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Host−Guest Interactions, Uniform vs Fragmented Linear Atom Chains and Likeliness of Peierls Distortions in the $(Ca_7N_4)[M_x]$ (M = Ag, Ga, In) Phases[#]

Pere Alemany,*,[‡] Miquel Llunell,[‡] and Enric Canadell*,[§]

Departament de Química Física and Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain, and Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra, Spain

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The electronic structure of the recently reported $(Ca_7N_4)[M_x]$ (M = Ag, Ga, and In) phases has been studied by means of first principles density functional theory (DFT) calculations. It is shown that under the assumption of very weak host−guest interactions: (a) four calcium atoms per formula unit may be considered as $Ca^{1.5+}$, whereas the remaining three may be considered as Ca^{2+} so that the guest atoms would be neutral, and (b) the Peierls distortions which could set in the guest linear chains are unlikely. These results are compatible with the experimental information. However, the first principles DFT calculations clearly show that very sizable host−guest interactions occur and drastically modify this situation. As a result, there is a substantial electron transfer from the framework to the guest atoms, and all calcium atoms of the framework are better described as Ca^{2+}. The stoichiometry and structure of these systems result from a competition between the natural tendency of the bare guest atoms to form uniform linear chains within the reduced space of the channels and the attempt to optimize their positions within the channels through interactions with the calcium atoms. Model calculations suggest that indium has a weaker tendency to form uniform linear chains and interacts in a stronger way with the host. It is shown that, for the $(Ca_7N_4)[M_{1.33}]$ (M = Ag and Ga) phases, a structure built from three repeat units of the Ca_7N_4 host framework containing uniform linear chains with a repeat unit of four guest metal atoms is compatible with the strong interaction scenario and the lack of correlation between the different linear guest chains. These phases should be metallic conductors, and the carriers have both host and guest character. In contrast, the guest atoms in $(Ca_7N_4)[In_{1.0}]$ prefer to occur as a series of trimeric units. Although this phase is found to have a metallic band structure, the conductivity should be smaller than those of the $(Ca_7N_4)[M_{1.33}]$ (M = Ag and Ga) phases.

Introduction

Alkaline-earth nitrides exhibit a remarkable crystal chemistry. Among them, the strontium−nitrogen binary system is especially interesting. For a long time Sr_2N, with a $CdCl_2$ type structure, was the only well characterized strontium−nitrogen binary.[1] However, Kniep and co-workers[2,3] showed that at least three more exist: Sr_4N_3, SrN, and SrN_2. In these phases, the strontium atoms are found at the vertices of the octahedra in a $CdCl_2$ type structure, and the nitrogen atoms appear either as nitride N^{3-} or as diazenido N_2^{2-} anions lying in the octahedral holes of the structure. Simple electron counting arguments suggest that, whereas strontium is formally found as Sr^{2+} in SrN_2 $[(Sr^{2+})(N_2^{2-})]$ and SrN $[(Sr^{2+})_4(N^{3-})_2(N_2^{2-})]$, it is found in the more unusual $Sr^{1.5+}$ oxidation state in Sr_2N $[(Sr^{1.5+})_2(N^{3-})]$ and Sr_4N_3 $[(Sr^{2+})_4(Sr^{1.5+})_4(N^{3-})_4(N_2^{2-})]$. Although a clear electronic explanation is still lacking, this unusual oxidation state has

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[#] Dedicated to Professor Sason Shaik on the occasion of his 60th birthday.

* To whom correspondence should be addressed. E-mail: p.alemany@ub.edu (P.A.), canadell@icmab.es (E.C.). Telephone: +34 93 402 1239 (P.A.), +34 93 580 1853 (E.C.). Fax: +34 93 402 1231 (P.A.), +34 93 580 5729 (E.C.).

[‡] Universitat de Barcelona.

[§] ICMAB (CSIC).

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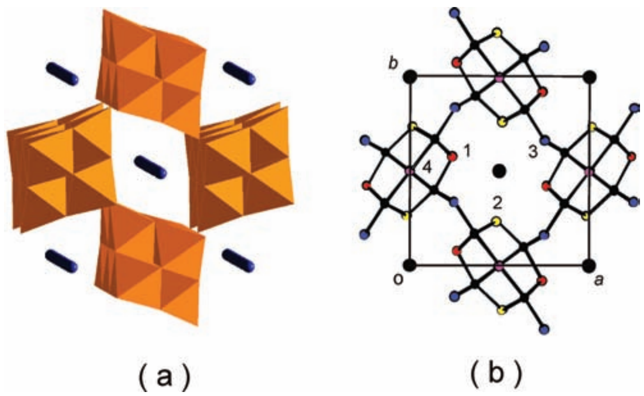

Figure 1. Crystal structure of the $(Ca_7N_4)[M_x]$ (M = Ag, Ga, In, and Tl) phases:[4] (a) view from a direction slightly tilted from the *c* axis; (b) projection of the structure along the *c* direction in which the four different types of calcium atoms are labeled. The red (Ca1) and yellow (Ca2) calcium atoms were assigned a charge of 1.5+ in the original structural report, whereas those in blue (Ca3) and purple (Ca4) were assigned a charge of 2.0+. The small and large black circles are the nitrogen and M atoms, respectively.

been considered to be a property of strontium atoms, which are associated with three condensed nitride-centered strontium octahedra.[3,4]

Many ternary alkaline-earth nitrides with main group or transition metal atoms are built from an elementary building block, which consists of a nitride ion surrounded by an octahedron of alkaline-earth atoms. Condensation of these elementary building blocks in different ways leads to a series of networks with cavities where the main group or transition metal atoms reside. A series of remarkable species of this type, $(Ca_7N_4)[M_x]$ (M = Ag, Ga, In, and Tl), has been recently reported.[4] These phases exhibit an orthorhombic structure with a Ca_7N_4 framework with open channels in which the metal atoms reside (see Figure 1). The Ca_7N_4 framework results from the condensation of 2 × 2 chains of edge- and corner-sharing nitride-centered calcium octahedra in such a way that large channels running along the *c* direction are built. It has been suggested that inside these channels there are uniform linear chains of Ag ($x \approx 1.36$) and Ga ($x \approx 1.33$), but only metal-chain fragments for In ($x \approx 1.02$) and Tl ($x \approx 0.97$).[4]

There are a number of quite fundamental questions that are brought about by these phases, and we would like to address them in this work. To begin with, there is the question of electron counting. Based on the above-mentioned observations on the strontium−nitrogen binary phases, Kniep et al.[4] assumed that two of the four crystallographically nonequivalent calcium atoms are found as Ca^{2+} (blue and purple in Figure 1b) and the other two as $Ca^{1.5+}$ (red and yellow in Figure 1b). This is an important point because it leads to the conclusion that the metallic guests are neutral. Based on the incommensurate host−guest arrangement and the lack of correlation between the guest chains in different channels (at least for the silver compound), as well as model density functional theory (DFT) type calculations, Kniep et al.[4] concluded that there is a weak host−guest interaction in these materials. However, this leads to a serious question concerning the fact that the silver chains in the channels seem to be linear and uniform. Silver, with a complete d block and a single electron in the s orbital, is a textbook case of a system that should undergo a Peierls type dimerization[5] when occurring as linear uniform chains. But, this seems not to be the case, and the system is metallic. The simplest explanation one can think is that the host−guest interaction is stronger than assumed, and there is a strong restoring force against the dimerization, which more than compensates for the electronic energy lowering provided by the silver chain dimerization. However, note that this strong interaction would implicate a considerable mixing of the silver chain orbitals with those of the Ca_7N_4 framework, and consequently, the silver atoms in the chain would not really be neutral as initially concluded. Another explanation would be that the initial counting for the Ca_7N_4 framework is not operative, and thus, the silver chain is not a half-filled band system (for instance, assuming that all calcium atoms are 2+, silver would have a partially filled p block). In that case, there is no need to assume sizable host−guest interactions to provide a rationalization since band occupations which are not integer fractions are associated with incommensurate modulations, and the driving force is considerably weaker in that case.[6] Finally, one could think that the host−guest interactions are indeed weak, but the energetic stabilization due to the Peierls dimerization is very small so the distortion either does not set in or is difficult to detect under the experimental conditions. It is clear that the nature of the host−guest interaction and the oxidation state of the calcium atoms are important features to consider before any attempt to understand the structure and transport properties of this phase may be attempted. Maybe even more surprising is the fact that the gallium and silver phases are similar, i.e., they both have uniform linear guest chains and are metallic despite the different atomic configuration of the guest atoms. In contrast, the indium and thallium phases have a different stoichiometry and exhibit broken guest chains and activated conductivity.

