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Article

Electronic Structure of Li_2Ga and Li_9Al_4, Two Solids Containing Infinite and Uniform Zigzag Chains

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The electronic structure of inorganic solids such as Li_2Ga and Li_9Al_4 containing infinite zigzag homoatomic chains is discussed. It is shown that Li_2Ga, a solid for which a Zintl-type electron-counting approach would suggest that a half-filled π-type band occurs as in *trans*-polyacetylene, is really a three-dimensional solid with strong covalent interchain connections and small effective charge transfer. The zigzag chains do not play a dominant role as far as the electronic structure near the Fermi level is concerned, and there is no reason for the occurrence of a Peierls distortion despite the possible analogy with *trans*-polyacetylene. It is suggested that even assuming that a Zintl-type approach is appropriate for electron counting purposes, the infinite zigzag chains in this compound and those in *trans*-polyacetylene are not isolobal. The bonding in Li_9Al_4 and Li_2Ga is very similar, and both phases are predicted to be stable three-dimensional metals.

Introduction

LiGa[1] ranks among those solid-state compounds whose preparation and structural characterization by Zintl and co-workers in the early 1930s[2] led to the development of one of the more simple and useful concepts in solid-state chemistry, that of Zintl phases.[3] A more systematic investigation of the Li/Ga phase diagram was initiated in the 1970s by Klemm, Stöhr, Schäfer, and co-workers, and compounds such as Li_3Ga_2, Li_5Ga_4, and Li_2Ga were characterized.[4−6] LiGa exhibits the NaTl structure, where the more electronegative Ga atoms form a three-dimensional network of locally tetrahedrally coordinated atoms, something which is rationalized formally assuming a full charge transfer. Increasing the Ga electron concentration should lead to occupation of antibonding states and thus lead to a progressive dismantling of this structure, as found for instance in Li_5Ga_4[6] and Li_3Ga_2,[5] where the crystal structure is build from double and single layers, respectively. The most interesting of these compounds is, however, Li_2Ga whose crystal structure contains isolated uniform zigzag chains of Ga atoms.[5]

Looking for analogies between the structure and properties of organic and inorganic (or organometallic) systems has been, and undoubtedly will remain, an extremely useful and suggestive approach to predict, understand, and generate new systems. However, the structure and properties are ultimately dictated by the electronic structure so that only when there is also a clear-cut relationship between the corresponding electronic structures, as illustrated for instance by the isolobal analogy,[7] these relationships can be fully endorsed. Probably there is no modern solid-state series of lectures or book in which the explanation of the Peierls distortion in *trans*-polyacetylene, i.e., a dimerization, does not play a starring role. The building of the π-type band structure based on the π and π^* orbitals of a C═C double bond leads to a transparent interpretation of the origin of this ubiquitous phenomenon and, maybe more importantly, illustrates how what otherwise would be an abstract physical concept may be understood in terms of well-known chemical concepts

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such as localization vs delocalization, metal−metal bonding in the transition metal related systems, etc. Thus, no chemist becoming aware of the Li_2Ga structure[5] can avoid some sense of surprise when realizing that despite formally having five electrons/Ga atom, and thus one electron/atom to fill the π-type levels as in *trans*-polyacetylene, the Ga chains in Li_2Ga do not exhibit any dimerization. Here we must point out that all along this manuscript the term *dimerization* is used in the sense that the ···M−M−M···· zigzag chains are not strictly uniform. The difference in the two M−M bond lengths can be large when the M atoms belong to the upper rows of the periodic table (i.e., the C−C bonds in *trans*-polyacetylene which really correspond to single and double bonds) but can be much smaller for heavier atoms as for instance Ga.

If we are trying to understand this observation, the obvious fact that in Li_2Ga the uniform Ga chains are not really isolated but embedded in a "sea" of lithium atoms immediately comes to the mind. And this fact can make us feel confortable because it can be argued that (i) the Li atoms connect the Ga chains so that they act as a kind of restoring force opposing the natural tendency toward dimerization of the Ga chains[8] or (ii) because of the Ga−Li nonnegligible interactions the Ga chains are less electron rich than when complete electron transfer is assumed and consequently the π-type bands are not really half-filled, decreasing the tendency toward dimerization. Once it is realized that solids such as Li_9Al_4[9], $CaSb_2$[10] or CrB-type phases such as CaSi or CaGe,[11] in which the more electronegative atoms, despite formally having electron concentrations larger than in Li_2Ga, still form analogous uniform zigzag chains, the second explanation seems more likely. Miller has thoroughly examined this kind of problems and made very perceptive comments.[12] However, it was found on the basis of semiempirical tight-binding calculations that in Li_2Ga the Fermi level exactly separates the π bonding from π^* antibonding bands. Consequently, the key question, i.e., why the Peierls distortion does not develop, still remains unanswered except if the Li−Ga interaction is strong enough to suppress the distortion. Although it cannot be completely discarded that these Li−Ga interactions are Coulombic in nature, it seems that orbital mixing between the Li and Ga should provide a more reasonable mechanism against the distortion. But this implicates only partial electronic transfer from Li which, at least at first sight, seems difficult to reconcile with Miller's observation that the Fermi level exactly separates the π bonding from π antibonding bands. Our recent work on phases such as K_5Bi_4,[13a] K_3Bi_2,[13b] $Ba_5In_4Bi_4$,[13c] etc., has clearly shown that a meaningful discussion of aspects related to the actual degree of charge transfer in Zintl-type phases must be based on accurate first principles calculations. Both strong Coulomb interactions and uncertainty in the relative values of the parameters used in semiempirical calculations for the alkali-metal and non-alkali-metal elements may seriously affect the degree of mixing of their orbitals, a central issue here. In view of the prominent role played by Peierls distortions in our understanding of the structure and properties of solids, we believe the problem deserves further analysis on the basis of accurate first principles calculations. Here we report the results of such a study on the basis of the consideration of the Li_2Ga and Li_9Al_4 phases. Both phases have been the subject of a previous first principles study,[14,15] but the focus of this work is very different.

