and an analytical face-indexed absorption correction was applied in that case. Furthermore, as noted above, the Ae:In (Ae = Sr and Ba) atomic ratios resulting from the partial occupancies for both compounds are in good agreement with the elemental analysis. Therefore, while we cannot be entirely confident about the fractional occupancy of the nitrogen sites, the Sr:In ratio, i.e. the value of the occupancy of the indium 16d site, is not in question.

The second question addresses the role of lithium in the reaction. The X-ray scattering power of lithium is very small when compared to strontium and indium; furthermore, the characteristic K\( \alpha \) emission energies of lithium cannot be detected by electron microprobe analysis. Therefore, neither technique can determine the presence or absence of lithium. The vapor pressure of lithium at 350 °C is approximately \( 10^{-3} \text{ Pa} \), approximately 4 orders of magnitude less than that of sodium at this temperature. Therefore, it is unreasonable to expect that all of the excess lithium could be removed via sublimation, along with the excess sodium. Thus, at the end of the reaction, much if not all of the lithium will remain in the product mass either in its elemental form or in a compound.

**Neutron Diffraction.** As discussed above, at this stage it was not clear whether lithium was present in the title compound. Neutron diffraction can help to answer this question because the neutron scattering factor of lithium is negative and of a magnitude more similar to that of strontium, indium, and nitrogen than their respective X-ray scattering lengths (see Supporting Information, Table S5). Inspection of the single-crystal derived unit cell reveals various possibilities for the location of the lithium. However, the most reasonable locations are either sharing the partially occupied In 16d site or being incorporated into interstices within the crystal.

The single-crystal derived unit cell and atomic parameters shown in Tables S2 and S3 (including the use of a split site model for N1) were used as the starting model in the Rietveld refinement. All system parameters, e.g. zero point error and peak shapes, unit cell parameters, and atomic coordinates, refined smoothly; however, when the occupancy of the In 16d site was allowed to vary, it fell from 16% to −0.4%. Both X-ray single crystal and electron microprobe data provide strong evidence for this site containing 16% indium; therefore, the fact that neutrons see an overall negative scattering length for this site is strong evidence for this site being shared by both indium and lithium. Lithium was introduced into the In 16d site, the indium occupancy was fixed at 16%, and the lithium occupancy was allowed to refine. It refined smoothly to a value of approximately 45%. In the final refinement cycles, the indium occupancy was fixed at 16% and the isotropic displacement parameters of the In 32e and 16d sites were refined as a single variable. The isotropic displacement parameters of the N 32e and 8a site were also refined as a single variable, but the occupancy of the N 8a site was allowed to refine freely. Independent, isotropic displacement parameters were used for the strontium and lithium atoms. All the aforementioned details lead to a final stoichiometry of Sr6In4(In0.32-Li0.92)N2.49, with the crystallographic details and atomic coordinates collected in Tables 1 and 2, respectively. The observed, calculated, and difference plots are shown in Figure 2.

**Ba6In4.78N2.72.** Following the removal of the sodium by washing with liquid ammonia, the single crystals contained in the crucible were black. Ba6In4.78N2.72 was present with two crystal habits, octahedral [maximum size (0.4 × 0.4 × 0.4) mm\(^3\)] and as triangular platelets [(1.0 × 1.0 × 0.2) mm\(^2\)] with a black metallic luster. A second phase, Ba9In6N8, whose structure has been reported elsewhere, was also present, and it formed as platelet crystals with a black metallic luster [(1.5 × 0.5 × 0.2) mm\(^3\)].

References:

Indium Subnitrides $\text{Ae}_6\text{In}_4\text{(In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}

Table 1. Crystallographic Details for $\text{Sr}_6\text{In}_4\text{(In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ and $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}$

