Inorg. Chem. **1992,** *31,* 115-118

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

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Received May 15, 1991

We have theoretically studied the bonding properties of $Ca_{14}GaAs_{11}$ using the ab initio, self-consistent pseudopotential method within the local density approximation of density functional theory. $Ca_{14}GaAs_{11}$ is an example of a new series of recently prepared compounds which have the stoichiometry $A_{14}MPn_{11}$ (A = Ca, Sr, Ba; M = Al, Ga, Mn; Pn = As, Sb, Bi). We have found that the electronic structure and bonding of the $Ca_{14}GaAs_{11}$ compound are consistent with the Zintl concept. In addition, the $GaAs_4$ tetrahedra and the linear As_3 groups contained in this compound are isolated units which are not arranged into an extended bonding network. The bonding within the $GaAs_4$ group is slightly more ionic than the bonding in a GaAs crystal. The linear As_3 unit can be accurately described as a hypervalent three-center, four-electron bonded structure. The $A_{14}MPn_{11}$ structure type contains the first example of a discrete, hypervalent group 15 linear anion.

Introduction

Electron-counting rules have long been important for interpreting the structures of compounds. A large number of solid-state compounds can be understood by using electron-counting rules in accordance with the Zintl–Klemm concept.[1] These so-called Zintl materials consist of a cation–anion pair in the simple binary compounds and monoatomic cations and polyatomic anions in the ternary and multiternary compounds. The electronic structures of these compounds can be modeled as a transfer of the valence electrons from the electropositive atoms to the electronegative atoms and polyatomic groups. These transferred electrons then form homo- or heteroatomic bonds within the polyatomic anions. Although the Zintl concept is used to understand the structure and bonding in a wide variety of crystal structures, not all compounds which might appear to be Zintl compounds can be fully understood with the Zintl concept. As an example, Alemany et al.[2] recently studied $Ba_7Ga_4Sb_9$ and concluded that its electronic structure could not be fully explained in terms of the Zintl concept.

A new series of compounds has recently been prepared with the stoichiometry $A_{14}MPn_{11}$ (A = Ca, Sr, Ba; M = Al, Ga, Mn; Pn = As, Sb, Bi).[3-10] If the Zintl concept is employed to describe the structure and bonding within this structure type, then one formula unit of the compound, $A_{14}MPn_{11}$, consists of 14 A^{2+} cations, one MPn_4^{9-} tetrahedron, one Pn_3^{7-} anion, and four Pn^{3-} anions. Although the formal charges assigned to the polyatomic anions are rather large, the Zintl concept provides a starting point for an understanding of the bonding in this structure. For example, the Pn_3^{7-} unit can be interpreted according to the Zintl concept if the central Pn atom is envisioned to expand its octet to become dsp^3 hybridized, thus rationalizing the linear structure of this anion.[3-10] Alternatively, since the Pn_3^{7-} anion is isoelectronic with X_3^- (X = halogen), the Pn_3^{7-} ion could be described as a hypervalent three-center, four-electron bonded structure.[11] If so, these Pn_3^{7-} ions would be the first examples of homoatomic, hypervalent group 15[12] anions that are not stabilized by a ligand.[13] However, the interatomic distances in the Pn_3^{7-} ions are long, and as the cation becomes a better electron donor, the distances in the Pn_3^{7-} anion increase to a point where the existence of a Pn_3 species is questionable. In addition, many of the Pn–A distances in all of these compounds are surprisingly short. For example, some arsenic–calcium distances[10] in $Ca_{14}GaAs_{11}$ are ~2.95–3.07 Å, *significantly smaller* than the estimates of the sum of the ionic radii (3.22 Å).[14] These two observations imply that the formal charges assigned according to the Zintl concept may be too restrictive to describe the bonding in these structures. In addition, although the high-temperature ($T > 60$ K) magnetic properties of the series of compounds $A_{14}MnPn_{11}$ (A = Ca, Sr, Ba; Pn = As, Sb, Bi) are consistent with the Zintl electron-counting scheme, all of these manganese analogues are ferromagnetic for $T < 60$ K (except for the compound where A = Ba, Pn = Bi, which is antiferromagnetic, and the compounds where A = Sr, Ba, Pn = As, which are simple paramagnets).[4-8] The low-temperature magnetic properties of the manganese analogues are difficult to justify if the bonding in these compounds is accurately described by the Zintl concept. In particular, the MPn_4 tetrahedra in these structures are separated by the Pn_3 anion so that, in the case of the manganese analogues, the closest Mn⋯Mn distance is about 10–11 Å. This large separation makes a direct magnetic interaction between the Mn atoms seem unlikely. The unexpected ferromagnetism found in the manganese compounds suggests that a sophisticated first-principles calculation is warranted to determine if the Zintl concept does provide an accurate description of the bonding in this type of structure.