Computational Details

First principles calculations for Li_2Ga and Li_9A_{l4} were carried out using a numerical atomic orbitals density functional theory (DFT) approach,[16] which has been recently developed and designed for efficient calculations in large systems and implemented in the SIESTA code.[17−19] The use of atomic orbitals instead of plane waves greatly facilitates a chemical analysis of the results. We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke, and Ernzerhof.[20] Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[21] factorized in the Kleinman−Bylander form.[22] 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.[23] The integrals of the self-consistent terms of the Kohn−Sham Hamiltonian are obtained with the help of a regular real space grid in which the electron density is projected. The grid spacing is determined by the maximum kinetic energy of the plane waves that can be represented in that grid. In this work, we used a cutoff of 150 Ry. The Brillouin zone (BZ) was sampled using grids of $(10 \times 10 \times 10)$ and $(6 \times 6 \times 6)$ k-points[24] for Li_2Ga and Li_9Al_4, respectively. We have checked that the results are well converged with respect to the real space grid, the BZ sampling, and the range of the atomic orbitals.

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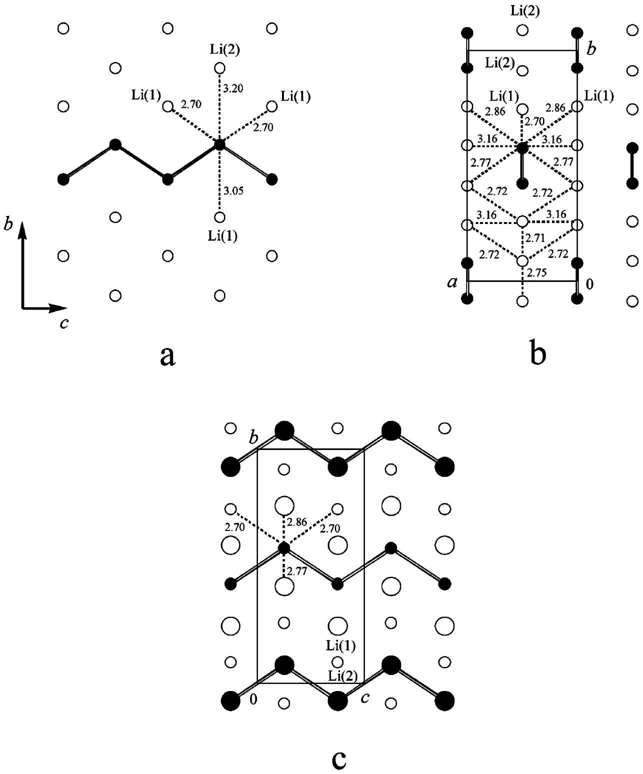

Figure 1. Crystal structure of Li_2Ga, where the full and empty circles refer to the Ga and Li atoms, respectively. (a) is a view of the approximately hexagonal (Li_2Ga) layers perpendicular to *a*; (b) and (c) are projections of the structure along the *c* and *a* directions, respectively. In (c) the atoms belonging to different (Li_2Ga) layers (i.e., those at *a* and *a*/2) are shown with circles of different sizes. Distances are in Å.

Qualitative aspects of the electronic structure were analyzed using semiempirical tight-binding band structure calculations based upon the effective one-electron Hamiltonian of the extended Hückel method.[25a] The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg−Helmholz formula.[25b] Single-ζ Slater-type orbitals were used in all cases. The exponents[26a] and ionization potentials[26b] used were 1.770 and −13.216 eV for Ga 4s, 1.550 and −6.049 eV for Ga 4p, 1.167 and −11.794 eV for Al 3s, 1.167 and −5.976 eV for Al 3p, 1.625 and −19.654 eV for C 2s, 1.165 and −11.129 eV for C 2p, and 1.30 and −12.565 eV for H 1s.