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<td>direct methods/SIR97</td>
</tr>
<tr>
<td>refinement method/program</td>
<td>full profile Rietveld/GSAS, EXPGUI</td>
<td>full-matrix least squares on F$^2$/SHELX</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>$\chi^2 = 1.062$</td>
<td>1.181 (on 1$^\text{st}$)</td>
</tr>
<tr>
<td>final R indices</td>
<td>$R_{\text{int}} = 0.0550$, $R_p = 0.0451$, $R(F^2) = 0.1746$</td>
<td>$I &gt; 2\sigma(I)$: $R_1 = 0.0238$, $wR_2 = 0.0530$</td>
</tr>
<tr>
<td>final R indices</td>
<td>$R_{\text{int}} = 0.0527$, $R_p = 0.0488$</td>
<td>all data: $R_1 = 0.0291$, $wR_2 = 0.0545$</td>
</tr>
<tr>
<td>largest dffractn peak and hole/e Å$^{-3}$</td>
<td>n/a</td>
<td>$0.912/-1.18$</td>
</tr>
</tbody>
</table>

$^a$ The different R values are defined in the Supporting Information. Note that the absorption coefficient of $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}$ is expressed in units of cm$^{-1}$.

$^b$ Used in the initial single-crystal X-ray analysis.

Table 2. Atomic Coordinates and Isotropic Displacement Parameters (10$^3$ Å$^2$) for $\text{Sr}_6\text{In}_4\text{(In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ and, Shown in Italics, for $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}$ (Both in Space Group $Fd3m$, Origin 2 (Origin at 3m))

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff posn</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{\text{iso}}$ or $U_{eq}$</th>
<th>occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}$</td>
<td>48f</td>
<td>0.31008(6)</td>
<td>0.125</td>
<td>0.125</td>
<td>13.3(6)</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Ba}$</td>
<td>48f</td>
<td>0.30796(4)</td>
<td>0.125</td>
<td>0.125</td>
<td>31.6(2)</td>
<td>1</td>
</tr>
<tr>
<td>$\text{In}$</td>
<td>32e</td>
<td>0.30044(2)</td>
<td>0.30044(2)</td>
<td>0.30044(2)</td>
<td>9(1)</td>
<td>1</td>
</tr>
<tr>
<td>$\text{In}$</td>
<td>32e</td>
<td>0.30278(2)</td>
<td>0.30278(2)</td>
<td>0.30278(2)</td>
<td>24.1(2)</td>
<td>1</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>32e</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>9(1)</td>
<td>0.16</td>
</tr>
<tr>
<td>$\text{Li}$</td>
<td>16d</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>15(15)</td>
<td>0.46(6)</td>
</tr>
<tr>
<td>$\text{In}$</td>
<td>16d</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>25.8(9)</td>
<td>0.389(5)</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>32e</td>
<td>0.0114(2)</td>
<td>0.0114(2)</td>
<td>0.0114(2)</td>
<td>13(1)</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>32e</td>
<td>0.0111(9)</td>
<td>0.0111(9)</td>
<td>0.0111(9)</td>
<td>40(7)</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>8a</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>13(1)</td>
<td>0.49(1)</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>8a</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>50(12)</td>
<td>0.72(8)</td>
</tr>
</tbody>
</table>

$^a$ The results for $\text{Sr}_6\text{In}_4\text{(In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$ are from the Rietveld refinement of powder neutron data; those for $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}$ from single crystal X-ray studies. For $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}^\text{a}$, the equivalent isotropic displacement parameter, $U_{eq}$, is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Figure 2. Observed (crosses), calculated (line), and difference plots for the full profile Rietveld refinement of $\text{Sr}_6\text{In}_4\text{(In}_{0.32}\text{Li}_{0.92})\text{N}_{2.49}$. The high level of background noise is due mainly to the large absorption and incoherent neutron cross sections of indium. At 150° in 2θ, the resolution is 0.8 Å.

Single crystals for X-ray diffraction were selected from the products in an argon-filled glovebox and sealed in glass capillaries under argon since the single crystals were not stable in air. The crystals of $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}$ were solved in space group $Fd3m$ (No. 227, origin at 3m) by direct methods;\textsuperscript{54} the crystallographic details and atomic coordinates are shown in Tables 1 and 2, respectively. A table and ORTEP\textsuperscript{53} representation of the anisotropic displacement parameters can be found in the Supporting Information, Tables S6 and Figure S2, respectively. Inspection of the Fourier difference map again indicated evidence that the N1 atom should be modeled as a split site. There was no effect on the R value and residuals when the N1 atom was moved from the 16c site to the 32e site with 50% occupancy [R1-(all data) = 0.0291 in both cases]. However, the displacement parameter, $U_{iso}$, halved to 0.040(7) from 0.078(8) Å$^2$. Following these steps in the refinement, it was noticed that the displacement parameter of the N2 (8a site) was unusually large [0.09(1)], and therefore, the site occupancy was allowed to vary. It refined smoothly to a final value of 72%, and $U_{iso}$ dropped to 0.05(1) Å$^2$.