Because of the different values of *x* for different guest atoms, it is not easy to address theoretically the problems raised by these interesting phases. In this work, we report first principles DFT calculations for different commensurate systems modeling these phases to provide some understanding of (a) the oxidation state of the different calcium atoms, (b) the strength of the host−guest interaction, (c) the likeliness of a Peierls distortion in these phases, (d) the origin of the differences between the silver/gallium and indium phases, and (e) the nature of the fragments in the indium phase.

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Computational Details

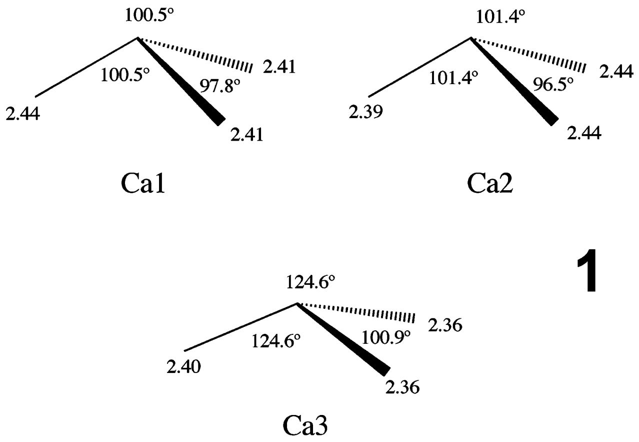
The first principles calculations for different models of (Ca_7N_4)[M_x] (M = Ag, Ga, and In) were carried out using a numerical atomic orbitals DFT approach,[7] which was developed for efficient calculations in large systems and implemented in the SIESTA code.[8−10] We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke, and Ernzerhof.[11] Only the valence electrons are considered in the calculation with the core being replaced by norm-conserving scalar relativistic pseudopotentials[12] factorized in the Kleinman−Bylander form.[13] Nonlinear partial core corrections to describe the exchange and correlations in the core region were used for Ag, Ga, In, and Ca.[14] We have used a split-valence double-ζ basis set, including polarization orbitals for all atoms as obtained with an energy shift of 100 meV.[15] The 4d orbitals of Ag and the 3d orbitals of Ca and Ga were considered explicitly in the calculations. The energy cutoff of the real space integration mesh was 150 Ry. Appropriately converged meshes of *k*-points[16] were used to sample the Brillouin zone of the different one-dimensional and three-dimensional models.

Results and Discussion

Host Ca_7N_4 Framework. As shown in Figure 1b, there are four different calcium atoms in the Ca_7N_4 framework. In the original structural report Ca1 and Ca2 (red and yellow atoms in Figure 1b) were assumed to be $Ca^{1.5+}$, whereas Ca3 and Ca4 (blue and purple atoms in Figure 1b) were considered to be Ca^{2+}. Ca4 is clearly structurally different from the other calcium atoms because it is shared by six octahedra so that it lies at the center of regular octahedra of nitrogen atoms. For the other three, the calcium atom is coordinated to three nitrogen atoms in a pyramidal geometry (see Scheme 1). Because of the higher coordination, the calcium orbitals of Ca4 must lie higher in energy than those of the other three calcium atoms, and, thus, it is natural to assume a Ca^{2+} oxidation state for Ca4. The situation is less clear cut for Ca1, Ca2, and Ca3. As shown in Scheme 1 (the structural details belong to the gallium compound, but they are very similar for all phases), the three calcium atoms are coordinated in a similar way by the nitrogen atoms. It is true that Ca1 and Ca2 are very similar, and they are in the same local environment as the strontium atoms in Sr_2N (i.e., as in the outer layers of the $CdCl_2$ type structure), whereas Ca3 plays a different structural role (i.e., connects different 2 × 2 chains), and this leads to a less acute pyramidalization. In principle, the smaller pyramidalization should keep the Ca s (+λp) orbital of Ca3 higher in energy because it is less stabilized through the smaller hybridization with the p orbital, which could justify a weaker participation in the filled levels of the system and a higher oxidation state. Thus, there are structural similarities but also differences among the three calcium atoms.

Table 1. Calculated Valence Electron Populations for the Different Atoms of the Ca_7N_4 Frameworks with the Geometry Found in the (Ca_7N_4)[M_x] (M = Ga and In) Compounds

	electron population	
atom	(M = Ga)	(M = In)
Ca1	1.65	1.66
Ca2	1.62	1.64
Ca3	1.25	1.23
Ca4	1.10	1.10
N1	5.95	5.95
N2	5.97	5.97



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Shown in Table 1 are the results of a Mulliken population analysis of the Ca_7N_4 framework of the gallium and indium compounds. The two sets of results are very similar (as they are for the silver compound) so that from now on, unless otherwise stated, we will only report the calculations for the gallium compound. The important result of Table 1 is that there is a significant difference, not far from 0.5 e, between the populations of the Ca1/Ca2 and Ca3/Ca4 atoms. These results, thus, provide a basis for the electron counting proposed by Kniep et al.[4]

However, let us remind that these results imply a nil host−guest interaction. Before examining to what extent this assumption may be valid by analyzing the results of DFT calculations for complete host−guest systems, we must see how these results translate into band structure calculations. In addition, an interesting question arises concerning the possible contribution of the Ca_7N_4 framework to the electrical conductivity of these materials. In principle, since a repeat unit of the solid contains two equivalent chains and each chain contains two Ca1 and Ca2 atoms, the s block Ca bands will appear as four pairs of bands and, thus, can be filled with 16 electrons per repeat unit. However, they contain only four electrons, so that it is one-quarter filled. Thus, it will crucially depend on the inner distortions of the chain whether the separation between the lower pair of bands and the next one is large enough or not. In the first case, there will be a

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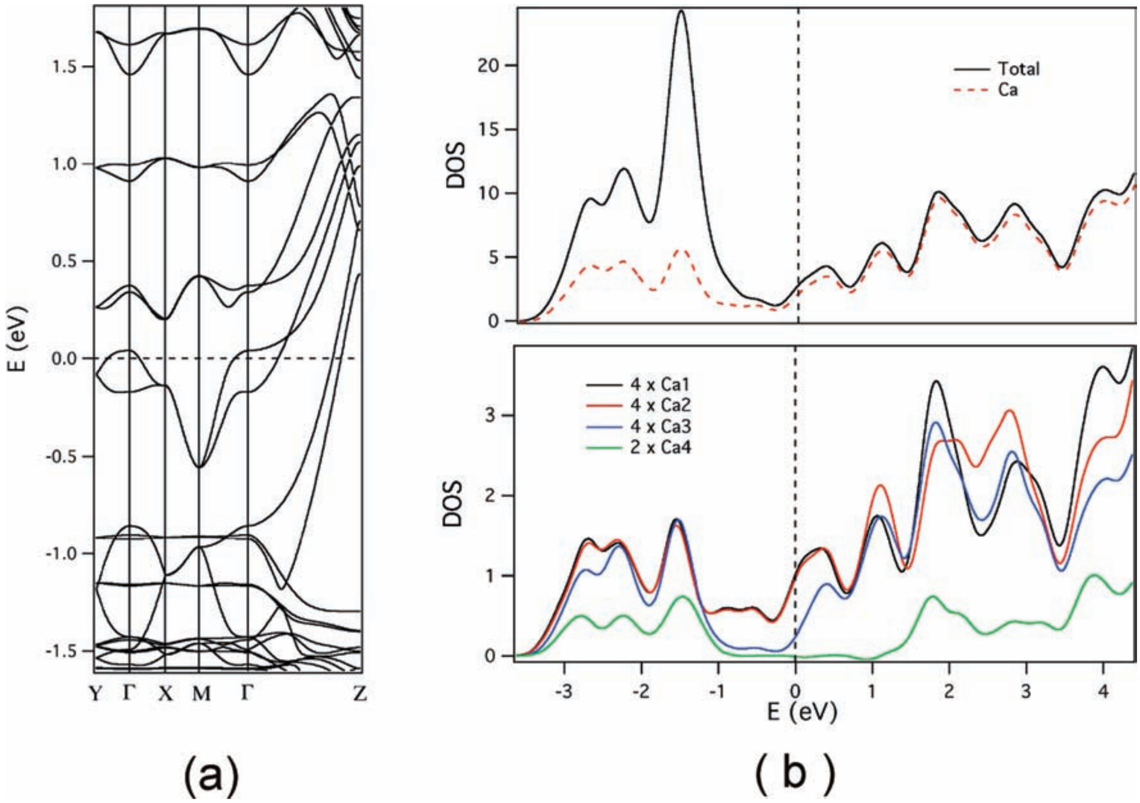

Figure 2. Calculated band structure near the Fermi level (a) and density of states (b) for the Ca_7N_4 isolated framework in the $(Ca_7N_4)[M_x]$ (M = Ga, $x \approx 1.33$) compound. The dashed line refers to the Fermi level and Γ = (0, 0, 0), X = (1/2, 0, 0), Y = (0, 1/2, 0), Z = (0, 0, 1/2), and M = (1/2, 1/2, 0) in units of the orthorhombic reciprocal cell vectors.

gap at the Fermi level, and the Ca_7N_4 framework will not contribute to the possible metallic conductivity of the compounds, whereas in the latter case, it will.