Results and Discussion

Crystal Structure and Absence of a Peierls Distortion. The crystal structure of Li_2Ga is shown in Figure 1. There are planar uniform zigzag chains of gallium atoms along the *c* direction and contained in the (*bc*) plane. Thus, in the following the π system of these chains will be considered to be built from the p_x orbitals. The Ga−Ga distance within these chains is 2.62 Å, and the Ga−Ga−Ga angle, 112.6°. The Ga−Ga distance is shorter that the typical Ga−Ga single bond distance found in LiGa (2.69 Å) or in Li_3Ga_2 (2.67 Å). The more simple way to describe the structure of Li_2Ga is to note that there are (Li_2Ga) layers perpendicular to the *a* direction (see Figure 1a) which can be described as being approximately hexagonal lattices with one-third of the positions being occupied by Ga atoms and two-thirds by Li atoms. The unit cell of Li_2Ga contains two of these layers, every layer being shifted by *b*/2 with respect to the adjacent ones (see Figure 1b). Thus, successive gallium zigzag chains along *a* are separated by double rows of Li(2) atoms; in fact, as it will be discussed below, these are better described as uniform zigzag lithium chains along *c* forming (Ga_2Li_2) layers parallel to the (*ac*) planes (see Figure 1b). These layers alternate along the *b* direction with layers of Li(1) atoms forming a centered rectangular lattice. In such a way, every Ga atom is surrounded by four Li(1) at 2.70 Å (×2) and 2.86 Å (×2) and two Li(2) at 2.77 Å (×2). Six additional Li atoms at distances between 3.05 and 3.20 Å are also found. As shown in Figure 1a, two of the six Ga−Li contacts smaller than 3.0 Å and two of the six contacts larger than 3.0 Å occur within the (Li_2Ga) layers. Several relatively short Li−Li contacts, both within these layers (2.71 and 2.75 Å) and between them (2.72 Å), must be noted. Except when otherwise stated, the terms inter- and intralayer interactions in the following discussion refer to these (Li_2Ga) layers.

To confirm the existence of regular chains in Li_2Ga, we optimized first the crystal structure without imposing constraints in the dimensions or symmetry of the cell. Since the unit cell contains two gallium atoms/gallium chain, the kind of distortion we are discussing, i.e., a dimerization, is perfectly feasible. The optimized structure is found to be orthorhombic ($a = 4.632$, $b = 9.693$, $c = 4.453$ Å) and contains uniform gallium chains with Ga−Ga distances of 2.68 Å and Ga−Ga−Ga angles of 112.3°, which are very similar to the experimental values. Thus, our calculations confirm that there is no tendency toward a dimerization in this phase.

Nature of the Gallium−Lithium Interactions and Actual Charge Transfer. Every zigzag gallium chain must lead to four filled σ-type bands, two mostly associated with the σ Ga−Ga bonding levels and two with mostly Ga sp^2-like lone pairs, and a pair of π-type bands. The four lower σ bands and the lower π one are those which by analogy with *trans*-polyacetylene should be filled assuming complete charge transfer from the lithium atoms. Since there are two zigzag chains/unit cell of the solid, the lower bands in the band structure of Li_2Ga are expected to be a set of eight σ-type bands originating from bonding or nonbonding σ levels of the zigzag gallium chains and two pairs of π bands. Even in such a naive description, some lithium character is of course expected to be found in these lower bands. The degree of mixing among the bands of the gallium zigzag chains and those associated with the lithium atoms is what makes more or less appropriate the use of a Zintl-type scheme to approach the electronic structure of the phase. The calculated band structure along the three main directions of reciprocal space is shown in Figure 2, where the two pairs of bands which originate mostly from the π-system of the Ga chains have been highlighted along the $\Gamma-Z$ direction (i.e., the c^* direction). Note a quite strongly avoided crossing

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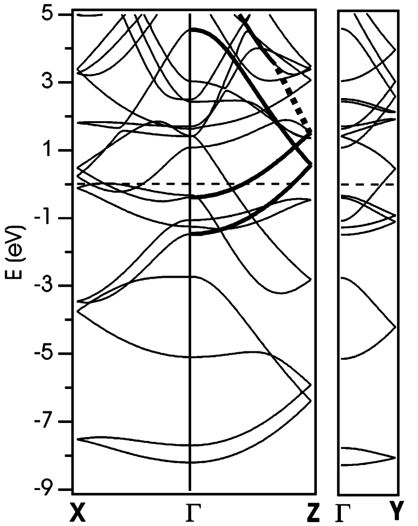


Figure 2. Calculated band structure for Li$_2$Ga where the horizontal dashed line refers to the Fermi level and $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, and $Z = (0, 0, 1/2)$ in units of the orthorhombic reciprocal lattice vectors. The four bands corresponding to the π system of the Ga chains have been highlighted in the $\Gamma - Z$ direction, with an avoided crossing indicated by a dashed curve.

between the upper of these bands near Z and a mainly lithium-based band with the same symmetry. As a matter of fact, at around 1 eV above the Fermi level several mostly lithium-based bands appear and mix strongly with the upper part of the set of above-mentioned bands which originate from the two π bands and the four lower σ bands of the uniform zigzag gallium chains. Although the bands based on the π levels of the gallium chains can be clearly recognized despite the mixing with lithium orbitals, this is quite difficult for the σ bands. Except for the lower two pairs of bands, with strong contributions of the gallium s orbitals, even for the three symmetry lines shown in Figure 2 it is difficult to clearly say if several of the bands are mostly gallium based. Of course, within most of the Brillouin zone, where the σ and π bands can mix, it is not easy to follow the so-called π bands. Thus, on the basis of the analysis of the nature of the bands plotted in Figure 2, it must be concluded that the mixing of the lithium levels into the occupied bands is considerably more heavy than expected from the simple naïve approach and thus that there are strong Ga−Li interactions in Li$_2$Ga.