Although a calculation of the electronic structure of one of the manganese analogues may provide insight into the magnetic properties of these compounds, application of first-principles calculational methods to a large unit cell which contains transition-metal elements is not currently possible. The present study was therefore undertaken on $Ca_{14}GaAs_{11}$ for several reasons. First, we wanted to determine the validity of the Zintl electron-counting rules for one member of the new series of compounds, $A_{14}MPn_{11}$. Second, we wanted to investigate the bonding within the $GaAs_4$ tetrahedra and the linear As_3 polyatomic groups. Finally, we

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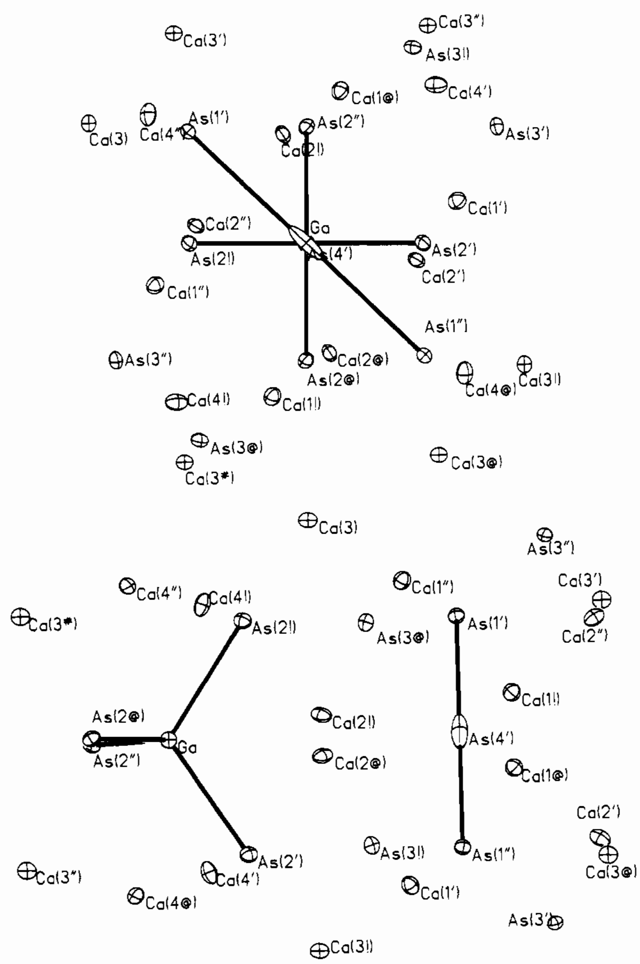

Figure 1. Projections of the 30 atoms in the partial unit cell onto a plane perpendicular to the (top) *c* axis and (bottom) *a* axis.

wanted to determine whether the $GaAs_4$ and As_3 groups exist as isolated units or as an extended network. The calculation techniques used in this study, the ab initio pseudopotential method with plane wave basis functions, is ideally suited to investigate the bonding in solid-state systems, since this method does not bias the electronic charge density in any way. This allows for the explicit investigation of bonding interactions between the cations and the anions and within the polyatomic groups without preconceived notions concerning the bonding arrangement.

Structure

$Ca_{14}GaAs_{11}$[10] forms tetragonal ($I4_1/acd$) crystals, with eight formula units per primitive unit cell. Each formula unit consists of 14 Ca cations, four As anions, a $GaAs_4$ tetrahedron, and a linear As_3 unit. The $GaAs_4$ tetrahedra have $\bar{4}$ point symmetry and are translated by $^1/_2$ along the *c* axis whereas the As_3 anions have 222 point symmetry and are staggered by 90° with respect to each other. The As anions are located between the $GaAs_4$ tetrahedra and the As_3 linear units and form a spiral along a screw axis coincident with the *c* axis. The closest As ion to an As anion in the spiral is another As anion in the spiral at 3.92 Å. The As atoms in the spiral are therefore considered to be isolated and not bonded to any other As atom. Additional details concerning the structure of $Ca_{14}GaAs_{11}$ can be found in refs 9 and 10.

