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# Electronic Structures of $KNa_3In_9$ and $Na_2In$, Two Metallic Phases with Classical Closed-Shell Electronic Configurations

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The cluster compounds $KNa_3In_9$ $[K_2Na_6(In_{12})(In)_6]$ and $Na_2In$ $[(Na)_8(In_4)]$, which contain $In_{12}$ icosahedra interbridged by 4-bonded In atoms and isolated $In_4$ tetrahedra, respectively, both have classical closed-shell electronic configurations but show metallic transport properties. These contrasts have been studied by means of first-principles density functional methods (LMTO-ASA). Several bands cross the Fermi level in both compounds, consistent with their metallic properties. In $KNa_3In_9$, the metal atom framework alone is sufficient to generate a metallic characteristic. The alkali-metal s and indium p orbitals mix considerably in both phases, providing for substantial covalent contributions to their stabilities as well as bands crossing $E_f$. The participation of Na atoms in the 3D bonding networks is more striking in cation-richer $Na_2In$ than in $KNa_3In_9$.

## Introduction

A large number and variety of phases result from reactions of the alkali metals with post-transition elements.[2] The bonding or, more precisely, the relationships between the structure and number of cation valence electrons have been successfully rationalized in most of the phases by means of simple guidelines for stable electron counts, as by Zintl–Klemm, octet, or Wade rules.[3] Some of these phases show metallic properties because they contain either an excess or deficiency of electrons according to these rules, such as $K_{10}Tl_7$[4] and $Na_8K_{23}Cd_{12}In_{48}$,[5] respectively, or because of the strong cation participation in the bonding, such as in $K_3Bi_2$ and $K_5Bi_4$, which contain small bismuth aggregates.[6] The electronic structures of the last two compounds were well-studied recently to show the decisive influences that K atoms have on the transport properties.[7] Interesting problems from the viewpoint of the bonding descriptions immediately emerge here: is it more accurate to describe the structures in terms of a 3D K–Bi network rather than with isolated bismuth dimers or tetramers? We have also recently given theoretical attention at the ab initio level to other types of compounds, the electron-rich $Na_6TlSb_4$[8] and electron-poor $Na_3MIn_2$ (M = Au or Ag),[9] in which a considerable mixing of sodium and post-transition element orbitals in extended networks provide substantial covalent bonding contributions to the stabilities of both compounds.

Another interesting category among the so-called Zintl phases contains those diverse compounds that classically should have electronically closed-shell configurations but which show metallic properties, such as $Na_{12}K_{38}Tl_{48}Au_2$,[10] $Na_{23}K_9Tl_{15.3}$,[11] $KNa_3In_9$,[12] and $Na_2In$.[13] Phases containing a triel element cluster are frequent members of this class, presumably because of their smaller electron affinities and weaker homoatomic bonds.[2a] The $Cr_5B_3$-type $Ca_5Ge_3$ and its numerous relatives with alkaline-earth metals as cations also belong to this category.[14] An extensive theoretical study on the latter family reveals that the empty d orbitals of and

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polarization by the cations have decisive influences on their bonding, cluster configurations, and metallic characteristics.[15] As part of our continuing efforts to understand the structures and properties of alkali-metal−indium systems, we report here on electronic structure studies of $KNa_3In_9$ [$K_2Na_6(In_{12})(In)_6$] and $Na_2In$ [$(Na)_8(In_4)$], the first with a visually attractive network structure built from, in part, $In_{12}$ icosahedra and the second, with isolated $In_4$ tetrahedra. Traditional extended Hückel tight binding methods do not handle the alkali-metal atom contributions well, so first-principles density functional calculations have been utilized to analyze the pronounced metallic properties of these two nominally electron-precise Zintl phases.