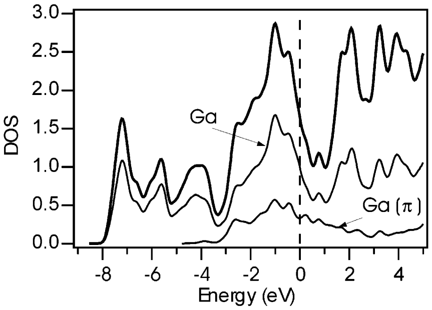
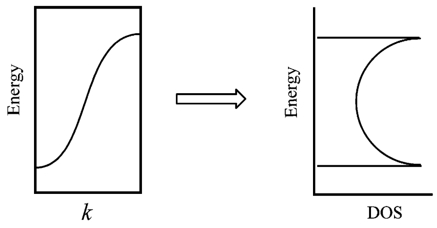


Figure 3. Calculated density of states for Li$_2$Ga. The total contribution of the gallium orbitals and those of the gallium $p_x(\pi)$ are also shown.

The extent of these gallium−lithium interactions is more simply seen on the density of states plot of Figure 3. The calculated DOS is overall in good agreement with the previous calculations based on a different approach (i.e., the linear muffin tin orbitals (LMTO) method).[14] The lithium contribution is important everywhere. (Let us remind that in DFT approaches using localized basis sets as the present one the total DOS is simply the addition of those of the different atomic contributions. Thus, the lithium contribution in Figure 3 is just the difference between the total and gallium contributions shown.) Even in the region dominated by the Ga s orbitals (from −8 to −3 eV), almost one-third of the DOS comes from lithium orbitals. This participation is larger above this region, and at the Fermi level it is practically 40%. In fact, the calculated Mulliken charges are +0.241 for Ga, −0.187 for Li(1), and −0.054 for Li(2). Even bearing in mind the possible shortcuts of the Mulliken analysis, these figures are quite clear in showing a very important mixing of the lithium and gallium orbitals. The calculated overlap populations are also quite informative. That for Ga−Ga bonds is large, 0.188, and some of those associated with the Li−Li interactions are far from negligible, 0.045, 0.039, 0.037, and 0.034. The first and third of these contributions are associated with the intralayer contacts of 2.75 and 2.71 Å, respectively, whereas the second and fourth are associated with the interlayer contacts of 2.72 and 3.16 Å, respectively. This very clearly shows the existence of a 3D network of Li−Li interactions. Alternatively, it can be noted that the overlap populations of 0.045 are associated with the uniform zigzag chains of Li(2)−Li(2) interactions along the c direction and those of 0.034 with the Li(1) atoms of the centered rectangular lattice. Those of 0.039 and 0.037 interconnect these two systems leading to the 3D network. Let us emphasize that the lithium participation in the filled levels really comes from orbital mixings with gallium orbitals and not from the existence of mostly lithium bands which dip below the Fermi level. This is at the origin of the many positive Ga−Li overlap populations. In fact all Ga−Li contacts shorter than 3.25 Å are associated with positive overlap populations. Those associated with the Ga−Li(1) contacts of 2.70, 2.86, and 3.05 Å are 0.127, 0.086, and 0.048, respectively, whereas those associated with the Ga−Li(2) contacts of 2.77, 3.16, and 3.20 Å are 0.097, 0.043, and 0.038, respectively. The somewhat smaller overlap populations with the Li(2) atoms harmonize with the smaller electron density associated with these atoms. Thus, on the basis of these results, we can conclude that Li$_2$Ga must be considered as a tight 3D network in which the gallium chains are strongly connected through Ga−Li and Li−Li bonding interactions. Consequently, there should be a strong restoring force opposing the possible distortion of the gallium chains.

The question is now: are the gallium chains really susceptible to such a distortion? If the answer is yes, then we must consider what kind of distortion. Let us remind that the calculated charge transfer is very different from the expected one on the basis of the simple reasoning. Thus, it seems unlikely that there are two electrons in the π system associated with the gallium chains and a dimerization may not be favorable. Here we should be aware, however, of the difference between the real and formal electronic distribution, i.e., the difference between the real charge and oxidation state of an atom. The real question we must ask is: are there really gallium based one-dimensional features in the DOS near the Fermi level of this phase, whatever their actual gallium−lithium percentage contribution is?