Shown in Figure 2 are the calculated band structure near the Fermi level for the empty Ca_7N_4 framework, as well as the density of states (DOS) and different local projections useful for a chemical analysis of these results. The band structure of Figure 2a shows that four different bands cross the Fermi level. Thus, the isolated Ca_7N_4 framework should be already metallic. This is a consequence of the overlap of the two highly dispersive lower bands along $\Gamma \rightarrow Z$, which overlap with the next pair of bands. Note that the ratio between the band dispersion along the chain and interchain directions is not too large (i.e., approximately two and four for the upper and lower pairs of partially filled bands, respectively) so that although the isolated framework should be better conducting along the chain direction, it is really a three-dimensional conductor. The DOS results of Figure 2b are very clear in showing that there are two electronically different types of calcium atoms in the framework. As expected, the DOS above the Fermi level is dominated by the calcium orbitals and below the Fermi level by the nitrogen ones. However, the calcium atoms' contribution to the filled levels is very substantial, suggesting a quite important covalent contribution to the bonding within the Ca_7N_4 framework. Let us note that the calculated charges for the calcium atoms (between +0.90 and +0.35, see Table 1) are significantly smaller than those calculated with the same computational details for a typically ionic system as CaF_2 (+1.11). The interesting result of Figure 2b is that when looking at the different calcium contributions, the region between the Fermi level and 1 eV below exhibits a large difference among the Ca1/Ca2 and Ca3/Ca4 contributions. There is a very small contribution of the Ca3/Ca4 atoms while there is a sizable one of the Ca1/Ca2 (when comparing the different calcium contributions of Figure 2b note that there are four calcium atom of types 1, 2, and 3 per unit cell, but only two of type 4). It is mostly that region of the DOS which is responsible for the different oxidation state of the Ca1/Ca2 and Ca3/Ca4 atoms. The bands carrying out the two pairs of extra electrons, i.e., those resulting from a standard electron counting analysis in which all calcium atoms would be considered as 2+, which are the four lower partially filled bands of Figure 2a, strongly concentrate in Ca1 and Ca2. Thus, these atoms are less positively charged than Ca3 and Ca4. However, further analysis of this region of the DOS shows that these levels have large contributions of the s and p_x/p_y orbitals of Ca1/Ca2 (the p_z orbitals are directed along c), so that they are very well prepared to interact with the atoms filling the channels.

In conclusion, the results of this section provide an electronic basis for the different oxidation state for the Ca1/Ca2 and Ca3/Ca4 atoms of the Ca_7N_4 framework suggested by Kniep et al.,[4] if there are very weak host−guest interactions. However, they also suggest that there may be important host−guest interactions strongly implicating Ca1 and Ca2, which could considerably alter this conclusion.

Isolated Guest Chains. We now consider the isolated chains of silver, gallium, and indium atoms because we need to know their relative tendency to form uniform chains within

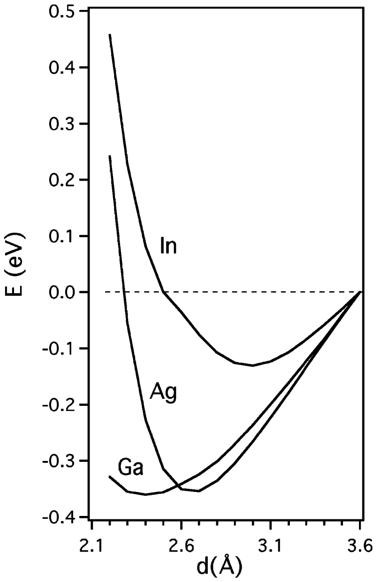

Figure 3. Relative energies per atom for the isolated uniform linear chains of silver, gallium, and indium atoms with respect to the chain with interatomic distance 3.6 Å, i.e., the distance they would have in a phase with the Ca_7N_4[M] stoichiometry.

the channels. Let us emphasize that we use isolated linear chains as an approximation to the weak host−guest interaction case. We first consider the stability of the different uniform linear chains as a function of the interatomic distance with respect to the situation in which there would be just one atom per repeat unit of the channel (i.e., $x = 1$). Shown in Figure 3 are the calculated energy per atom vs interatomic distance curves for the uniform linear chains taking the chain with interatomic distance 3.6 Å, i.e., the distance they would have in a phase with the Ca_7N_4[M] stoichiometry, as the reference. The calculated equilibrium distances are 3.0, 2.7, and 2.4 Å for In, Ag, and Ga, respectively. The values for In and Ag are in good agreement with those calculated by Kniep et al.[4] (3.05 and 2.66 Å, respectively) with a different implementation of DFT. In contrast, the calculated value for Ga clearly differs, 2.40 vs 2.78 Å. Although the similarity in the values for Ag and Ga was used by these authors to rationalize the similar value of x for the two compounds, we believe that the present values are more reasonable. It is well known that both the atomic and covalent radii of Ag and Ga differ by ~0.3 Å,[17] the values for Ga being smaller. This is also the difference in our calculated values of the optimal interatomic distance in the Ag and Ga uniform linear chains. Anyway, the calculation of a larger value for Ga than Ag in ref 4 seems at odds with this basic information. In addition, a Ga−Ga distance of 2.78 Å is larger than the distance in the elemental gallium, which is not reasonable since the number of neighbors is smaller in the chain. To have a better appreciation of this feature, we optimized the structure of elemental Ag, In, and Ga using exactly the same computational approach as for the chains. For Ag, we calculated an interatomic distance of 2.97 Å which is 3% larger than the experimental value, 2.88 Å.[17] For In, we calculated an In−In distance of 3.38 Å which is 4% larger than the experimental value of 3.25 Å.[17] Finally, elementary gallium has a slightly more complex structure in which the shorter interatomic distance is 2.48 Å, and then there are a series of Ga−Ga distances around 2.7 Å.[17] Our shortest Ga−Ga calculated distance was 2.55 Å, which is 2.7% larger than the experimental value. Thus, we confirmed that the Ga−Ga distance should be shorter than the Ag−Ag one. Let us note that these values, obtained with the same computational details that we used for relatively large commensurate models of the (Ca_7N_4)[M_x] (M = Ag, Ga, and In) phases, seemed to be mutually consistent, since the relatively small error in the three systems is very similar.

Looking at the optimized M−M distances we would predict that the x values for Ag, Ga, and In, assuming weak host−guest interactions, would be approximately 1.33, 1.5, and 1.2 Å, respectively. The calculated value for silver was in excellent agreement with the experimental one. As done by Kniep et al.,[4] this result can be taken as suggestive of very weak host−guest interaction in that case. However, for both gallium and indium, the agreement was not as good, and this observation may cast a shadow on the validity of the weak host−guest scenario (at least for the group 13 atoms). Note that in Figure 3 the relative stabilization energy for gallium with a Ga−Ga distance of 2.7 Å (i.e., leading to a value of $x \approx 1.33$) is only slightly smaller than that for the optimized distance. In other words, if there is something besides the stability of the chain which favors occupation of the channels with x values around 1.33 (see later), then it will be easy in the gallium case to also adopt this stoichiometry. It is worth noting that the relative stabilization energies of Figure 3 are very similar for the silver and gallium chains, whereas for the indium chain it is clearly smaller (i.e., less than half). The calculated relative stabilization energies are −0.36, −0.35, and −0.13 eV/atom. Of course, this is largely a result of the smaller size of silver and gallium. For (Ca_7N_4)[M_x] phases of silver and gallium with x values around 1, a uniform distribution of guest atoms is not very favorable because they are too far apart, and, thus, there will be a definite tendency to increase the x value. In the case of indium, there is also some tendency to increase the x value, but since the energy gain would be considerably smaller, it is likely that a fragmented chain situation with smaller indium content may become an alternative. Thus, assuming weak host−guest interactions, it appears that the tendency to form uniform linear chains should be similar for silver and gallium, but substantially less for indium (and presumably thallium).