## Computational Details

Self-consistent electronic band structure calculations were performed using the linear muffin-tin orbital (LMTO) method in its scalar relativistic version (program LMTO-ASA 4.7).[16] Reciprocal space integrations were carried out using the tetrahedron method.[17] The radii of the Wigner−Seitz spheres were assigned automatically so that the overlapping potentials would afford the best possible approximation to the full potential. The results seemed reasonable; the muffin-tin radius for K was 4.56 Å, and the In and Na values ranged from 3.19 to 3.41 Å and 3.57 to 3.64 Å, respectively. The basis sets of short-range, atom-centered tight-binding- (TB-) LMTOs contained 5s, 5p, and 5d wave functions for In; 4s and 4p for K; and 3s and 3p for Na. The d orbitals of In and the p orbitals of the alkali metals were treated by downfolding techniques.[18] Fat band methods were utilized to aid interpretation of the contributions of a given set of atomic orbitals via increased widths of the bands involved. To quantify the overall interactions between pairs of atoms, the integrated crystal overlap Hamiltonian populations (−ICOHPs)[19] were also determined for $KNa_3In_9$. The −ICOHPs obtained by means of such first-principle methods are more meaningful analogues of the Mulliken overlap populations from extended Hückel methods and are better measures of relative bond strengths. The structural data employed for both compounds were as reported.[12,13]

## Results and Discussion

**$KNa_3In_9$.** The visually attractive structure of $KNa_3In_9$, Figure 1, occurs in the orthorhombic space group *Cmca* ($Z = 8$) and can be described as a three-dimensional indium network composed of icosahedra, each with 12 exo bonds, together with three types of 4-bonded In atoms that interconnect the clusters, viz., $In_{12}(In)_6$. There are no direct bonds between clusters; rather, the 4-bonded indium atoms In5, In6, and In7 are respectively bonded to three, two, and one icosahedra, and at the same time, In6 and In7 define bonded and relatively flat zigzag chains that run along the *a* direction. All cations bridge between faces or edges of different clusters. A more thorough structural description can be found in ref 12. According to traditional understanding, the empirical electronic distribution in the ideal Zintl phase $KNa_3In_9$ would be approximated as $[(K^+)_2(Na^+)_6(In_{12}{}^{2-})(In^-)_6]$ with the superscripts emphasizing oxidation states, not charges. (Such icosahedra require $2n + 2 = 26$ skeletal electrons less one electron for each exo bond to another In; i.e., as $In_{12}{}^{2-}$ individually.) Thus, this compound is structurally closed-shell according to the apparent electron balance and, therefore, ideally a semiconductor. A semiconducting property of this phase was also suggested by semiempirical extended Hückel band calculations on just the $In_9{}^{4-}$ network.[12] Although both approaches have proven useful in providing a simple understanding of the electronic structures of many solids,[3] $KNa_3In_9$ in fact behaves as a metallic compound with a resistivity at 298 K of about 49.4 $\mu\Omega$ cm and mean temperature dependence of +0.46%.[12] A more thorough theoretical investigation of the electronic structure of this compound, both of the network and of the influence of the cations, seemed clearly needed in order to learn where and why simple views of the bonding fail and, in the longer term, to understand the details that govern the bonding and properties of these and similar apparent Zintl salts.