Remember that the π system of the *trans*-polyacetylene zigzag chain like that of the gallium chains in Li_2Ga is just a folded one-dimensional band so that it should appear in the DOS as a single one-dimensional contribution. In other words, even if strongly connected, do the gallium zigzag chains show up in the electronic structure near the Fermi level? After all one-dimensional electronic features in structurally two- or three-dimensional solids do exist and have strong consequences for their physical behavior in phases such as the purple bronzes, monophosphate tungsten bronzes, etc.[27,28] A one-dimensional feature occurs in the DOS with a very characteristic shape, i.e., a double-peaked contribution with maxima at the borders and a minimum near the middle (**1**). In contrast, two- and three-dimensional features tend to be more spread out and have maxima around the middle.[28] These one-dimensional features can be easily seen in the DOS even if there is quite extensive orbital mixing between the more and the less electronegative elements and several bands overlap, as for instance in K_5Bi_4.[13a]



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When we look at the gallium π-type contribution to the DOS in Figure 3, it is very clear that it is very spread and tends to peak around the middle of the broad contribution. Thus, the p_x gallium orbitals apparently do not give rise to a one-dimensional contribution to the electronic structure of Li_2Ga. In other words, from the electronic viewpoint, the crystal structure does not contain chains. Consequently, there are no partially filled one-dimensional bands and there is no driving force for any kind of Peierls distortion within the gallium chains, in good agreement with the uniform chains found in the experimental structure.

Are Zigzag One-Dimensional Chains of Main Group Atoms with Five Electrons/Atom and Those of *trans*-Polyacetylene Equivalent? The end point of the previous discussion is that although it may be appealling to consider Li_2Ga as containing infinite zigzag gallium chains immersed in a sea of lithium atoms, strong Ga−Li and Li−Li interactions make it really a three-dimensional solid from the electronic point of view. At this point the question of why there is not a Peierls distortion becomes irrelevant. However, does that mean that infinite gallium zigzag chains in any solid must lose their identity? Of course not. In that case the possibility of a Peierls distortion, whose nature will depend on the number of electrons in the chain, remains. The question we should examine now is if there is some intrinsic difference between the *trans*-polyacetylene and zigzag gallium (or in general, any main group atom) chains with the same formal number of electrons (i.e., five electrons/atom). For this purpose, let us just consider a single gallium chain completely isolated from the rest of the solid and in the absence of any Coulomb field. To highlight the relationship between the nature of the topology and electronic structure, let us just consider a simple tight-binding extended-Hückel band structure (i.e., a calculation in which the actual filling of the bands does not modify the band structure itself).

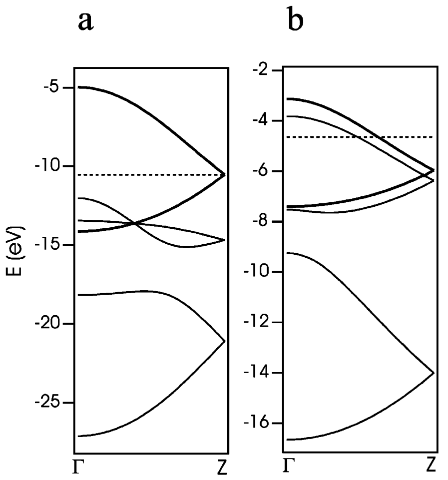

Figure 4. Calculated extended Hückel band structures for the uniform zigzag chains of (a) *trans*-polyacetylene (C−C, 1.40 Å; C−C−C, 120°) and (b) gallium as in Li_2Ga. The dashed line refers to the Fermi level which in (b) corresponds to $(Ga^{2-})_\infty$.

The calculated band structures for uniform *trans*-polyacetylene and gallium zigzag chains are shown in Figure 4a,b, respectively (note the different energy scales in these figures). The high-lying antibonding σ^* bands (i.e., the σ^*_{CC} and σ^*_{CH} of *trans*-polyacetylene and σ^*_{GaGa} of the zigzag gallium chain) are not shown in these figures. We assume that the chains run along the z direction and stay in the (yz) plane. The lower pair of bands originate from the s orbitals of gallium (which mix in p_z contributions to better describe the Ga−Ga bonding) and the two next pairs of bands originate from the p_x and p_y orbitals, respectively. Here, as well as in *trans*-polyacetylene, the two bands can cross because they are of different symmetry with respect to the (yz) plane. The p_x-type bands, i.e., the π-type ones, are highlighted in Figure 4. The band structure of *trans*-polyacetylene has been discussed in detail many times. We refer the reader to ref 29 for a very detailed, chemically oriented, discussion of the nature of the different bands. The important feature for the problem at hand is that in Figure 4b the p_x and p_y bands are not very different in energy and thus, since there is a total of six electrons to fill them, both are partially filled. In contrast, the two bands are clearly separated in *trans*-polyacetylene (Figure 4a) so that only the upper π-type band