Peierls Distortions in the Guest Chains. We now consider the likeliness of Peierls distortions in these isolated linear chains. Kniep et al.[4] first proposed, and the results of the previous section seem to confirm the idea, that the weak host−guest scenario applies for the silver compound. Since silver possesses just one electron to fill the s level, the s band of the uniform linear chain of silver atoms should be half-filled. This is the typical situation were a Peierls distortion (i.e., a dimerization in this case) occurs. However, analyzing the experimental data, this does not seem to be the case. On the other hand, if the weak host−guest scenario

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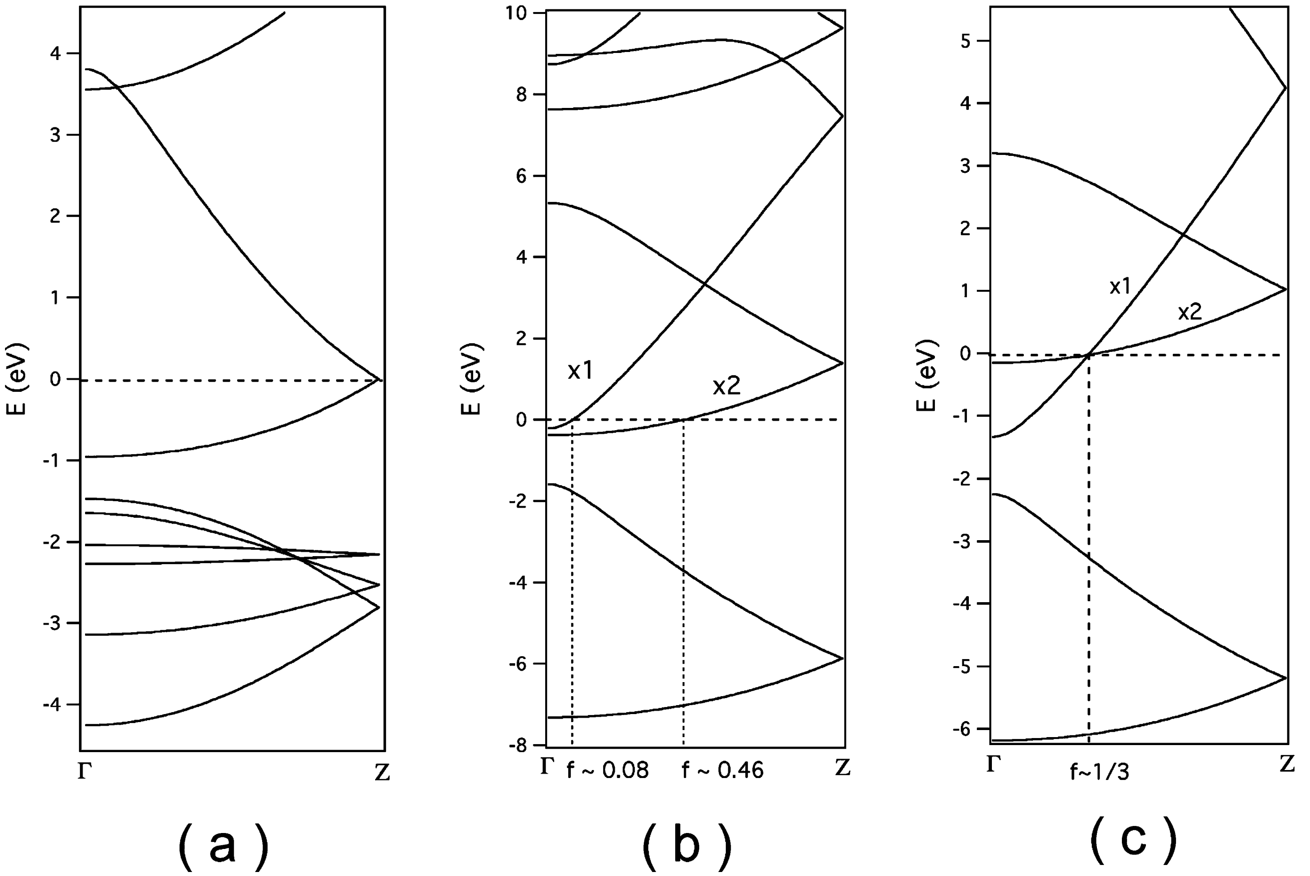

Figure 4. Calculated band structure for the uniform linear chains of silver (a), gallium (b), and indium (c) at their optimized structures using a double unit cell. The dashed lines refer to the Fermi level. In (b) and (c) × 2 and × 1 refer to the degeneracy of the p-type bands.

was valid for the phases with the group 13 atoms, then it is difficult to understand why the gallium phase exhibits uniform linear guest chains, whereas the indium (and thallium) phase contains fragmented chains. One could think that this fragmented chain results from a Peierls distortion, which does not condense in the gallium phase. The question is why, having the same electron count, the gallium and indium chains behave differently. Thus, this point deserves some discussion.

Since the d block is completely filled, the chain of silver atoms is in principle equivalent to the hydrogen atom chain. The band structure in Figure 4a, which was calculated using a double unit cell and a Ag−Ag distance of 2.7 Å, shows that this is indeed the case. However, when we carried out structural optimizations allowing the dimerization, we found that the lowest energy structure is indeed that of the uniform chain. Of course, the dimerization opens gaps at the border of the Brillouin zone, but the gaps are small and, thus, are associated with a small energy gain, which does not compensate for the cost in elastic energy. A careful study showed that our calculations are well converged. We note that a negligible stabilization only for stretched chains has been reported for the linear gold chain.[19] We believe that this unexpected result mostly originates from d−s mixing. The d block bands lie immediately below the bottom part of the s band (see Figure 4a), and the d−s interaction does not allow the opening of a sizable gap under dimerization. This leads to a very small electronic stabilization, which does not compensate for the loss in elastic energy.[20] In addition, the d^{10}−d^{10} repulsions strongly disfavor the dimerization providing a substantial contribution to the elastic force opposing the distortion. Thus, this finding seemingly solves one of the apparent contradictions raised in the Introduction: in principle, there is no conflict in assuming a weak host−guest interaction and noticing the metallic behavior and the absence of a Peierls distortion in the silver compound.

The situation is different for the chains of the group 13 atoms. Here, two of the three valence electrons will fill the s band, and the remaining electron will be most likely shared by the three p bands. In the case of the uniform linear chain, two of the bands (the π type bands) are degenerate, while the other is implicated in σ-type interactions and is more dispersive. Because of the symmetry of the chain, the s band can interact with the p_σ band, but not with the p_π bands. Thus, although the p_σ band is more dispersive than the p_π, the lower region will be raised by the s−p interaction so that the bottom part of the three bands will not lie very far and the remaining electron will be shared by the three bands.

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[20] For a more in depth analysis of the reasons behind the absence of a Peierls distortion in uniform linear chains of the group 11 atoms see: Alemany, P.; Llunell, M.; Canadell, E. *Theor. Chem. Acc.* **2009**, in press.

How the electron is distributed among the three bands depends on the nature of the atom, the atom–atom distance, and the extent of s–p mixing. The band structures calculated for the uniform linear chains of gallium and indium at their optimized geometries are shown in Figure 4b,c. For gallium (Figure 4b) the overlap is such that each of the two p_π bands is 46% filled (i.e., $2k_f = 0.46$), and the p_σ band is 8% filled (i.e., $2k_f = 0.08$). If only the p_σ band had been occupied (i.e., 50% filled), then $2k_f = 0.50$, and since our unit cell contains two atoms a tetramerization would be expected. Note that even if the 3d electrons were explicitly included in the calculations, the associated bands are much lower in energy, and, thus, in contrast with the situation for the silver chains, they do not play an important role in the discussion.

In the case of the indium chain the occupation of the p_σ band increases, whereas that of the p_π bands decreases, such that for the particular case of the In–In equilibrium distance, the occupation is approximately 33% for each of the three bands. The difference in band filling between the gallium and indium chains originates from the stronger interactions in the gallium case, but also from the stronger s–p mixing, which pushes the bottom of the p_σ band at approximately the same energy as the bottom of the p_π bands. In the indium chain, the situation is more usual with the bottom of the p_σ band lower in energy than the bottom of the p_π bands. Not much attention should be paid to the fact that the occupation of the three bands is practically the same for the indium chain, since this will change with small variations of the In–In distance. For instance, with the 3.6 Å distance (the periodicity of the host) the occupation would be 23% (i.e., $2k_f = 0.23$) for each of the two p_π bands and 54% (i.e., $2k_f = 0.54$) for the p_σ band. It is quite clear that since there is one electron to be shared by three bands, in general, the filling of the bands for the group 13 atoms will not be given by the inverse of an integer number, and, consequently, the kind of Peierls distortions which could occur in these chains would be incommensurate. Since, as mentioned above, the driving force for these structural modulations is considerably smaller than those for typical dimerizations,[6] it is very likely that they will not occur for the linear chains of group 13 atoms.[21] In short, the absence of a Peierls distortion in the silver and gallium chains of the $(Ca_7N_4)[M_x]$ phases, although having a different origin, seems not to be in contradiction with the weak host–guest scenario. Thus, at this point of the discussion, we crucially need to assess the strength of the host–guest interactions.