The single-crystal results lead to a Ba:In ratio of 6:4.78, and in support of this stoichiometry, the Ba:In ratios found in two samples of hand-picked single crystals of $\text{Ba}_6\text{In}_{4.78}\text{N}_{2.72}$ were 6:4.83 and 6:4.87, in reasonable agreement with each other. This compound was made without the presence of lithium, and therefore, there is no reason to believe that lithium is incorporated. A reaction between

by nitrogen; in the η-carbide structure type, only the 16c site is occupied.

The indium or indium–lithium sublattices in Sr$_6$In$_4$N$_{2.49}$ and Ba$_6$In$_4$N$_{2.72}$ are isostructural and have partial occupancy on a face-sharing octahedron. The inner tetrahedra are formed from the In 32e site and are, in both compounds, fully occupied. The capping 16d site is partially occupied by either lithium or indium [Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$] or indium (Ba$_6$In$_4$N$_{2.72}$). As can be seen from Table 3, the intratetrahedral indium separations (32e–32e site distance) are shorter than the capping-tetrahedral indium separations (32e–16d site distance) in both compounds.

All the near-neighbor indium–lithium distances in Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and Ba$_6$In$_4$N$_{2.72}$ are shorter than 3.25 Å, the nearest neighbor distance in indium metal, and compare well to the indium–lithium separations in (the nonisostructural compounds) SrIn$_2$ and BaIn$_2$. In SrIn$_2$ and BaIn$_2$, the four indium–lithium separations range from 2.98 to 3.30 Å and from 2.97 to 3.12 Å, respectively. In Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$, the indium–lithium interactions created by the mixed occupancy of the 16d site lead to indium–lithium separations of 3.04 Å. This compares well to the indium–lithium separations in Li$_3$In$_2$ that range from 2.85 to 3.43 Å, with a mean value of 3.16 Å. Mixed indium–lithium site occupancy has been observed before in the binary compound LiIn, which has a wide composition range that, although relatively ill-defined, extends over ca. 2 at. % at 100 °C and from 47 to 63 at. % at 415 °C, indicating mixed site occupancy at relatively low temperatures.

An indium or indium–lithium, stellar quadrangular network has, as far as the authors can tell, not been previously reported; furthermore, isolated indium tetrahedra are also rare within extended structures. According to the Zintl concept, an isolated In$_4$ tetrahedron would be expected to have a charge of $-8$ and In$_4^8$ tetrahedra are indeed observed within the binary compound Na$_3$In, but to our knowledge, there is only one further extended structure type that is able to support the In$_8^-$ cluster, namely, Ael$_9$In$_3$N$_{12}$ (Ael = Ca and Sr). Molecular In$_n$ species are also rare, but in the past decade compounds such as In$_4$(SiMe$_3$)$_3$ have been successfully synthesized. The molecules contain an In$_4$ tetrahedral core in which every vertex is ligated. Indium–indium bond lengths are typically 3.00 Å in the molecular compounds and range from 3.07 to 3.15 Å in Na$_3$In, in good agreement with that found here.

The basis of the Ael$_9$N$_3$ subn in the supercapped tetrahedron that consists of five, face-sharing octahedra. This unit can be observed in Figure 4, and it can be seen that each Ael atom of the central octahedron is shared by three nitrogen atoms. The central, hatched octahedron is ideal but the four

![Figure 3.](image)

Table 3. Important Interatomic Separations in Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and Ba$_6$In$_4$N$_{2.72}$