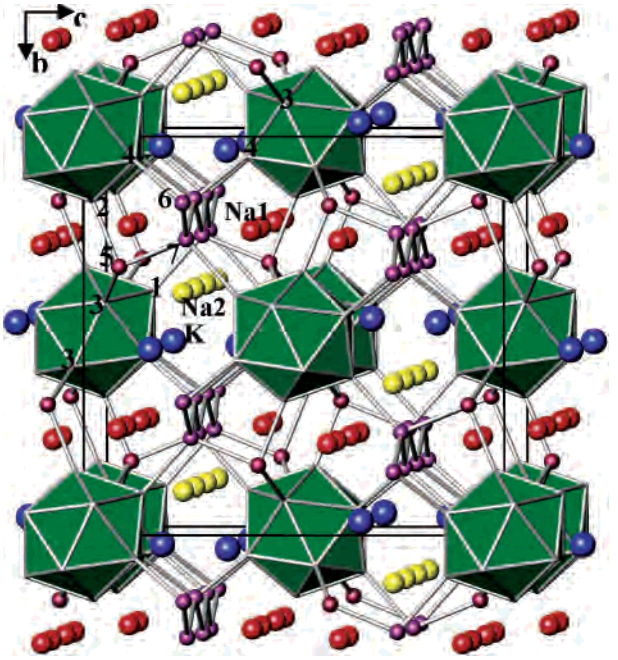

**Figure 1.** ~[100] view of the centered orthorhombic cell of $KNa_3In_9$ [$K_2Na_6(In_{12})(In)_6$]. The icosahedral $In_{12}$ units are green; 4-bonded In5−In7 atoms are purple; and K, Na1, and Na2 are blue, red, and yellow, respectively. Some individual In atoms are also identified.

The calculated total densities of states (DOSs) for $KNa_3In_9$ [$K_2Na_6(In_{12})(In)_6$] obtained from LMTO-ASA calculations are shown in Figure 2 (black line) along with the projected partial DOS contributions from In (blue) and the alkali-metal atoms (red). As expected, In contributions dominate the filled bands, but the alkali-metal contributions to DOS are not negligible. (The In 5s orbital contributions are small, ≤2 in DOS, over the bonding region shown.) At the Fermi level, the total DOS contributions are very small but *not zero*, consistent with the observed poorly metallic

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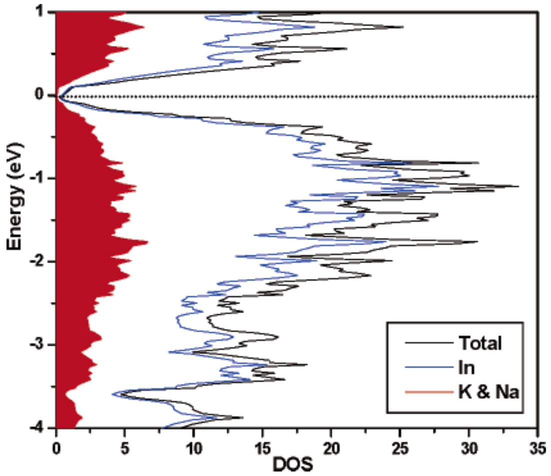

**Figure 2.** Total DOSs for $KNa_3In_9$ (black line) plus partial contributions of indium (blue) and alkali metals (red).

property. Some of the small densities of states at the Fermi level in Figure 2 may be related to inherent approximations in the LMTO-ASA program.[15] The most serious approximations in this approach are the use of a spherically symmetric form for the potentials, the atomic-sphere approximation to the Wigner−Seitz cell, and the local-density approximation, especially for a highly directional bonding situation.[20] The considerable mixing between the In and the alkali-metal orbitals must be important in terms of their covalent bonding. Both Wade's rules and Hückel theory fail to explain the transport and bonding property here, in part because both methods assume that alkali-metal atoms simply transfer their valence electrons to an anionic network.

