Intermetallic Phases

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YAlC: A Bonding Chameleon with Heteropolyacetylene Features**

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Dedicated to Professor Arndt Simon on the occasion of his 75th birthday

Abstract: *YAlC was prepared by a flux method. It crystallizes as a partially filled-up TlI structure, showing remarkable structural aspects at the border between Zintl phases and intermetallics. This novel ternary aluminide–carbide exhibits a unique one-dimensional multi-center bond and a polyacetylene-related aluminum carbide substructure. The different functionalities of aluminum and of yttrium are quite remarkable. While the latter behaves more like a trivalent ion, aluminum contributes considerably to covalent bonding with carbon. Still yttrium d states contribute, but hardly in a directed manner.*

Silicon carbide and aluminum carbide are extremely stable refractory compounds demonstrating the strength of the Si–C and the Al–C bonds, respectively. If stoichiometric, both of them are semiconductors with bandgaps in the optically most attractive range between 2 and 3 eV. Ternary aluminum carbides exhibit remarkable combinations of structural and physical properties, therefore being investigated for applications, for example, as highly shear-resistant or thermoelectric materials.[1,2] Ternary carbides show a variety of structures with different (and sometimes novel) arrangements of similar building blocks. A few examples like $Th_2Al_2C_3$ and Mo_3Al_2C already indicate the higher structural complexity that ternary carbides can achieve and thus make their classification as intermetallic phases questionable.[3,4] Despite numerous attempts, no ternary or multinary compound of the Zintl phase type is yet known, which comprises common Zintl anions of silicon and carbon or aluminum and carbon.[4,5] We report herein on YAlC, the first aluminide carbide with a polyanionic structure featuring a polyacetylene-related geometry in a fascinating compromise of chemical bonding.

The compound was synthesized from the pure elements yttrium and aluminum, together with perylene as active carbon source, at the melting point of Al at 670 °C. This low reaction temperature may be essential for the formation of multinary compounds in competition with the highly stable binary phases. The crystal structure, which is displayed in Figure 1, was determined from single-crystal XRD, and the structure parameters were refined to high accuracy.

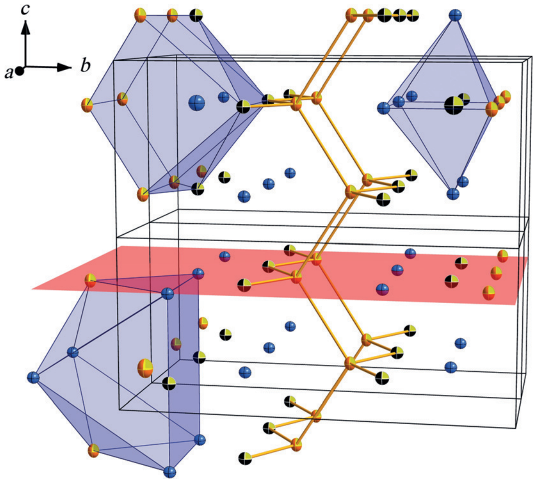

Figure 1. Crystal structure of YAlC as a skew view along the crystallographic *a* axis (C black, Al white, Y blue spheres). Semipolar bonds are drawn in yellow.

The structure of YAlC is a partially stuffed YAl (TlI structure type), by filling part of the octahedral voids with carbon.[6] It is perhaps worth mentioning that there is yet another more stuffed (and more distorted) variation of YAl, namely $Th_2Al_2C_3$, in which both types of octahedral voids are filled with carbon.[3] The carbon coordination sphere in YAlC is Y_4Al_2. Both yttrium and aluminum have ten-fold coordination, of which only four and two neighbors are carbon atoms, respectively. From the relatively high coordination number, one can infer a methanide interpretation according to $Y^{3+}Al^{3+}C^{4-}(e^{-})_2$. Paradoxically, we are left with the fact that there are many relatively short Y–Al contacts and an Al–Al separation of only 2.98 Å, which is too short for neighboring Al^{3+} cations. However, the resulting "ionic" sizes of Al, and Y fall fairly well around those occurring in the respective pure metals. Taking into account the two remaining electrons, which do not fit in the closed shell count, the system can be seen as C^{4-} anions embedded in a positively charged, and polarized, metallic background. The shortest Y–Al distance occurs precisely opposite to the shortest Al–C contact, which fits to the idea that the other valence electrons try to avoid the highly charged anion. All remaining Al–Al, and Y–Al, distances are slightly larger than the respective sums of the atomic radii, which is presumably due to the reduced number of electrons left for the metallic bonding.