Host–Guest Interaction. To have a hint on the strength of this interaction, we started carrying out a calculation for $Ca_7N_4[M]$ (M = Ag, Ga, and In) in which we kept the structure of the Ca_7N_4 framework constant, and the M atom was displaced along the *c*-direction through a line just at the center of the channels. The origin of the atomic displacement ($r = 0.0$) was taken in the plane containing the Ca1 and Ca2 atoms (see Figure 1). The plane at $r = 1.8$ Å is the plane of the Ca3 atoms. The results are shown in Figure 5a where it is clear that for the three different atoms the behavior is qualitatively similar. The energy values in this figure clearly prove that *there is a very sizable interaction between the Ca_7N_4 framework and the guest atoms*. The more favorable situation for all three guest atoms is to lie at the center of the plane of the two Ca3 atoms. However, it is also clear that there is a quantitative difference between both the gallium and silver atoms and the indium atoms, which goes through a larger barrier when moving along the *c*-direction. In other words, it is more difficult to move the indium atoms from their equilibrium position than it is for the gallium and silver atoms. Because of the strength of these host–guest interactions, it is clear that they will be in competition with the tendency of the guest atoms to form linear chains, and, consequently, they must definitely be taken into account when discussing the structure of these phases.

Before having a closer look at this point, we need to have a working knowledge of this interaction. This is easily done by looking at the DOS diagrams in Figure 5b–d, which correspond to the case of gallium at the center of the plane defined by the Ca3 atoms (the DOS diagrams do not qualitatively depend on the nature and position of the guest atoms). Several observations can easily be made. First, the participation of the calcium and gallium atoms is very similar at the Fermi level (see Figure 5b). This may have important consequences in understanding the transport properties. Second, the fact that the calcium and gallium contributions overlap for a broad energy range is not due to a mere superposition of contributions, as would be the case in the very weak host–guest interaction scenario, but to a real orbital mixing leading to bonding interactions as shown by the results of an overlap population analysis (see Table 2). These overlap populations indicate strong bonding interactions. Third, the partial DOS for Ca1, Ca2, and Ca3 (see Figure 5c) now practically overlap all along the region of the occupied states. Thus, there is no reason to expect a different oxidation state for these calcium atoms anymore. Fourth, comparing Figures 5c and 2b, it is clear that the partial DOS of Ca4 is kept unaltered. At the same time, it is also clear that the Fermi level has been lowered by approximately 1 eV (when comparing the two figures keep in mind the energy scale is set at zero at the Fermi level for each calculation) since it is now placed at the point that the Ca4 partial DOS becomes practically nil, whereas in the isolated framework, it was 1 eV above this point. This means that there is an important depopulation of the Ca1 and Ca2 atoms, which are those contributing almost exclusively to the filled levels after this point for the isolated Ca_7N_4 framework. Consequently, their oxidation states should become similar to that of Ca3. Although not shown in Figure 5, the nitrogen levels stay unaltered so that there must be an important electron transfer from the Ca1 and Ca2 atoms of the framework to the gallium atoms. All these observations are substantiated by the valence electron populations of Table 3. Fifth, the nature of the gallium levels that receive the electrons is somewhat dominated by the p_x and p_y contributions (note that we represent the total p_x and p_y contribution and the isolated p_z one), which are implicated in the

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(21) For a similar discussion in the case of zigzag chains of group 13 atoms see: Alemany, P.; Llunell, M.; Canadell, E. *Inorg. Chem.* **2005**, *44*, 374.

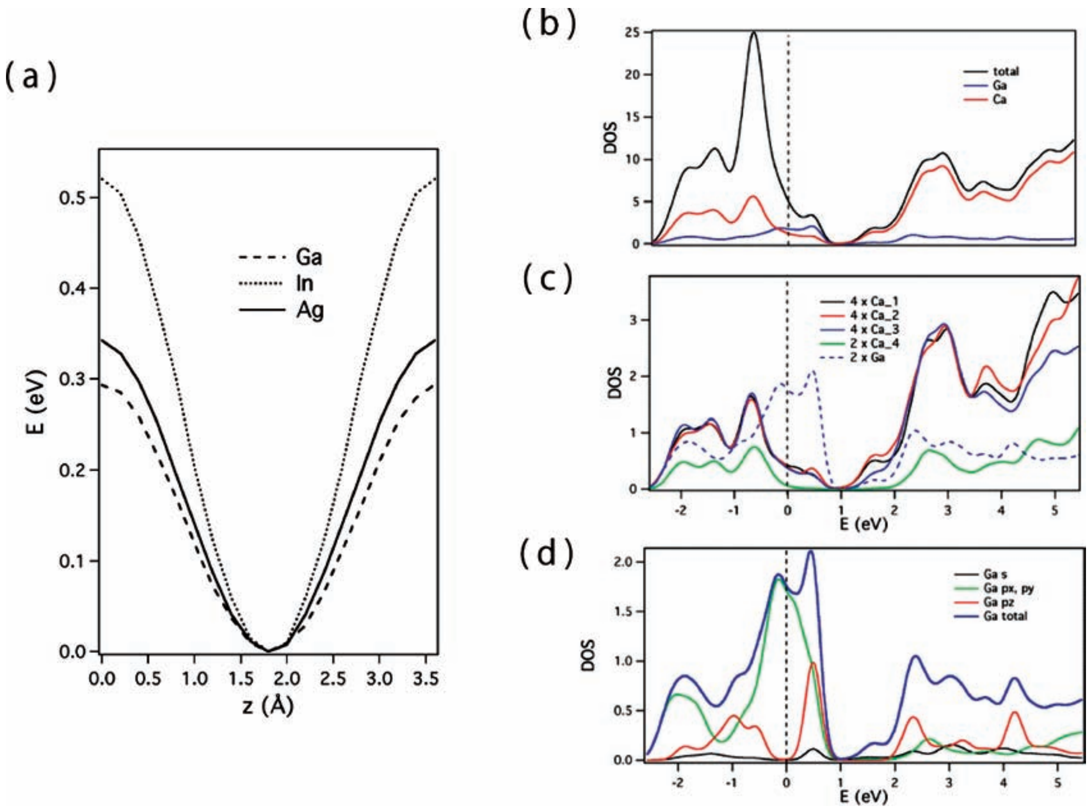

Figure 5. (a) Energy of the Ca_7N_4[M] system as a function of the position of the M atom along the chain line. The energy zero corresponds to the situation in which the M atom sits at the center of the plane defined by the Ca3 atoms ($r = 1.8$) (see Figure 1). (b) Density of states for the Ca_7N_4[M] system where M is gallium and sits at the center of the plane defined by the Ca3 atoms ($r = 1.8$). Shown in (c) and (d) are local projections associated with different calcium and gallium contributions.

Table 2. Calculated Mulliken Overlap Populations for the Different C(i)−M Interactions in the (Ca_7N_4)[M] (M = Ag, Ga, and In) Model Compounds[a]

X−M interaction	(Ca_7N_4)[Ga]	(Ca_7N_4)[In]	(Ca_7N_4)[Ag]
	M at $r = 0.0$ Å		
Ca1−M	0.149	0.148	0.125
Ca2−M	0.143	0.135	0.122
$Ca3_s$−M	0.029	0.038	0.029
$Ca3_l$−M	0.000	0.001	0.000
	M at $r = 1.8$ Å		
Ca1−M	0.079	0.079	0.070
Ca2−M	0.074	0.077	0.067
$Ca3_s$−M	0.066	0.070	0.051
$Ca3_l$−M	0.006	0.013	0.007

[a] The $Ca3_s$ and $Ca3_l$ labels refer to the Ca3 atoms whose distance to the center of the $r = 1.8$ Å plane is short and long, respectively (see Figure 1).

Table 3. Calculated Valence Electron Populations for the Different Atoms of the (Ca_7N_4)[M] (M = Ag, Ga, and In) Model Compounds with M at $r = 1.8$ Å and the Isolated Ca_7N_4 Framework of (Ca_7N_4)[$Ga_{1.33}$]

atom	Ca_7N_4	(Ca_7N_4)[Ga]	(Ca_7N_4)[In]	(Ca_7N_4)[Ag]
Ca1	1.65	1.36	1.31	1.42
Ca2	1.62	1.33	1.29	1.39
Ca3	1.25	1.35	1.35	1.36
Ca4	1.10	1.15	1.16	1.15
N1	5.95	5.95	5.96	5.95
N2	5.97	5.98	5.99	5.98
M	–	3.91	4.02	1.66

interaction with the Ca3 atoms, but there is also a considerable participation of the p_z orbitals, which are used together with the p_x and p_y to interact with the Ca1 and Ca2 atoms (we are examining the results for Ga atoms at $r = 1.8$Å). When the gallium atom moves toward $r = 0.0$ Å, there is a decrease of the participation of the p_z orbitals because the gallium atoms depart from the plane containing two interacting calcium atoms (Ca3) to go toward a plane containing four interacting calcium atoms (Ca1 and Ca2), and the decreased p_z participation allows keeping, as much as possible, the interaction with all atoms through a larger participation of the p_x and p_y orbitals.