<table>
<thead>
<tr>
<th>Feature</th>
<th>Sr$<em>6$In$<em>4$(In$</em>{0.32}$Li$</em>{0.92}$)N$_{2.49}$</th>
<th>Ba$_6$In$<em>4$N$</em>{2.72}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–N1(32e)</td>
<td>2.543(15)</td>
<td>2.667(13)</td>
</tr>
<tr>
<td>N1–N1(16c)</td>
<td>2.543(15)</td>
<td>2.667(13)</td>
</tr>
<tr>
<td>Ae–N1(32e)</td>
<td>3.5649(5)</td>
<td>3.8265(8)</td>
</tr>
<tr>
<td>Ae–N1(16c)</td>
<td>3.5649(5)</td>
<td>3.8265(8)</td>
</tr>
<tr>
<td>Ae–In1</td>
<td>3.836(3)</td>
<td>4.0364(7)</td>
</tr>
<tr>
<td>Ae–In2</td>
<td>3.7252(6)</td>
<td>3.9717(6)</td>
</tr>
<tr>
<td>Ae–Ae</td>
<td>3.7578(12)</td>
<td>3.9373(9)</td>
</tr>
<tr>
<td>In1–In1 (intratetrahedral)</td>
<td>3.0277(1)</td>
<td>3.1084(14)</td>
</tr>
<tr>
<td>In1–In2 (or Li)</td>
<td>3.046(1)</td>
<td>3.2088(4)</td>
</tr>
<tr>
<td>N1(16c)–In1</td>
<td>4.434(1)</td>
<td>4.745(1)</td>
</tr>
<tr>
<td>N1(32e)–In1</td>
<td>4.346(1), 4.531(1)</td>
<td>4.655(1), 4.848(1)</td>
</tr>
<tr>
<td>N2–In1</td>
<td>4.362(2)</td>
<td>4.686(1)</td>
</tr>
<tr>
<td>N1(16c)–N2</td>
<td>3.108(1)</td>
<td>3.294(1)</td>
</tr>
<tr>
<td>N1(32e)–N2</td>
<td>2.825(1), 3.392(1)</td>
<td>3.003(1), 3.586(1)</td>
</tr>
</tbody>
</table>

*Note that, in both Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and Ba$_6$In$_4$N$_{2.72}$, the N1 atom does not occupy the 16c site (0, 0, 0); rather, it occupies the 32e site (0.01, 0.01, 0.01) with 50% occupancy.*

(57) Bailey et al. 1979, 85, 6932.
(58) Bailey et al. 1993, 6932.
(59) Bailey et al. 1993, 6932.
neighboring octahedra (solid color) are slightly distorted. The supertetrahedra share corners to build up a diamond-like net in which all octahedra share faces and all nitrogen atoms continue to be shared by three alkaline earth atoms.

Within the alkaline earth octahedra, there are two distinct sites for nitrogen occupation, the 16c (N1) and 8a (N2) sites. The 16c and 8a nitrogen atoms reside in the slightly distorted and ideal octahedra, respectively. As shown in Table 3, the interatomic spacing from the 8a site to the Ae site is shorter than the distance from the 16c site to the Ae site. However, in both SrIn$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and BaIn$_4$N$_{2.72}$, the nitrogen atom in 16c site shifts to the more general 32e site of ($x$, $x$, $x$; $x = 0.01$), which results in the generation of the two sets of three Ae–N1 distances detailed in Table 3. One set of these Ae–N1 distances is shorter than the Ae–N2 distance and the other is longer, but all the Ae–N separations detailed in Table 3 compare well to those found in SrIn$_2$ and BaIn$_2$, which have Sr–N or Ba–N distances of 2.61 and 2.76 Å.\(^{(60)}\)

It is postulated that the shift of the N1 atom from the 16c to the 32e site is in response to the presence or absence of the neighboring N2 atom; the 16c and 8a sites are separated by only 3.11 Å in SrIn$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and 3.29 Å in BaIn$_4$N$_{2.72}$. Such a Coulombic repulsion between the nominally highly charged N$^-$ anions has been observed before in the compound Na$_{14}$Ba$_{14}$CaN$_{6.61}$\(^{(61)}\). This compound contains the cluster Ba$_4$CaN$_6$, which is a fragment of a cubic close packed layer of cations with nitrogen in the six octahedral holes. An equally valid representation of the Ba$_4$CaN$_6$ cluster is of a superoctahedron formed by the edge-sharing of six, nitrogen-centered BaCa octahedra—the calcium atom is shared by all six octahedra and is at the center of the close packed layer. The octahedral holes within this cluster that are occupied by the N$^-$ are in close proximity to one another, and to minimize repulsion between the closed shell anions, they are observed to have radially “breathed out” from the central calcium cation to create inter-nitrogen separations of 3.64 Å.