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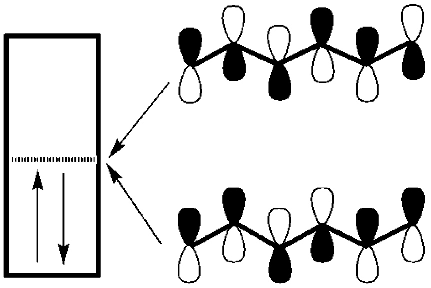
is empty. This leaves the band orbitals at the Fermi level (i.e., the out of phase combinations of the π (**2a**) and π^* (**2b**) orbitals) half-filled and provides the driving force for the Peierls distortion. The similarity in the two pairs of bands and as a consequence the fact that the two upper bands are partially filled does not depend on the actual values of the Ga−Ga distance or the Ga−Ga−Ga angle as far as they are reasonable. Of course, a dimerization opens a gap at *Z* and stabilizes the system in the case of *trans*-polyacetylene because the Fermi level lies just where the gap opens. In the case of the gallium chain the opening of a gap at *Z* does not stabilize the system because both the states lowered and raised are filled.

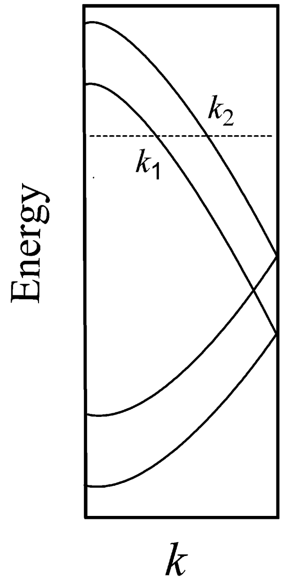


2b

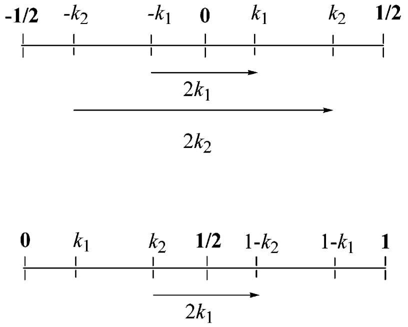
2a

The kind of Peierls distortion which can occur in a one-dimensional system with partially filled bands can be understood by analogy with the situation in *trans*-polyacetylene. If the size of the unit cell becomes *n* times larger, the Brillouin zone becomes *n* times smaller and the original band structure must be folded into the new smaller Brillouin zone to contain exactly the same information. For a one-dimensional 1/*p* filled band, if the unit cell is taken *p* times larger, the Brillouin zone will be *p* times smaller. The Fermi level will thus occur at the border of the new Brillouin zone so that a distortion which increases *p* times the unit cell will open a gap at the Fermi level exactly for the same reason as in *trans*-polyacetylene. Thus, it is the filling of the band what determines the new periodicity, i.e., the structural distortion. More formally, the repeat unit after the distortion is $1/2k_f$ times larger than the initial one, where k_f is the Fermi wave vector (in units of the associated reciprocal vector). For instance, for a half-filled one-dimensional band, $k_f = 0.25$ and $1/2k_f = 2$ so that the system will dimerize.

For the band structure of Figure 4b there are two Fermi wave vectors, k_1 and k_2 (**3**), associated with the lower and upper partially filled bands, respectively. Although in principle it can be thought that a different kind of distortion must be associated with each of the two bands, it is easy to show that a single distortion will suffice to open gaps in both of the bands at the Fermi level. Since every level can be filled with two electrons, $2(2k_1)$ is the number of holes/unit cell associated with the lower band and $2(2[1/2 - k_2]) = 2(1 - 2k_2)$ is the number of electrons associated with the upper band. Since there are two electrons to fill the two bands, this means that the number of holes in one band must be equal to the number of electrons in the other band, i.e., $2k_1 = 1 - 2k_2$. Thus, as schematically shown in **4**, where two different representations of the Brillouin zone are given, a distortion which leads to a unit cell which is $1/2k_1$ times larger should open a gap simultaneously in both bands. For instance, if k_1 is 1/8, then k_2 must be 3/8 and, consequently, a tetramerization must open a gap for both bands.



3



4

It is obvious that the kind of distortion appropriate for a one-dimensional zigzag chain of this type will be in general incommensurate; i.e., $1/2k_1$ will not be an integer so that the new lattice will not be commensurate with the original one. The driving force for a structural modulation or Peierls distortion is weaker for incommensurate distortions.[30] To this intrinsic weakness one must take into account that in real solids, even in very favorable situations, the one-dimensional character will be somewhat disturbed by some kind of interchain interaction. This will lead to some warping of the otherwise planar Fermi surface for the ideal one-dimensional system[28] and will even decrease the driving force for the distortion. In practice, the tendency to undergo the incommensutate modulation will be very small.