More convincing evidence regarding the metallicity as well as the bonding is found in the complete band structure in which several bands cross the Fermi level, Figure 3a. Here, the roles of alkali metals are easier to see in their fat band representations in the calculated band structures, as shown here in blue for Na1 alone. Unpaired electrons at the Fermi level are the carriers in metallic systems, and here, only Na1 among the cations makes appreciable contributions at $E_F$. [Neither Na2 nor K does so visibly (Supporting Information).] The transport is clearly 3D, however, because eight bands cross at $E_F$, some rather steeply, especially along Γ → Y and Γ → Z. The fat band descriptions for the p orbitals of each In (Supporting Information) reveal that In6 and In7 atoms alone make major contributions at or near all crossings of the Fermi level and in the same regions as Na1, as their structural proximities might suggest (Figure 1, 3.74 and 3.50 Å, respectively), but least along Γ → Z. (This aspect is also supported by −ICOHP data, below.) Although the separate In5−In7 atoms do not afford obvious means for communication along *b** and *c**, the presence of more moderate contributions by other In atoms does supply the answer (Supporting Information). Thus, one can expect obvious conduction in the *a** direction largely from the In6−In7 chain coupled with Na1; in *b** via In6, In7, and Na1 plus moderate (intracluster) contributions from atoms In2, In3, and In4; and in *c**, what might be judged the difficult direction on the basis of the structure, by In6, In7, and moderate contributions by cluster atoms In1−In4 and by interbridging In5 atoms. Thus, conduction in the *b** and *c** directions logically involves the icosahedra as well. Unfortunately, this compound is very air-sensitive, and the growth of large single crystals for anisotropic resistivity measurements will be difficult.

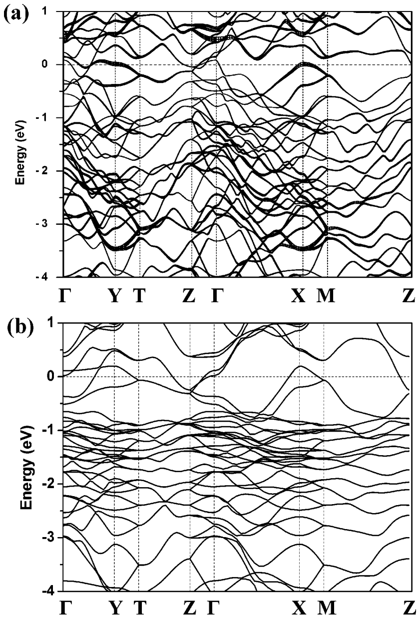

**Figure 3.** (a) Band dispersions of $KNa_3In_9$ with a fat band representation of Na1 s contributions in blue; (b) band structure for $\square_8[In_{18}]^{8-}$ with the same In atom structure and number of electrons but without cations. [$\Gamma = (0\ 0\ 0)$, $Y = (-{}^1/_2\ {+}{}^1/_2\ 0)$, $T = (-{}^1/_2\ {+}{}^1/_2\ {+}{}^1/_2)$, $Z = (0\ 0\ {}^1/_2)$, $X = ({}^1/_2\ {}^1/_2\ 0)$, and $M = ({}^1/_2\ {}^1/_2\ {}^1/_2)$ in the primitive cell.]

Band calculations for the In framework alone and with the same number of valence electrons, namely, $(\square^{1+})_8[In_{18}]$,$^{8-}$ Figure 3b, afford a good deal more information about the nature of the bonding. First, a comparison of the two diagrams in Figure 3 shows that the alkali-metal cations are clearly "pulled down" from higher-lying conduction band states and mix with the indium states, generally increasing the band dispersion over much of *k* space, particularly from Γ to the special points *X*, *Y*, and *Z* (that is, parallel to *a**, *b**, and *c**). This mixing also noticeably increases the DOS over the entire region shown above about −0.7 eV. The other striking feature is that the metal host alone would also be metallic, as artificial as the lone In lattice may be, although the DOSs in this region are clearly less than when in the presence of the cations. Many of the states near $E_F$ again arise from the bridging and chain atoms In5, In6, and In7 (Supporting Information) together with smaller contributions by the same cluster atoms In3 and In4. Thus, the metal structure alone does not produce a clear valence-conduction band gap, some of this presumably originating (among many such triel systems) because of generally weakened Tr−Tr bonding and reduced electron affinities relative to networks generated by later, main-group elements.[2,3]

The strength of pairwise interactions between atoms can be better quantified by crystal overlap Hamiltonian population (COHP) analyses as a function of energy. Integrated