The difference between the results for the gallium at $r = 0.0$ Å and $r = 1.8$ Å (see Figure 1b) is that in the first case the gallium makes two interactions with both Ca1 and Ca2 and four interactions with every one of the two different Ca3s, whereas in the second, the gallium makes four interactions with both Ca1 and Ca2 and two interactions with every one of the two different Ca3s. A simple calculation using these values and the overlap populations of Table 2 shows that the total host−guest (Ga−Ca) overlap populations are 0.700 for $r = 0.0$ Å and 0.756 for $r = 1.8$ Å. In other words, the host−guest bonding interactions are large when the guest atom moves along the channel, but they are stronger when they reach the plane of the Ca3 atoms, and this leads to the energetic preference for this position. The only difference between the results for the group 13 atoms and silver systems is that the guest levels which receive the electrons in the latter case are more heavily weighted on the s levels than on the p_x and p_y levels. For silver, the difference in total overlap populations is almost the same (0.054) as for gallium (0.056), whereas for indium it is larger (0.068), which is in agreement with the energetic results. It is clear from Figure 5d and the results of Table 2 that, although gallium as well as silver and indium usually act as electron donors, here they behave as electron acceptors from the framework (∼1 electron for gallium and indium and ∼2/3 electrons for silver in these model calculations) because they interact with the best electron donor calcium atoms of the host. As expected, the charge transferred from the calcium atoms of the host is dominated by contribution of the s orbitals.

We summarize this model study by noting that there is an important host−guest interaction in the $(Ca_7N_4)[M_x]$ (M = Ag, Ga, and In) phases, that the guest atoms prefer to be in the plane of the Ca3 atoms, and that this preference is stronger for indium. This host−guest interaction competes with the natural tendency of the guest atoms to form uniform linear chains with M−M bonds. The interaction is associated with an equalization of the oxidation state of the Ca1/Ca2 and Ca3 atoms, which are better described as formally being Ca^{2+}. However, the bonding within the 2 × 2 Ca_7N_4 chains has a sizable covalent character, and this is why the calculated charges are smaller than those calculated for typically ionic systems. This very sizable covalent character of the bonding is most likely behind the rigidity of the 2 × 2 Ca_7N_4 chains in all of these phases.[4]

Actual Systems. If we now try to integrate the results of all the previous model calculations in a simple description of these phases, then we must take into account several pieces of information. First, the host−guest interactions are strong, and they are stronger for indium. Second, the guest chains within the channels tend to form uniform linear chains within the channels in the three cases, although this tendency is smaller for indium. The electron transfer induced by the host−guest interaction should not change this feature, at least in a first approximation, because it would lead to incommensurate modulations with small driving forces. The guest−guest and host−guest interactions in these phases are in conflict because they tend to favor structures with different periodicity for the guest chains (and of course different stoichiometry). With these results of the model calculations in mind, it seems that in the indium phase the host−guest interactions should dominate, while in the silver and gallium cases the competition should be more complex. Given this situation, the simplest approach is to examine the situation in appropriate supercell models approaching the real stoichiometry of the systems.

A. $(Ca_7N_4)[Ga_{1.33}]$. As mentioned in our discussion of the isolated linear guest chains, the optimum structure found for the gallium chain corresponds to a Ga−Ga distance of 2.4 Å. However, the lengthening of the Ga−Ga distance to 2.727 Å costs only around 0.05 eV per atom. This is an important observation because a uniform gallium chain with this Ga−Ga distance is commensurate with a triple cell of the C_4N_7 framework. This is the simplest supercell model that can be built for the gallium containing phase. The important feature of this model is that it is also compatible with the strong host−guest interaction scenario. This may be easily understood by looking at Figure 6. There we have represented the interaction energies of the framework with a gallium atom along the chain in the triple cell model, based on the results for the $Ca_7N_4[Ga]$ model calculations of the previous section. If one of the gallium atoms is placed at the position of minimum energy, the remaining three atoms of the uniform linear chain must be placed as shown in this figure. Thus, one of the atoms lies at the position of maximum energy and two on the same intermediate energies. It is clear that if the gallium chain slides in any way, the energy loss of the atom initially located at the minimum energy position will be compensated by the energy gain of the atom initially placed at the maximum energy, and the same compensation would occur for the other pair of atoms. Thus, this simple reasoning suggests that although the host−guest interaction is strong, such interaction is almost invariant to a sliding of the gallium chain along the *c*-direction. Of course, this simple argument should be tested against actual calculations for the sliding process. Indeed, our first principles calculations show that the complete sliding of the gallium chain goes through a tiny barrier of 0.01 eV. This gives strong support to the proposed structural model and explains the complete lack of correlation between the different gallium chains within the strong host−guest scenario. The very small energy cost of the stretching of the optimum linear gallium chain allows a situation in which the tendencies of the gallium atoms to interact along the chain, as well as with the framework are made compatible, leading to a stable structure where the different chains are uncorrelated. We believe that this is the simplest model compatible with both the experimental and theoretical evidence concerning the gallium-containing phase.

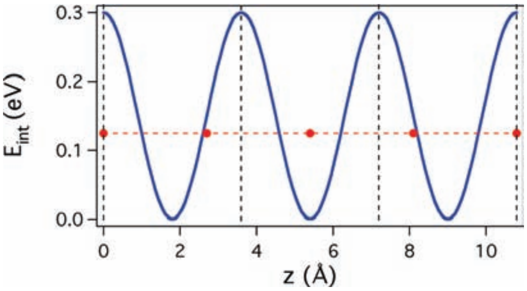

Figure 6. Schematic representation of the interaction between the Ca_7N_4 framework and a series of four gallium atoms along the channel using the triple cell model discussed in the text and the results of Figure 5a (blue curve). The dashed lines represent the limits of each of the three cells of the host, and the red circles represent the gallium atoms in the channel. The origin of the distances along the chain is the same as in Figure 5a.

Concerning the electronic structure of the material, we report in Figure 7a,b the calculated band structures of the isolated Ca_7N_4 host and the full system, $(Ca_7N_4)[Ga_{1.33}]$. Note, that these calculations have been carried out using the triple cell structure, and this is why the band structure of the host may appear to differ in details from that in Figure 2a (which was calculated using a single repeat unit), although they are completely equivalent. The important host−guest interaction can be appreciated by looking at the evolution of the two mainly calcium-based pairs of bands near the Fermi level of the isolated framework. One of them, the upper one that was partially filled in the isolated framework, is ejected approximately 1 eV above the Fermi level and, thus, becomes completely empty (i.e., the lowest fully empty band of Figure

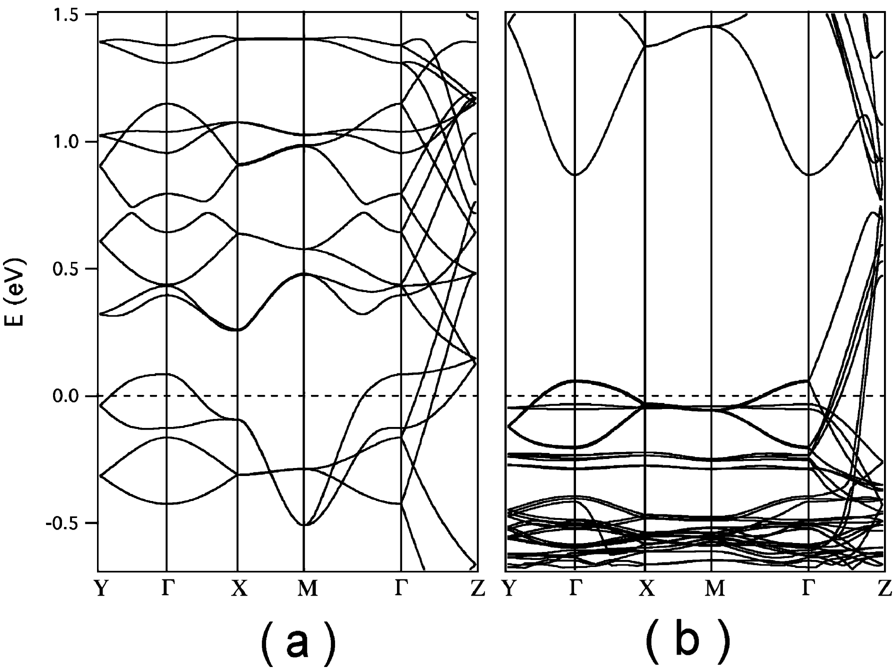

Figure 7. Calculated band structure near the Fermi level for (a) the Ca_7N_4 isolated framework and (b) the full $(Ca_7N_4)[Ga_{1.33}]$ compound, according to the triple cell model discussed in the text. The dashed lines refer to the Fermi level and Γ = (0, 0, 0), X = (1/2, 0, 0), Y = (0, 1/2, 0), Z = (0, 0, 1/2), and M = (1/2, 1/2, 0) in units of the orthorhombic reciprocal cell vectors.