An interesting comparison can be made by comparing how the interatomic separations differ between SrIn$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$, which has a smaller unit cell, and BaIn$_4$N$_{2.72}$, which has a larger unit cell. The increase in the unit cell size is due to the larger size of the alkaline earth cation, leading to the observed expansion within the Ae–N sublattices. However, for the structure of the two subnets to remain commensurate, there must also be an expansion within the indium sublattice, and by inspection of Table 3, it can be seen that the majority of this expansion occurs in the separation between the capping, 16d, site and the tetrahedral, 32e, site rather than between the indium atoms within the tetrahedra: the difference between the intratetrahedral distance in Sr$_6$-In$_{(0.32)Li_{0.92})$N$_{2.49}$ and in Ba$_{6}$In$_4$N$_{2.72}$ is only 0.08 Å, which is smaller than 0.17 Å, the comparable difference between the capping, 16d, site and the tetrahedral, 32e, site, in the two title compounds. This suggests that the intratetrahedral bonding is more important than the capping-tetrahedral bonding (q.v. the Indium or Indium/Lithium Network in the Supporting Information).

The final comparison to be made is that between the two subnets. The separation between the Ae–N and In (and Li) subnets also increases with the replacement of strontium by barium, but in both Sr$_6$In$_{(0.32)Li_{0.92})$N$_{2.49}$ and Ba$_{6}$In$_4$N$_{2.72}$, the Ae–In (Ae = Sr and Ba) separations are longer than those found in, for example, SrIn$_2$\(^{(55)}\) (6 × 3.33 Å) and BaIn$_2$\(^{(55)}\) (6 total, ranging from 3.53 to 3.87 Å). This inconsistency emphasizes the separation of ionic and covalent bonding that can be visualized in these compounds; i.e., of primary concern to the Ae–N and In(Li) networks is the intra-subnet bonding rather than the inter-subnet bonding.

All the above results have established the actual stoichiometries of the title compounds to be Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and Ba$_{6}$In$_4$N$_{2.72}$. At this point it is worth noting that, despite the stoichiometric differences, the excess electron count for the two compounds is, within experimental error, the same; i.e., on the basis of valence electron counts derived from “expected” oxidation states, Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ can be written as (Sr$^{2+}$)$_6$(In$^{3+}_{3.12}$Li$^{+}_{0.32}$)N$_{2.49}$, and Ba$_{6}$In$_4$N$_{2.72}$ can be written as (Ba$^{2+}$)$_6$(In$^{3+}_{3.72}$N$^{2-}$)$_2$N$_{2.72}$(e$^-$)$_n$, where $n = 18.4$ and 18.2, respectively. Such a similarity between electron counts suggests that there is an electronic “explanation” for these stoichiometries, and to that now turn.

**Extended Hückel Calculations.** To understand the partial occupancies of Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ and Ba$_{6}$In$_4$N$_{2.72}$, extended Hückel calculations were carried out with the program YAEHMO.\(^{(46)}\) As mentioned above, the parent structure of both phases is the hypothetical compound Ae$_2$In$_3$N (Ae = Sr and Ba) whose primitive unit cell contains 30 atoms, distributed as either Sr$_{12}$In$_4$(In,Li)$_4$N$_2$ or Ba$_{12}$In$_4$N$_2$, where the two sites that exhibit partial occupancy in the experimental structures are highlighted with italics. The partially occupied indium (and lithium) site is the 16d site that caps the faces of the In$_4$ tetrahedra. For ease of discussion throughout this section, the stoichiometry of both the experimental and theoretical compounds will be written in terms of the population of the primitive unit cell; for example, Sr$_6$In$_4$(In$_{0.32}$Li$_{0.92}$)N$_{2.49}$ will be written as Sr$_{12}$In$_4$(In$_{0.64}$Li$_{1.84}$)N$_{4.99}$ and Ae$_2$In$_3$N as Ae$_{12}$In$_3$In$_4$N$_2$.