The difference between the two band structures of Figure 4 is very simple to understand. Let us assume that the gallium (or in general any main group atom) chain, with two atoms/repeat unit, is linear. In that case the cylindrical symmetry makes the p_x and p_y orbitals completely equivalent and the corresponding pairs of bands degenerate. Lowering the

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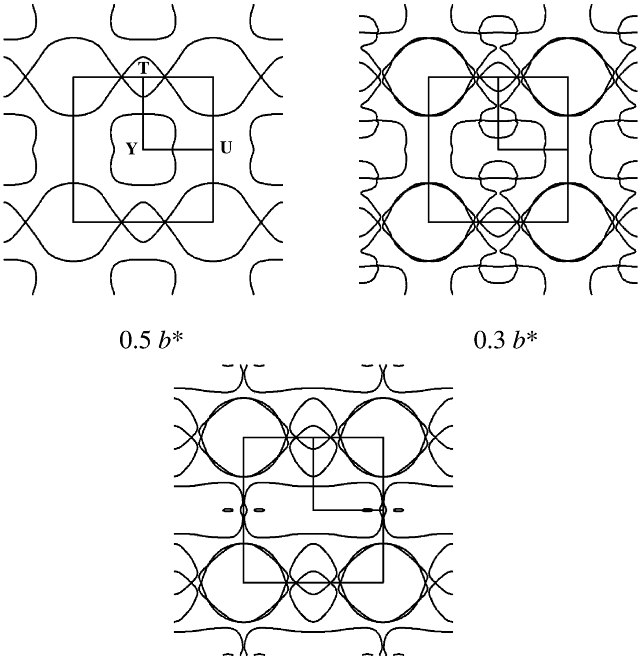
(30) Whangbo, M.-H. In *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*; Rouxel, J., Ed.; Reidel Publ.: Dordrecht, The Netherlands, 1986; pp 27−85.

symmetry toward a zigzag chain makes the two pairs of bands different (by decreasing the p_y-p_y overlap while keeping the p_x-p_x and allowing the mixing of p_y with the s and p_z orbitals), but they keep a strong memory of their initial equivalence. The orientation of the p_x and p_y orbital is however completely different. If some atom or group of atoms having a σ orbital higher in energy than the p_y orbital approaches the main group atoms along the y direction, as for instance the hydrogen atoms in *trans*-polyacetylene, the p_x band will remain unaltered whereas the p_y will be lowered. In that way the pair of p_y based bands become completely filled whereas only the lower one of the p_x pair of bands can be filled and the driving force for a dimerization of the zigzag chain occurs.

In summary, the additional ligand to locally create three σ bonds/atom is necessary to leave all the σ (s, p_y, and p_z) bands completely filled and the π (p_x) bands half-filled. The observation that a zigzag chain of gallium atoms must have both the p_x- and p_y-based bands partially filled is general for any main group atom as the above qualitative argument and extended-Huckel calculations show. Consequently, even if the interchain interactions could be reduced so that the main group metal atom zigzag chains would keep their identity in the solid, it is not expected that they will exhibit a dimerization as in *trans*-polyacetylene, simply because although both chains are structurally related, they are too different from the electronic viewpoint.

Dimensionality and Fermi surface. As shown in the band structure of Figure 2, the Fermi level cuts several dispersive bands so that the system is predicted to be metallic. For a system with partially filled bands the Fermi surface[28] separates the regions of the Brillouin zone which are associated with filled levels from those which are associated with empty levels. Since the carriers of metallic systems are those electrons at the Fermi level, the Fermi surface contains much information concerning the conductivity of the system. However, as discussed in the previous section for the purely one-dimensional case, the Fermi surface is also important in explaining the origin of electronic instabilities of systems with partially filled bands, like the Peierls distortion. Some sections of the calculated Fermi surface of Li_2Ga are shown in Figure 5. If the conductivity had been dominated by partially filled bands of the gallium chains, the Fermi surface would had been one or several pairs of more or less warped planes perpendicular to the chains direction, i.e., the c direction, the warping being proportional to the strength of the interchain interaction. The calculated Fermi surface is however quite complex and different but contains valuable information concerning the problem at hand.

Let us consider first the section for $k_y = 0.5$. Because of the nonsymmorphic symmetry elements, all band levels are doubly degenerate in this plane of reciprocal space (see for instance the bands at the Y point in Figure 2) so that the corresponding section is really the superposition of two identical ones. Using an extended zone scheme, this section can be described as containing pairs of very warped lines running along the borders of the Brillouin zone perpendicular to the direction of the gallium chains (i.e., the c direction). These contributions are associated with the π-type bands of the gallium chains. The very strong warping indicates a strong coupling along the a direction. In addition there is a pair of closed contributions which are associated with the σ-type levels of gallium. When sections for smaller values of the k_y component are considered, the two identical components separate progressively and interact and for very small values new contributions appear. As a whole, the Fermi surface is very complex, typical of a three-dimensional metal and without large parts which can be superposed with others (i.e., nested). Thus, Li_2Ga is predicted to be a stable three-dimensional metal. Some memory of a strongly perturbed one-dimensional behavior associated with the gallium chains is detected, but it is so strongly perturbed that it is not relevant for the physics (i.e., three-dimensional conducting properties) nor the structural properties (i.e., absence of a structural modulation along the zigzag chains direction).