7b). The second one that was completely filled along large zones of the Brillouin zone in Figure 7a is considerably emptied and constitutes, in fact, the highest partially filled set of bands. In addition, gallium based bands now also cross the Fermi level. Bands mostly calcium in character, which were empty, but very near the Fermi level for the isolated host, were raised and appear at energies higher than those shown in Figure 7b through antibonding interactions with the gallium levels. Thus, from this perspective, it is also quite clear that the host−guest interaction is strong, and that there is a considerable electron transfer from the host to the guest.

What is clear from Figure 7b is that $(Ca_7N_4)[Ga_{1.33}]$ with this structure must be a metal. Although the Fermi level cuts more bands along the c^* direction (i.e., Γ→Z), it also cuts bands in directions perpendicular to c^*. Thus, $(Ca_7N_4)[Ga_{1.33}]$ should be a three-dimensional metal although with much better conductivity along c. From the preceding discussion, it is clear that the host must contribute in a considerable way to the conductivity of the system. In order to make this observation more quantitative, we have decomposed the density of states at the Fermi level into the contributions of the Ca_7N_4 host and the gallium chain. We found that 30% is associated with the gallium chains and 70% with the host framework, making clear again the strong host−guest interaction. Finally, we have analyzed in detail the DOS of the system and have found that it shares most of the main features of that already analyzed for $(Ca_7N_4)[Ga]$. The most relevant finding was that the projections of the Ca1, Ca2, and Ca3 atoms almost overlap all along the filled part of the DOS, thus leading to very similar charges. The calculated valence electron populations for the different atoms are reported in Table 4. According to these values, there is a transfer of ∼2/3 electrons per gallium atom (i.e., ∼1 electron per Ca_7N_4 unit) as a result of the interaction.

Table 4. Calculated (Average) Valence Electron Populations for the Different Atoms of the Models for the $(Ca_7N_4)[Ga_{1.33}]$, $(Ca_7N_4)[Ag_{1.33}]$, $(Ca_7N_4)[In_{1.0}]$, and $(Ca_7N_4)[In_{1.2}]$ systems discussed in the text

atom	$(Ca_7N_4)[Ga_{1.33}]$	$(Ca_7N_4)[Ag_{1.33}]$	$(Ca_7N_4)[In_{1.0}]$	(Ca_7N_4) $[In_{1.2}]$
Ca1	1.38	1.41	1.30	1.35
Ca2	1.36	1.39	1.28	1.33
Ca3	1.33	1.36	1.35	1.35
Ca4	1.16	1.16	1.15	1.15
N1	5.93	5.95	5.96	5.96
N2	5.99	5.98	6.00	6.00
M	3.62	1.48	3.99	3.74

B. $(Ca_7N_4)[Ag_{1.33}]$. This compound shares most of the relevant features with the gallium phase, and, thus, it will be only very briefly discussed. Now the situation is even more favorable because the calculated optimum Ag−Ag distance in the chain is 2.70 Å. Thus, there is practically no price for the chain to pay in order to adapt to the framework and to adopt the same triple cell type structure discussed above. This result is not surprising in view of the similarity noted in the model studies for gallium and silver concerning the energetic aspects of the interaction with the host framework and the tendency to form uniform linear chains.

The calculated band structure for $(Ca_7N_4)[Ag_{1.33}]$ using the triple cell model discussed above is shown in Figure 8. The most relevant feature of this figure is that now the Fermi level cuts bands only along the c^* direction (i.e., Γ→Z). Since these bands are quite dispersive, this phase is predicted to be a one-dimensional metal. It should be noted that the Fermi level lies quite near the top of the upper filled bands along directions perpendicular to c^* so that it cannot be completely discarded that the Fermi level may touch these bands, creating small closed pockets. However, the silver compound seems to be more one-dimensional than the gallium compound. Analysis of the density of states at the Fermi level shows that 34% is associated with the guest atoms and 66%

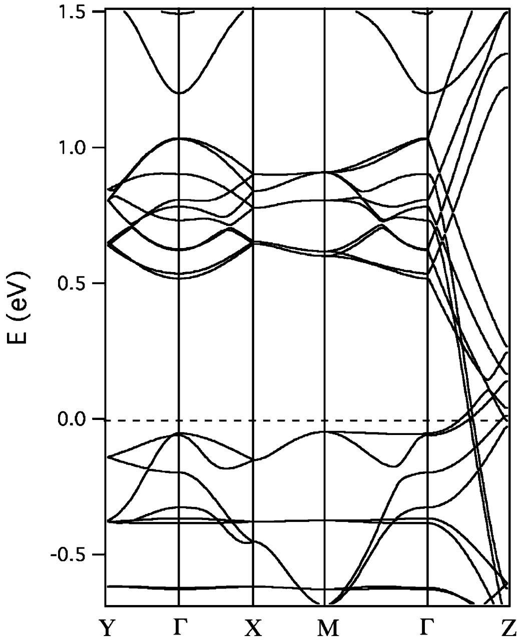

Figure 8. Calculated band structure near the Fermi level for (Ca_7N_4)[$Ag_{1.33}$] using the triple cell model discussed in the text. The dashed line refers to the Fermi level and Γ = (0, 0, 0), X = (1/2, 0, 0), Y = (0, 1/2, 0), Z = (0, 0, 1/2), and M = (1/2, 1/2, 0) in units of the orthorhombic reciprocal cell vectors.

with the host framework. As shown in Table 4, the calculated valence electron populations for Ca1, Ca2, and Ca3 are again very similar. The only difference was that the electron transfer to the guest atoms is a little bit smaller, 0.48 per silver atom (i.e., ~2/3 electrons per Ca_7N_4 unit). Thus, the geometric and electronic structures of the silver and gallium phases are essentially similar except for an increased one-dimensionality of the conductivity and a 22% smaller electron transfer for the silver phase. In contrast with the results of Kniep et al.,[4] we did not find a clear difference on the magnitude of the density of states at the Fermi level.

C. (Ca_7N_4)[$In_{1.0}$]. In this case, the situation is more complex because the optimal In−In distance for a regular chain of indium atoms is too short compared with the periodicity of the framework, and lengthening the In−In bonds to the value required by the framework periodicity would destabilize the chain too much. Since the model calculations suggest that the host−guest interaction is stronger for indium than for gallium or silver, it seems natural to assume that the indium chains will try to maximize their interaction with the calcium atoms of the host and, therefore, break into fragments, as suggested by Kniep et al.[4] Since from the available experimental information it is not possible to know what type of fragments are most likely to be found in (Ca_7N_4)[$In_{1.0}$], we decided to tackle this point using computational tools. We considered a large model which contains six repeat units of the host along *c* and six indium atoms per channel. A sufficiently large series of commensurate approximations to the real structure of the system may be studied in this way. For instance, the indium atoms may be taken as fragmented into a series of hexamers, a pentamer and an isolated atom, a tetramer and a dimer, two trimers, etc., so that practically all likely possibilities are taken into account. We considered all these possibilities as the initial structures for the structural optimization. Since the positions of the guests in one channel do not influence those in the other channels, we optimized the positions of the guests in one of the two channels of the unit cell while keeping the guest atoms fixed and equidistant in the other channel to avoid unnecessary problems during the optimization process. The possibility that the different initial units were not linear was also taken into account. In all cases, the optimization led to the same minimum energy structure in which the indium atoms occur as two practically identical trimeric fragments with In−In distances of 3.25 Å separated by a 4.43 Å gap and with the central In atoms residing on the plane of the Ca3 atoms. Thus, this study suggests that even if a perfectly commensurate model may not be completely appropriate, the indium atoms inside the channels must have a strong tendency to exist as a series of trimeric units.