Calculational Model and Method

The full unit cell of $Ca_{14}GaAs_{11}$ contains eight formula units—a total of 208 atoms.[10] A calculation of the electronic structure of the full unit cell is currently impossible due to a variety of technical limitations. Therefore, in order to investigate the bonding in this material, a partial unit cell consisting of one-eighth of the full unit cell was considered. Expressed in terms of the lattice constants of the full unit cell defined in ref 10, the coordinates of the corners of the partial unit cell are (0.25, 0.00, 0.00), (0.25, 0.00, 0.50), (0.25, 0.50, 0.00), (0.25, 0.50, 0.50), (0.75, 0.00, 0.00), (0.75, 0.00, 0.50), (0.75, 0.50, 0.00), and (0.75, 0.50, 0.50).

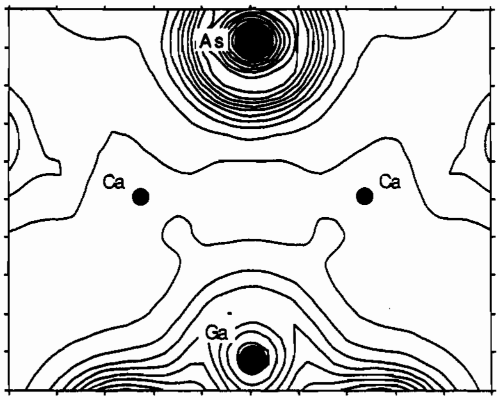

Figure 2. Total valence electron charge density plotted through two Ca's, the Ga from the $GaAs_4$ tetrahedron, and the central As in the linear As_3 unit.

This partial unit cell is tetragonal with lattice constants along the *a* and *b* axes of 7.808 Å, and a lattice constant along the *c* axis of 10.569 Å. The partial unit cell contains one $GaAs_4$ tetrahedron and one linear As_3 unit in addition to four isolated As atoms and 18 Ca atoms—a total of 30 atoms. Schematic diagrams of the projection of this 30-atom group onto a plane perpendicular to the *c* axis and the projection onto a plane perpendicular to the *a* axis are given in Figure 1. Six of the Ca atoms (3, 3′, 3″, 3#, 3!, and 3@) are located on the surface of the partial unit cell, however, and it is unclear which of these Ca's on the surface should be included to most accurately model the bonding in the full unit cell.

In order to investigate whether the number of included surface Ca's affects the calculated electronic structure of $Ca_{14}GaAs_{11}$, two calculations were performed. In the first calculation, all six surface Ca's were included in the partial unit cell. This partial unit cell contains one Ga atom, 11 As atoms, and 18 Ca atoms. The stoichiometry of this partial unit cell ($Ca_{18}GaAs_{11}$) is therefore not the same as in the full unit cell ($Ca_{14}GaAs_{11}$). In the second calculation, only two surface Ca's, 3 and 3!, were retained. This partial unit cell contains one Ga atom, 11 As atoms, and 14 Ca atoms. The stoichiometry of the full unit cell is therefore maintained in this partial unit cell.

The calculations for the two partial unit cells described above yield similar electronic structure results. The number of included surface Ca's therefore does not affect the qualitative conclusions presented in this paper. However, since the partial unit cell with two surface Ca's preserves the stoichiometry of the full unit cell, we consider this partial unit cell to be a more accurate model of the full unit cell than the partial unit cell which contains all six surface Ca's. Therefore, the results for the partial unit cell with two surfaces Ca's will be presented in the remainder of this paper. For simplicity, this partial unit cell will be referred to as the reduced unit cell of $Ca_{14}GaAs_{11}$.

Calculations of the electronic structure of the reduced unit cell were performed using the ab initio, self-consistent pseudopotential method[15,16] within the local density approximation of density functional theory.[17] The Kohn–Sham equations of density functional theory were solved for the electronic wave functions and eigenvalues using a local optimization method proposed by Woodward et al.,[18] rather than the standard method of matrix diagonalization.[16] The interactions between the valence electrons and the ionic cores were described using Kleinman–Bylander nonlocal pseudopotentials[19] for the Ca, Ga, and As atoms. The exchange and correlation interactions between the valence electrons were treated using the Ceperley–Alder potential[20] as parametrized by Perdew and Zunger.[21]

Plane waves were used to construct the valence electron wave functions. Because plane waves are independent of the positions of the atoms in the unit cell and do not bias the electronic wave functions (and, therefore, the electronic charge density) in any way, plane wave basis