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Our view of the title compounds is one based upon the decomposition of the hypothetical crystal structure of Ae12-In8In4N2 into a covalent indium/lithium network and a predominantly ionic alkaline-earth—nitrogen network. This viewpoint suggests that the electronic requirements of Ae12-In8-In4N2 can be expressed as the sum of the electronic requirements of each subnet. To a first approximation, the electronic requirements of the predominantly ionic alkaline-earth—nitrogen subnet are straightforward; the alkaline earth atoms will formally become fully oxidized and the nitrogen atoms will formally become fully reduced, creating Ae2+ and N3− ions.

The electronic requirements of the partially complete stellar quadrangular subnet are not so clear but are developed within the Supporting Information. It is shown that the electronic requirements of the partially complete stellar quadrangular subnet of both Ba6In78N2.72 and Sr6In4In32-Li0.92N2.49 can be expressed as 20 valence electrons/inner In4 tetrahedron, irrespective of the number of indium or lithium atoms occupying the capping 16d site. Indeed, the occupation of the capping 16d site by indium or lithium serves merely to modify the electron count of the stellar quadrangular subnet because no new bonding states are introduced; i.e., the central In4 tetrahedron sets the number of bonding crystal orbitals, into which the capping atoms’ orbitals are assimilated.62

The electronic requirements of the two subnets within Ae-x-InyInzN3 have been stated, and just as the complete crystal structure of Ae-InyInzN3 is the sum of the two subnets, it is suggested that the electronic requirements of the generic compound Ae-InyInzN3 is the sum of the valence electron requirements of each subnet; i.e., 20e−/inner In4 tetrahedron + 8e−/nitrogen atom. Our hypothesis is that the fractional/mixed occupancies of the 16d and 8a site act in a coordinated fashion to optimize the bonding within Ba6In78N2.72 and Sr6-In32-Li0.92N2.49. A test of this hypothesis is contained in Figure 5, which shows the COOP analysis of the partially complete stellar quadrangular subnets of the compounds Sr12-In8(InLi2)N5 and Ba12In8In2N5. Both Sr12In8(InLi2)N5 and Ba12In8In2N5 contain five nitrogen atoms and two inner tetrahedra/primitive cell, suggesting a required electron count of 80 valence electrons/primitive cell. As shown in Figure 5, the transition from bonding to antibonding within the stellar quadrangular network indeed occurs at 80 valence electrons/primitive cell.

Figure 5. COOP analyses of the partially complete stellar quadrangular networks of (a) Sr12In8(InLi2)N5 and (b) Ba12In8In2N5. According to our model, the stellar quadrangular subnet and the five nitrogen atoms each require 40 valence electrons/primitive cell, giving a total requirement of 80 valence electrons/primitive cell. As shown, the transition from bonding to antibonding within the stellar quadrangular network indeed occurs at 80 valence electrons/primitive cell.

Do the experimental and calculated electron counts match? If it is assumed that lithium, strontium, barium, indium, and nitrogen each have 1, 2, 2, 3, and 5 valence electrons, respectively, and the number of valence electrons within the primitive cells of Sr12-In8(In0.64Li1.84)N4.98 and Ba12In8In1.56N5.44 is 76.7(4) and 79.9(9), respectively. Both these values are approximately three electrons short of attaining the expected magic electron count. This small deviation arises because we have oversimplified the bonding within the alkaline-earth—nitrogen subnet. Our viewpoint was that this was a completely ionic network whose electronic structure would consist of a set of mainly nitrogen p bonding states well below the Fermi energy and a set of mainly alkaline-earth s antibonding states well above the Fermi energy. Such a wide separation of bonding and antibonding levels would be insensitive to the position of Fermi energy; however, the bonding within nitrides always has considerable covalent character. The effect of this covalent character is to distribute the antibonding states of the alkaline-earth—nitrogen network both above, around and below the Fermi energy. In fact, as shown in Figure S9 of the Supporting Information, an antibonding interaction is present at the Fermi energy; therefore, the observed electron count in Sr12In8(In0.64Li1.84)N4.98 and Ba12In8In1.56N5.44 is the result of the attempts to maximize the bonding of both the stellar quadrangular and the alkaline-earth—nitrogen subnets.