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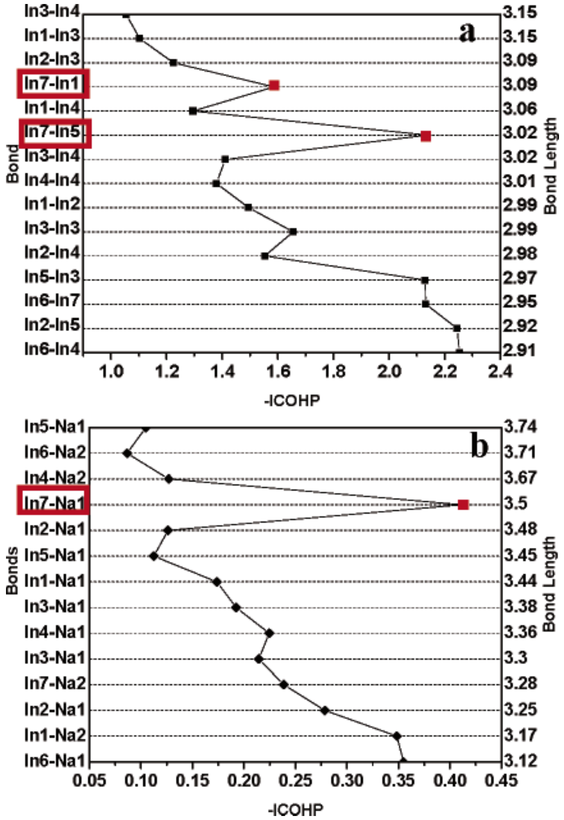

**Figure 4.** Comparisons of −ICOHP values (eV/bond) and bond lengths (Å) for different pairwise interactions in $[K_2Na_6(In_{12})(In)_6]$: (a) In−In and (b) In−Na. Note the difference in scales for the two −ICOHP sets. Some notable contrasts between −ICOHP and distance values are marked in red.

−ICOHP values for pairwise In−In and In−Na interactions are plotted in Figure 4 relative to their respective distances. The −ICOHP/bond values are more accurate reflections of relative bond strengths than the usual Mulliken overlap populations,[19,21] and both may greatly contrast with more intuitive indications according to interatomic distances.[9,22,23] All In−In bonds within the icosahedra (In1−4) have smaller −ICOHP values than those for exo bonds to and between In5, In6, and In7, consistent with the more delocalized and electron-deficient character of the bonding within closed polyhedra. Some of these values are in notable contrast with their relative bond lengths, such as for the large In7−In1 and In7−In5 values for longer distances, and other values to and between In5, In6, and In7 are the largest in the structure. Likewise, the In7−Na1 and In6−Na1 examples, Figure 4b, have the largest −ICOHP values among those for all of the Na−In contacts, consistent with the strong involvement of Na1 with these neighbors, and reflected in the fat band representations. Other pairs involving Na1 with cluster In atoms and a few with Na2 are not far behind. The effective strength of the long In7−Na1 (3.50 Å) distance is particularly striking. Although the transport properties originate with a very small subset of levels at $E_F$, these are obviously not those primarily responsible for the structure and the major bonding therein. Note also the much smaller magnitudes of the integrated Na−In functions, for which close packing and Coulombic rather than covalent interactions are more important. The above contrasts between bond lengths and quantities more related to bond strengths are better-quality representations of what have long been recognized as “matrix effects”, plus or minus variations in distances that arise more because of packing effects and that do not parallel bond strengths at all well, and vice versa.[9,22,23]