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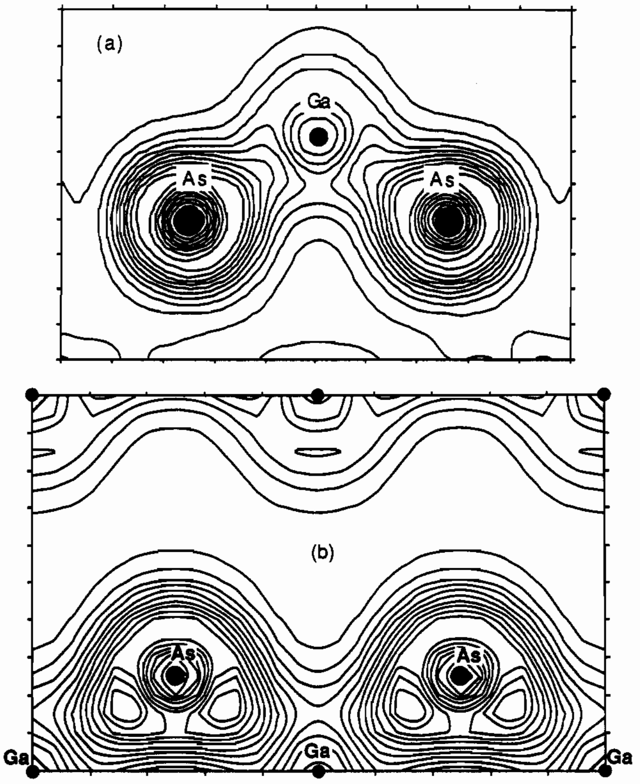

Figure 3. Total valence electron charge density along two of the Ga–As bonds in (a) the $GaAs_4$ tetrahedra of $Ca_{14}GaAs_{11}$ and (b) the GaAs crystal.

functions are useful for determining the bonding properties of solid systems. Plane waves with kinetic energies up to 12.3 Ry (~3200 plane waves) were included in the calculation, and the convergence of the electronic eigenvalues with respect to plane wave basis size was better than 10^{-3} Ry.

Finally, in the iterations to self-consistency, the charge density was approximated by its value at the Γ point of the Brillouin zone.[22] This approximation has been found to be sufficient to determine the qualitative features of the bonding in a solid.

Results and Discussion

We begin by showing that the Zintl concept does provide a reasonable description of the electronic structure and bonding in the $Ca_{14}GaAs_{11}$ crystal. Specifically, a contour plot of the total valence electron charge density is shown in Figure 2. The plane of this plot contains two Ca atoms, the Ga from the $GaAs_4$ tetrahedron, and the central As from the linear As_3 unit. In this figure, the total valence charge density is a minimum near the locations of the Ca atoms, whereas the charge density is a maximum on the $GaAs_4$ tetrahedron and the As_3 groups. This contour plot indicates that valence electrons have been transferred from the Ca's to the polyatomic units to form Ca cations and polyatomic anions. The Zintl concept therefore does apply to the electronic structure of this main-group compound. Figure 2 also suggests that the $GaAs_4$ tetrahedron and the As_3 linear groups exist as isolated units in $Ca_{14}GaAs_{11}$ rather than as an extended network. This conclusion will be verified as the bonding properties of the two polyatomic groups are considered.

To investigate the bonding between the Ga and the As atoms in the $GaAs_4$ tetrahedron, we have plotted the total valence electron charge distribution along two of the Ga–As bonds in Figure 3a. Although most of the electronic charge is concentrated around the more electronegative As atoms, the presence of charge density along the Ga–As bonds indicates that these bonds also have a significant covalent component. In addition, the total charge contours are spherical around the As atom except along the Ga–As bonds. The $GaAs_4$ tetrahedra are therefore not bonded covalently to the other atoms in the reduced unit cell. The $GaAs_4$ groups do not participate in a 3-dimensional bonding network as is found, for example, in the GaAs semiconducting crystal. To provide a comparison with the GaAs crystal, the total valence charge density of a GaAs crystal is plotted in Figure 3b.[23] This plot shows the total charge density in a (110) plane which passes through both Ga and As atoms. The contours around the As atom in the GaAs crystal are not as spherical as in the $GaAs_4$ group because of the formation of Ga–As chains along the $[1\bar{1}0]$ GaAs crystal directions.