**Band Structure and Density of States.** Shown in Figure 6 is the calculated band structure and total density of states.

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(62) This result that capping atoms have no effect on optimal electron count is very similar to the capping principle outlined by Mingos and Wales.63

Indium Subnitrides \( \text{Ae}_6 \text{In}_4 (\text{In}_x \text{Li}_{1-x})_N \)\n
The measured resistivity of a pressed pellet of \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) is shown in Figure 7. The resistivity data for \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) are consistent with a highly defective, high carrier concentration metal, which is also consistent with the metallic behavior suggested by extended Hückel calculations but with low mobility carriers. The low mobility is due to random partial occupancies in \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) which produce considerable disorder scattering. The concentration of partial and mixed occupancies does not depend on temperature, and hence, a flat, relatively high resistivity vs temperature behavior is expected. The data for Figure 7 are also consistent with a degenerately doped semiconductor, and as neither the highly pure reagents nor the clean-room environment required for highly pure semiconductor fabrication were employed, it is also possible that \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) is a semiconductor with a small quantity of impurity carriers.

**Conclusion.** Two new indium nitrides have been synthesized and characterized. Like all other ternary indium nitrides of this class, their structures can be visualized in terms of interpenetrating nets, one ionic and the other covalent in bonding character. Considerable partial and/or mixed occupancies are present in both compounds. Even though the stoichiometries are different in \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) and \( \text{Ba}_6 \text{In}_4.78 _N_{2.72}\), they are electronically similar and the electron count in both compounds is the result of attempts to optimize the bonding requirements of the subnets of both compounds. \( \text{Sr}_6 \text{In}_4 (\text{In}_{0.32} \text{Li}_{0.92})_N_{2.49} \) is found to have a room-temperature resistivity of 6.3 m\( \Omega \)cm, with a weak temperature dependence.

**Acknowledgment.** This work was supported by NSF Grant No. DMR-0245462 and by a grant from the Ministry of Education, Culture, Sports, Science, and Technology of the Japanese Government. We thank Dr. Emil Lobkovsky for help with the single crystal data collection and structure solution and Mr. John Hunt for help with the SEM microprobe. The microprobe is supported by the Cornell Center for Materials Research Shared Experimental Facilities, funded through the National Science Foundation Materials Research Science and Engineering program DMR-0079992. We thank a reviewer for very insightful comments concerning the balance of interactions at the Fermi level.

**Certain commercial products are identified to document experimental procedures. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that these products are necessarily the best available for this purpose.**

**Supporting Information Available:** A table of \( H_{ij} \) and \( \xi_j \) values used in the electronic structure calculations, Table S1; single-crystal
X-ray crystal structure refinement data, atomic coordinates, and anisotropic displacement parameters of the partial model, Sr_6In_{4.32}N_{2.47}, Tables S2–S4; an ORTEP representation of the anisotropic displacement parameters of Sr_6In_{4.32}N_{2.47}, Figure S1; definition of crystallographic R values, a table of neutron cross sections, Table S5; a table and ORTEP representation of the anisotropic displacement parameters of Ba_6In_{4.78}N_{2.72}, Table S6 and Figure S2, respectively; the coordination environments of the Ae, In1, and In2 atoms, Figure S3; the development of the electronic requirements of the stellar quadrangular networks of Sr_6In_{4(In_{0.32}Li_{0.92})}N_{2.49} and Ba_6In_{4.78}N_{2.72}; the COOP analysis of the alkaline-earth–nitrogen network in Sr_6In_{4}In_{1}Li_{1}N_{5}, Figure S9; an input file used for YAeHMOP, including the primitive unit cell and atomic coordinates; and crystallographic information files (CIF) for Sr_6In_{4(In_{0.32}Li_{0.92})}N_{2.49} and Ba_6In_{4.78}N_{2.72}. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files are also deposited at the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, with depository numbers 415294 [Sr_6In_{4(In_{0.32}Li_{0.92})}N_{2.49}] and 415293 (Ba_6In_{4.78}N_{2.72}).