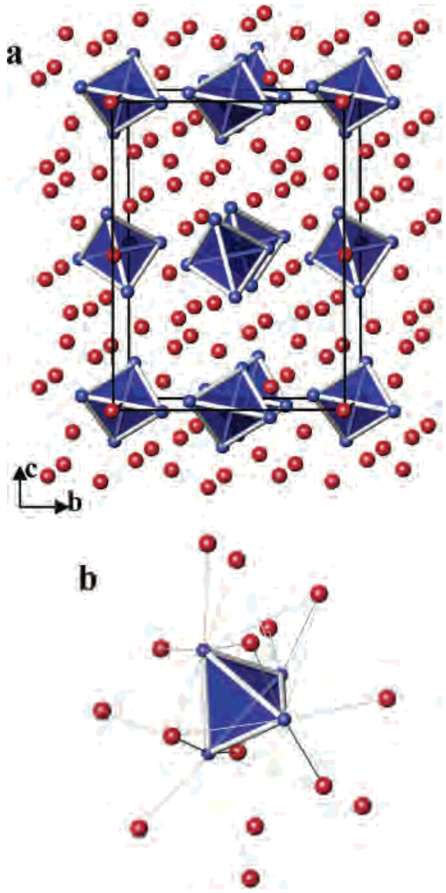

**Figure 5.** (a) ~[100] view of the centered orthorhombic cell of $Na_2In$ $[(Na)_8(In_4)]$ with $In_4$ tetrahedra (blue) located on 2-fold axes along *a*. (b) Sodium dispositions around an $In_4$ cluster with Na−In distances of 3.22−3.71 Å.

**$Na_2In$.** In the foregoing, the influence of alkali-metal atoms on the transport properties is strongly coupled with the 3D indium lattice. To show an importance of cations alone, $Na_2In$, another nominally electron-precise but metallic phase, was also studied by the same calculation methods. The structure of $Na_2In$,[13] isostructural with $Na_2Tl$[24] in space group $C222_1$ ($Z = 16$), contains isolated, deformed $In_4$ tetrahedra ($C_2$ point symmetry) immersed in a sodium sublattice, Figure 5a. The multifunctional Na atoms lie above all faces, edges, and vertexes of the $In_4$ clusters, Figure 5b, with Na−In distances of 3.22−3.71 Å and Na−Na distances of 3.39−3.84 Å, the shortest of which are, in each case, about 0.02 Å less than the shortest in $KNa_3In_9$. The shortest intercluster In−In distance is 5.39 Å, so the $In_4$ clusters appear to be isolated. However, the $In_4$ clusters and the surrounding Na naturally share the same symmetry elements, and their

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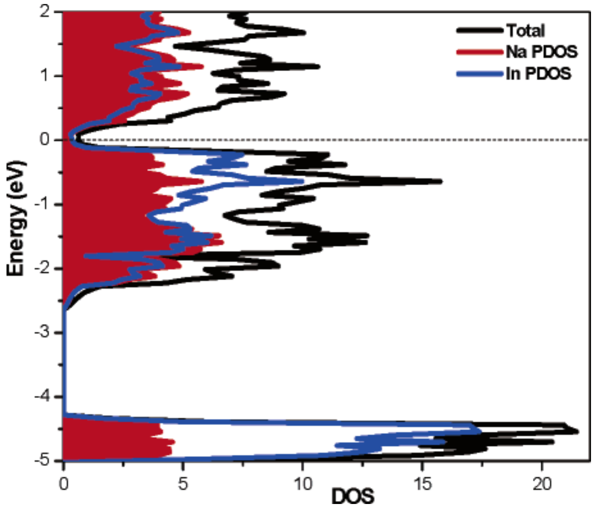

**Figure 6.** Total densities-of-states for $Na_2In$ (black line) plus partial contributions of indium (blue) and sodium (red).