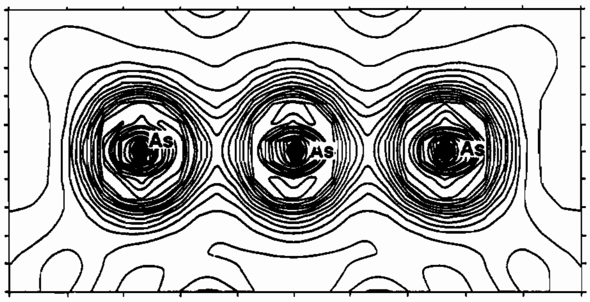

Figure 4. Total valence electron charge density in a plane which passes through all three As atoms in the linear As_3 group.

The Ga–As bonds in the $GaAs_4$ tetrahedron appear to be slightly more ionic than the Ga–As bonds in crystal GaAs. This appearance may result from a greater amount of electronic charge being concentrated around the As atoms in the tetrahedron as compared to the As atom in the GaAs crystal. Figure 2 indicates that valence electrons have been transferred from the Ca's to both the $GaAs_4$ and the As_3 units. In fact, if the Zintl concept is applied to this structure, the formal charge on the tetrahedron is predicted to be −9. Because the As atoms are more electronegative than the Ga atom, most of the transferred charge will be concentrated around the As atoms in the $GaAs_4$ tetrahedron. We therefore anticipate that the amount of charge on the As atoms in the $GaAs_4$ group is greater than the charge on the As atom in crystal GaAs. As a result, we expect the Ga–As bonds to be weaker in the $GaAs_4$ group than in the GaAs crystal. This conclusion is supported by the experimental result that the Ga–As bonds are longer in the tetrahedra (~2.532 Å[9,10]) than in the GaAs crystal (2.447 Å[24]). In conclusion, the $GaAs_4$ tetrahedra appear to be covalently bonded anions with most of the excess electronic charge on these groups concentrated on the more electronegative As atoms.

We next consider the linear As_3 group. Figure 4 shows the total valence electron charge density in a plane which passes through the three As atoms in this linear unit. As was found for the $GaAs_4$ tetrahedron, this As_3 group is isolated and not bonded covalently to the other atoms in the reduced unit cell. This figure also indicates that the As atoms in the As_3 group are bonded together to form a polyatomic anion.

As was mentioned in the Introduction, the bonding within the As_3 group might be described in one of two ways. First, the central As atom could be dsp^3 hybridized. The axial p orbitals on the apical As atoms would then overlap and form bonds with two of the dsp^3 hybrids. The remaining three dsp^3 hybrids would then be distributed around the central As atom in a plane perpendicular to the axis of the As_3 group. This model therefore correctly predicts the linear structure of the As_3 unit. Alternatively, the As_3 group could be modeled as a hypervalent, three-center, four-electron bonded structure. In this model, the axial p orbitals on each As atom overlap to form three molecular orbitals: a bonding orbital which localizes electronic charge between the atoms, a nonbonding orbital which is localized on the apical As atoms, and an antibonding orbital which diminishes electronic charge between the atoms (see Figure 5). All three of these molecular orbitals have σ symmetry with respect to the As_3 axis.

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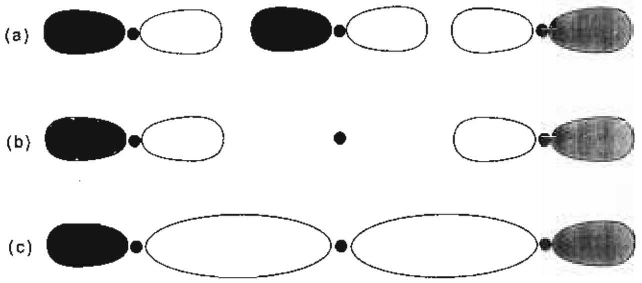

Figure 5. Molecular orbitals formed by overlap of the axial p orbitals on each As atom in the hypervalent three-center, four-electron bond model of the linear As_3 group: (a) an antibonding orbital which diminishes electronic charge between the atoms; (b) a nonbonding orbital which is localized on the apical As atoms; (c) a bonding orbital which localizes electronic charge between the atoms. All three of these molecular orbitals have σ symmetry with respect to the As_3 axis.