0.5 b^* 0.3 b^*

0.1 b^*

Figure 5. Calculated Fermi surface for Li_2Ga shown as different sections perpendicular to the $\Gamma-Y$ direction (i.e., b^*) of the Brillouin zone: (a) $0.5b^*$; (b) $0.3b^*$; (c) $0.1b^*$. $Y = (0, 1/2, 0)$, $U = (1/2, 1/2, 0)$, and $T = (0, 1/2, 1/2)$ in units of the orthorhombic reciprocal lattice vectors.

Li_9Al_4, a Solid in Which the Zigzag Chains Are More Spaced. As shown in Figure 6a, Li_9Al_4 contains zigzag uniform chains of aluminum atoms along the c direction.[9] These chains are more far apart from each other than in Li_2Ga, and thus, if the interactions with the Li atoms were not as strong as in that phase, there could be some chance for them to keep their identity in the solid. Here the formal number of electrons/aluminum atom assuming a complete charge transfer is however somewhat higher, 5.25. As discussed by Müller and Stöhr,[5] the packing in Li_2Ga is strongly related with that in Li_9Al_4 but also with that in the LiGa phase.

Our first principles calculations for this phase led to a very similar picture of the electronic structure for the Li_2Ga and Li_9Al_4 phases. The DOS of Figure 6b is overall in good

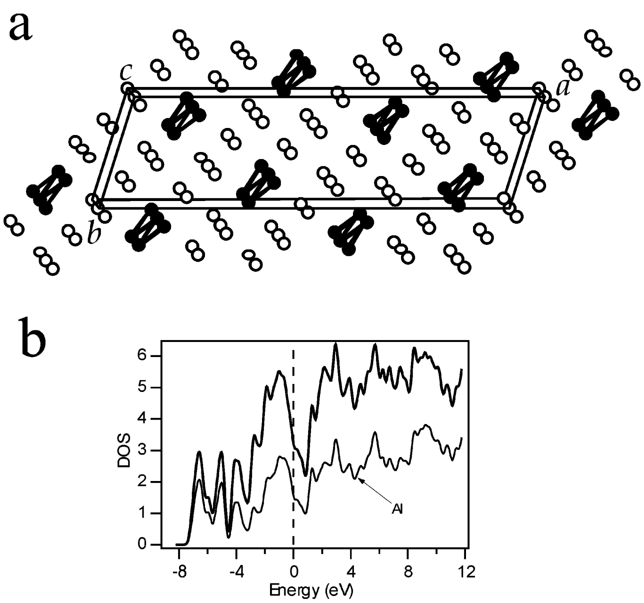


Figure 6. (a) Crystal structure of Li_9Al_4, where the full and empty circles refer to the Al and Li atoms, respectively. (b) Calculated density of states for Li_9Al_4. The total contribution of the aluminum orbitals is also shown.

agreement with the previous full-potential linearized augmented plane wave (FLAPW) results.[15] As shown in Figure 6b, there is again a very strong mixing of the lithium orbitals into the filled levels, the mixing being even larger than in Li_2Ga, simply because of the larger proportion of lithium atoms. The calculated Mulliken charges for the two different Al atoms are $+0.377$ and $+0.397$ whereas those for the five different Li atoms are -0.095, -0.099, -0.152, -0.207, and -0.258. The calculated overlap populations are also of the same order as those in Li_2Ga. The calculated tight-binding band structure for the isolated aluminum chain is practically identical with that of Figure 4b. Although we will not comment in any detail, the study of the Mulliken analysis, DOS and Fermi surface shows that in this phase there is a three-dimensional network of Al−Li, Li−Li, and Al−Al interactions in which the aluminum zigzag chains cannot be considered as a building block dominating the electronic structure near the Fermi level, as found for the gallium chains in Li_2Ga.

Conclusion

The electronic structure of Li_2Ga and Li_9Al_4, two phases which are closely related in terms of packing and contain uniform zigzag chains of gallium and aluminiun, respectively, have been studied on the basis of first principles DFT calculations. It is clear that in both phases there is a three-dimensional network of M−M, M−Li, and Li−Li (M = Ga, Al) bonding interactions, within which the zigzag chains do not play a dominant role as far as the electronic structure near the Fermi level is concerned. In addition, it is found that from the electronic structure perspective the zigzag chains of group 13 metal atoms are fundamentally different from that of *trans*-polyacetylene in that two orbitals lead to partially filled bands in the first case but only one in the second. In other words, the zigzag chains of doubly charged group 13 metal atoms and that of *trans*-polyacetylene are not isolobal.[7] Even though it is appealing, the analogy between the appropriately charged zigzag chains of main group atoms in solids and that of the prototypical *trans*-polyacetylene lacks any basis from the electronic structure viewpoint. Both Li_2Ga and Li_9Al_4 are predicted to be stable three-dimensional metallic conductors. The electron transfer in these phases is found to be very different from that suggested by the traditional Zintl approach, a fact whose consequences in related phases deserves further study.

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