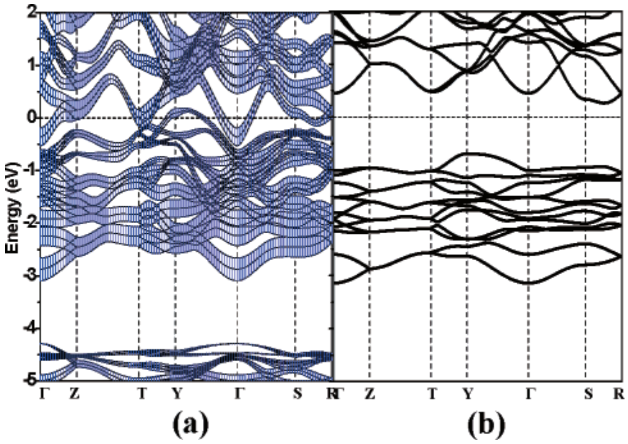

**Figure 7.** (a) Band dispersions of $Na_2In$ with a blue fat band representation for Na s orbitals; (b) band structure for $\square_8[In_4]^{8-}$ in the same structure.

orbitals will mix, so they are less isolated than it might appear at first view. The empirical electronic formula of this compound can be described classically. According to traditional views, $(Na^{1+})_8(In_4)^{8-}$ should be closed shell with $2n + 4 = 12$ skeletal electrons for the nido polyhedra, and a semiconductor property is so suggested. Nonetheless, the phase is metallic with a $\rho_{298}$ of about 270 $\mu\Omega$ cm and a mean temperature dependence of +0.27% $K^{-1}$.[13]

Correspondingly, the calculated densities of states for $Na_2In$ shown in Figure 6 contain an appreciable number of open states at the Fermi level, and as shown, both the indium and sodium orbitals make strong contributions to the filled bands, reflecting the covalent bonding character in this phase in the presence of a numerically larger number of sodium atoms. The fat bands for the Na s orbitals, Figure 7a, illustrate the very substantial involvement of sodium at about nine crossings of $E_F$ as well as in the valence bands. In striking contrast, an analogous band calculation for $(\square^{1+})_8In_4,^{8-}$ Figure 7b, reveals a direct gap of about 1.2 eV, without the continuous metal lattice so important in $KNa_3In_9$.

The 3D network character of $Na_2In$ is different from those in a similar family of compounds $(A^+)_4(Tt_4)^{4-}$, A being one of the alkali metals Na−Cs and Tt being a group 14 (tetrel) element Si−Pb. These again contain only isolated tetrahedra of the Tt atoms immersed in a sea of half as many A atoms.[23] Extensive electronic structure studies of these compounds by means of LMTO or the augmented-spherical-wave calculations, such as for NaSi (*mC*32), NaGe (*mP*32), KGe (*cP*64),[26] β-NaSn (*tI*64),[27] NaPb (*tI*64), and KPb (*tI*64),[20] all indicate that they should have semiconducting properties, the alkali-metal atoms making relatively fewer contributions to the electronic structures. These also demonstrate that the widths of the band gaps depend on the interactions between the tetrahedra both directly and indirectly through the cations. In $Na_2In$, the shortest intercluster distance is 5.39 Å, so there is no question of direct interaction between tetrahedra. However, the shortest Na−In (3.22 Å) and Na−Na (3.39 Å) distances in $Na_2In$ are less than the shortest Na−Sn, 3.35 Å, and Na−Na, 3.64 Å, distances in NaSn, even though an In atom would probably be considerably intrinsically larger than Sn. The larger contribution of sodium to the electronic structure of $Na_2In$ is not surprising. Of course, the $In_4$ anions should be considerably more polarizable than $Sn_4$ as well.

## Conclusions

The contrasts between their metallic conductivities and the ideal electron-precise configurations have been investigated for both $KNa_3In_9$ and $Na_2In$ by ab initio LMTO methods. Several bands cross the Fermi levels for both compounds. It is impossible to understand the details of the electronic structures without realizing that the alkali-metal atoms do far more in bonding than just providing electrons to satisfy the electronic requirements of the more electronegative In clusters. Coulombic attractions also exist, of course.

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**Supporting Information Available:** Graphical fat band representations for Na2, K, and In1−7 in $KNa_3In_9$ and for In5−7 in the cation-free calculation and COHP data for In6−Na1 and In7−Na1 in the former. This material is available free of charge via the Internet at http://pubs.acs.org.

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