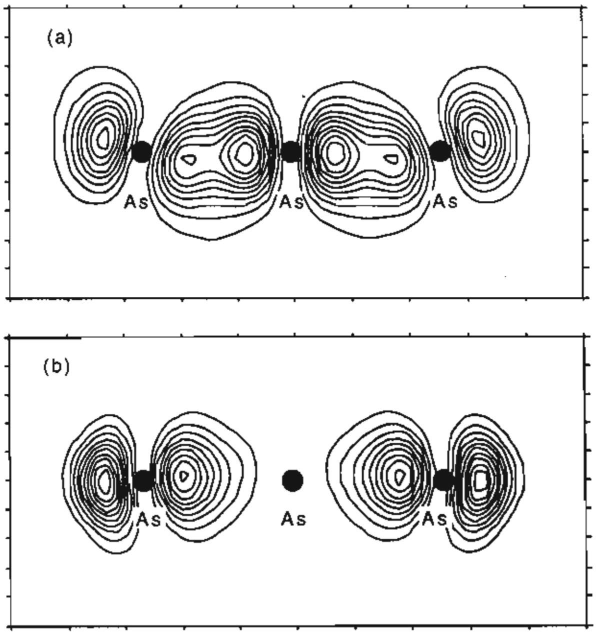

Figure 6. Charge density contour plots of (a) an electronic state 3.9 eV below the top of the valence band of $Ca_{14}GaAs_{11}$ and (b) the electronic state at the top of the valence band of $Ca_{14}GaAs_{11}$. The planes of these plots pass through the three As atoms in the linear group.

Since As_3^{7-} is isoelectronic with X_3^- (X = halogen), the bonding and nonbonding orbitals would be expected to be filled whereas the antibonding orbital would be expected to be empty.[11]

The individual electronic energy states were investigated for evidence to support either of the two possible models outlined above. Figure 6a shows a charge density contour plot for an electronic state which is deep within the filled valence band of $Ca_{14}GaAs_{11}$. Specifically, this state is 3.9 eV below the top of the valence band. (The valence band has a total width of 11.7 eV.) The plane of this plot is the same as in Figure 4 and passes through the three As atoms in the linear group. The charge density of this state is concentrated in the bonds between the As atoms and resembles a filled three-center, two-electron bonding orbital which was mentioned above. The distortion of this state from axial symmetry is most likely due to the presence of other atoms in the reduced unit cell.

A charge density contour plot of the state at the top of the valence band of $Ca_{14}GaAs_{11}$ is shown in Figure 6b. The plane of this plot is the same as in Figure 6a. The charge density of this state is localized on the apical As atoms and can be identified as a filled three-center, two-electron nonbonding orbital.

As illustrated in Figure 6, our results support the three-center, four-electron model of the bonding in the As_3 group. In addition, according to Cahill et al.,[11d] the defining characteristic of all hypervalent molecules is the presence of at least one occupied high-energy molecular orbital which is σ rather than π in symmetry with respect to a central atom to ligand bond. Figure 6b illustrates an occupied high-energy molecular orbital for the As_3 group which has σ symmetry. We therefore conclude that the As_3 unit is a hypervalently bonded, three-center, four-electron structure and that this structure type contains the first evidence of a hypervalent group 15 Pn_3^{7-} anion.

Our conclusion that the As_3 group can be described as a hypervalent anion is also supported by the experimentally determined As–As distance in the As_3 group. This distance is 2.956 Å,[10] a value which is considerably larger than a normal As–As single-bond length (about 2.4 Å[25,26]). This increased As–As bond length in the As_3 group is consistent with the presence of only one filled bonding orbital for the three-center, four-electron bond. (Two electrons occupy both the lower energy bonding state and the higher energy nonbonding state.) Since each As–As bond therefore only consists of 0.5 bond order, the As–As bond length is expected to be larger in the As_3 group than in the As–As single bond.

Finally, since we have shown that the bonding properties of $Ca_{14}GaAs_{11}$ are accurately described with the Zintl concept, we infer that the unexpected magnetic properties of the Mn analogues are not due to any anomalies in the valence bonding in this type of structure. Research on the $A_{14}MnPn_{11}$ and other transition-metal analogues is underway to further determine the properties and electronic requirements of this structure type.

Acknowledgment. We thank J. S. Nelson for technical assistance with the calculations and D. J. Webb for useful discussions. R.F.G. is supported in part by the U.S. Department of Energy under Contract W-ENG-7405-48. C.Y.F. is supported in part by the San Diego Supercomputer Center. S.M.K. is supported by NSF Grant DMR-8913831.

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