According to these results, the simplest model which should grasp the essential features of (Ca_7N_4)[$In_{1.0}$] may be built from a repeat unit containing a triple cell of the host and three indium atoms, forming a linear trimer with In−In bond lengths of 3.25 Å with the central In atom residing on the plane of the Ca3 atoms. Since, as mentioned before, the relative location of the trimers in one channel does not have a detectable influence on the location of the trimers in the neighboring chains, there is a large number of possible commensurate models, but the differences among them are almost nondetectable in the electronic structure. In Table 4, we report the average charges for the different atoms. As for all other cases, the Ca1, Ca2, and Ca3 atom charges are very similar. Note that the calculated charges are very similar to those obtained in the model study, where an indium atom was displaced along the *c* direction (see Table 3). This is normal since in the optimized structure one indium atom (the central one) is in the same plane as Ca3, and the other two are quite near the planes of the other Ca3 atoms. According to the values in Table 4, there is a transfer of practically one electron per indium atom (i.e., ~1 electron per Ca_7N_4 unit as for (Ca_7N_4)[$Ga_{1.33}$]) as a result of the interaction. The calculated In−Ca overlap populations are also practically identical to those obtained in the model study (see the values for $r = 1.8$ Å in Table 2), and the calculated In−In overlap populations are 0.325 and 0.046 for the intra- and intertrimers contacts. Thus, there is a definite stabilizing interaction between the trimeric units inside the channels. In other words, the guest atoms should be described as forming a chain of interacting indium trimers. It is interesting to compare these results with those of the (Ca_7N_4)[$In_{1.2}$] phase in which the In−In distances are those appropriate for the linear uniform chain, 3.0 Å. In that case, if the first indium atom is chosen to be in the lower energy position, i.e., the plane of the Ca3 atoms, then the fourth atom must be located in the highest energy position, i.e., the plane of the Ca1/Ca2 atoms. In other words, whereas in the case of the (Ca_7N_4)[$In_{1.0}$] phase the host−guest interaction is quite near being optimum, in the case of the (Ca_7N_4)[$In_{1.2}$] phase we are far from this situation. As we know from the model calculations that among the

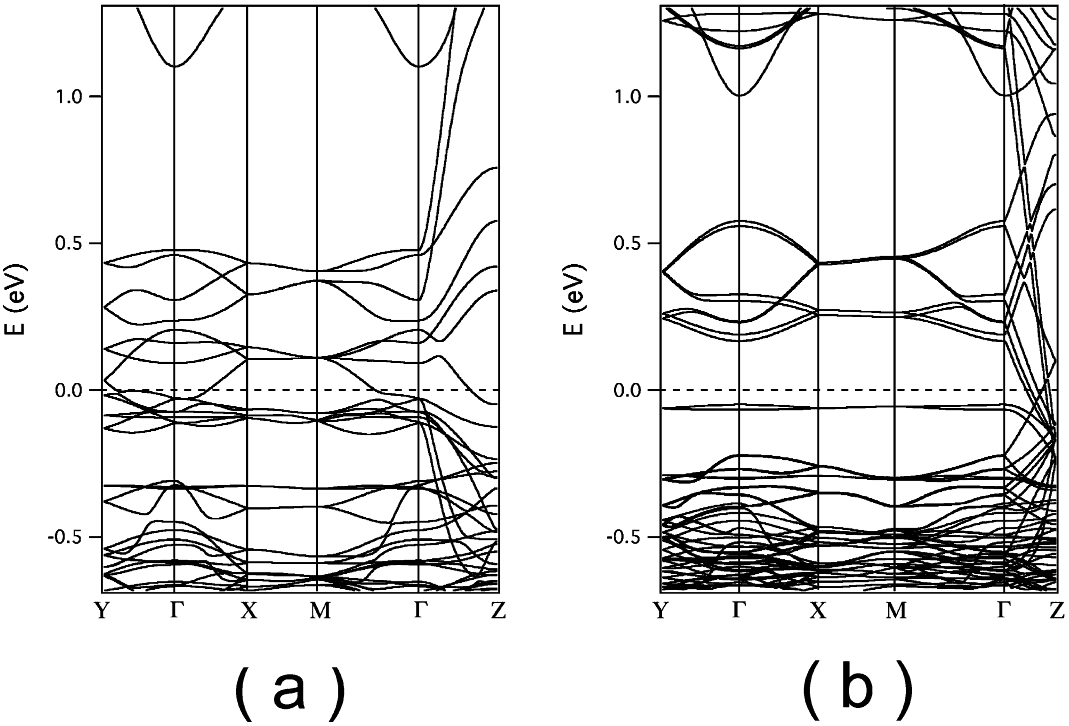

Figure 9. (a) Calculated band structure near the Fermi level for $(Ca_7N_4)[In_{1.0}]$ using the calculated triple cell model discussed in the text. (b) Calculated band structure near the Fermi level for $(Ca_7N_4)[In_{1.2}]$ using the quintuple cell model discussed in the text. The dashed lines refer to the Fermi level and Γ = (0, 0, 0), X = (1/2, 0, 0), Y = (0, 1/2, 0), Z = (0, 0, 1/2), and M = (1/2, 1/2, 0) in units of the orthorhombic reciprocal cell vectors for every case.

three atoms considered, indium has the smaller tendency to form uniform chains but undergoes stronger interactions with the guest, it is understandable that $(Ca_7N_4)[In_x]$ prefers to adopt the x value allowing to optimize the host−guest interactions ($x \approx 1$) even if losing some indium−indium bonding. This situation is just the contrary of that discussed above for the gallium and silver phases with $x \approx 1.33$, in which the guest−guest interaction is optimized.

Shown in Figure 9a is the calculated band structure for the simplest possible model for $(Ca_7N_4)[In_{1.0}]$, i.e., that in which the central In atom of the trimers in all channels is located at the same plane. In Figure 9b, we report the calculated band structure for the hypothetical solid containing uniform linear guest chains, $(Ca_7N_4)[In_{1.2}]$. Note that for this calculation a quintuple cell of the host is needed so one must be careful in comparing the two band structures. Looking at the $\Gamma \rightarrow Z$ direction of these band structures (i.e., the c^* direction) the effect of the trimerization is clearly visible, i.e., opening of gaps at Γ and Z. In either case, when the channels are filled with uniform linear chains (Figure 9b) or with trimers (Figure 9a), the system is calculated to be metallic. However, whereas the phase with uniform linear chains would be a one-dimensional metal, that with the trimers would be a three-dimensional metal. Another difference is that the slope of the bands at the Fermi level is substantially smaller in the last case so that the system should be a weaker metal in that case. Thus, although as for the gallium and silver phases the density of states at the Fermi level is shared between the host and guest, the occurrence of discrete trimeric units (though in interaction) notably influences the conductivity. Comparing the band structures of $(Ca_7N_4)[In_{1.0}]$ (Figure 9a), $(Ca_7N_4)[Ga_{1.33}]$ (Figure 7b), and $(Ca_7N_4)[Ag_{1.33}]$ (Figure 8), which according to the present study should be a good representation of the electronic structure of the real materials, it is clear that: (a) the first and third should be three-dimensional metals, whereas the second should be a one-dimensional metal, and (b) the conductivity of the first should be clearly smaller than those of the other two. These results agree with the conductivity measurements for the gallium and silver phases, which clearly indicate a metallic behavior.[4] Those for $(Ca_7N_4)[In_{1.0}]$, which also suggests metallic behavior despite the existence of broken guest chains, are not necessarily in contradiction with the experimental measurements, indicating activated conductivity since these could not be carried out for single crystals, but on powdered samples. However, it would not be unlikely that the noncomplete commensurability, which implicates the occurrence of some defects along the chains of trimers as well as other sources of disorder (for instance the lack of correlation between the chains of trimers in different channels), may suppress the already not very strong metallic character and lead to an activated conductivity. Thus, the activated or nonactivated character of the conductivity of the indium (and thallium) phase remains as an interesting open question waiting for single crystal measurements.

Concluding Remarks

First principles DFT calculations for models of the $(Ca_7N_4)[M_x]$ (M = Ag, Ga, and In) phases have provided valuable hints concerning the structure and transport properties of these phases. For instance, it has been possible to show that if the assumption of very weak host−guest interactions is made: a) four calcium atoms per formula unit may be considered as $Ca^{1.5+}$, whereas the remaining three may be considered as Ca^{2+} so that the guest atoms would be neutral, and b) the Peierls distortions, which could set in the guest linear chains, are unlikely. These results are compatible with the experimental information, so it is understandable that this scenario was proposed in the original report on these phases even if some puzzling questions may arise from it. However, the first principles DFT calculations reported here also clearly show that very sizable host−guest interactions occur, drastically changing our view of these phases. For instance (a) the Ca1, Ca2, and Ca3 atoms of the framework are in the same oxidation state; (b) there is a considerable electron transfer from the framework to the guest atoms; and (c) the stoichiometry and structure of these systems result from the competition between the tendency of the bare guest atoms to form uniform linear chains within the reduced space of the channels and the tendency to optimize their positions within the channels. It has been possible to propose structural models for the three phases, which are consistent with the presently available experimental and theoretical information. For $(Ca_7N_4)[M_{1.33}]$ (M = Ag and Ga), a structure built from three repeat units of the host framework that contains uniform linear chains with a repeat unit of four guest atoms is compatible with the strong interaction scenario, but also with the lack of correlation between the different linear guest chains. These phases should be metallic conductors, and the carriers should have both host and guest character. For $(Ca_7N_4)[In_{1.0}]$, our study suggests that the guest indium atoms should exist as a series of trimeric units and the phase should be metallic though with a smaller conductivity.

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