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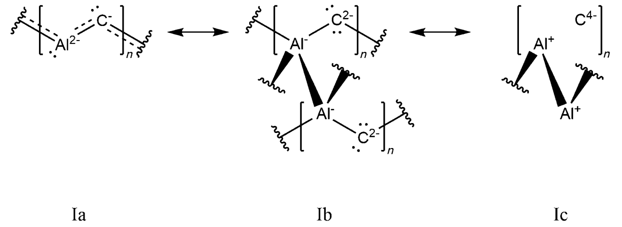
Depending on how far the idea of electron gas polarization is taken, the system can be interpreted in terms of covalently bonded models, which, despite not being fully satisfactory, are in agreement with the structural order. The shortest interatomic distance of 2.06 Å occurs between Al and C, in a planar one-dimensional zigzag chain, extending along the crystallographic *a* direction. Despite this planarity, the zigzag angle Al-C-Al of 110.8° falls between those of sp^2 and sp^3 configurations, actually closer to sp^3. With no other contact to carbon that could be classified as a semipolar bond, this angle seems to result from a compromise between the tendency to form polar covalent bonds to aluminum, and the preference for an octahedral coordination of the C^{4-} anion. Aluminum has a four-coordinate sp^3-like shell that consists of two Al−C (from the zigzag chain) and two homolytic Al−Al contacts. If this semi-polar covalent Al−C substructure is considered, the structure can be written as $Y^{3+}[AlC]^{3-}$. Here two lone pairs at carbon (C^{2-}) and a strongly distorted four-bonded tetrahedral Al^- are assumed. The elongated Al−Al bonds would have, at 2.98 Å, a Pauling bond order of 0.51,[7] which would bring us back to the yttrium-assisted (quasi-metallic or multi-center) bonding.

Interpretations taking the planarity of C−Al chain as a starting point are quite unsatisfactory. The $10e^-$ $^1_\infty[AlC]$ network isoelectronic to polyacetylene $(CH)_x$ (Scheme 1, Ia) would have one lone electron pair at carbon and one at the Al center, with a single–double bond alternation, in contradiction with the all-equal Al−C distances.



Scheme 1. Different Lewis formulations of the bonding situation.

Another semipolar network is represented in Scheme 1, Ib. If one still considers a methanide-like formulation according to the typical but distorted octahedral coordination of carbon, then a covalent two-electron substructure $^1_\infty[Al^+]_n$ results as given in Scheme 1, Ic, which however seems to be quite awkward.

To better unravel the chemical bonding we evaluated the DFT band structure, density of states (DOS), and selected surface sections of the electron localization function (ELF).[8] Occupied bands (see partial DOS in Figure 2) exhibit strong carbon contributions, with selective Al s and Al p in-mixing to certain bands only. Y d in-mixing is more of a general kind and concerns more-or-less all bands. The system is predicted to be metallic, with a low DOS at the Fermi level (Figure 2 and 3). The conduction electrons belong to two incompletely filled (Figure 3) bands originating mainly from p and d states. At the first sight, the overall picture fits acceptably the idea of carbon anions in metallic background; that is, $Y^{3+}Al^{3+}C^{4-}(e^-)_2$.

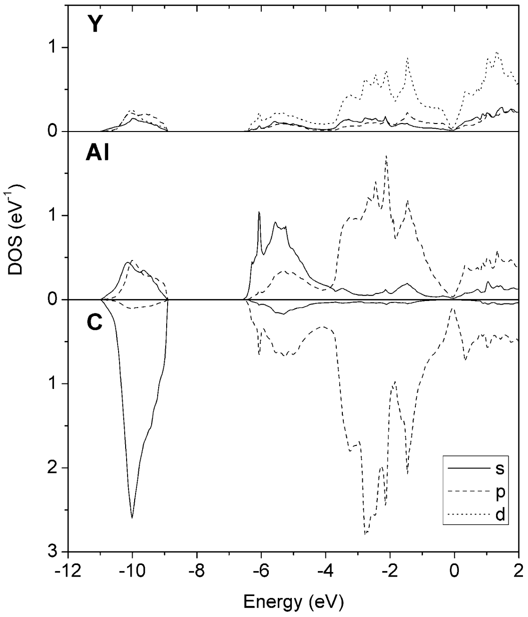


Figure 2. Partial density of states of YAlC.

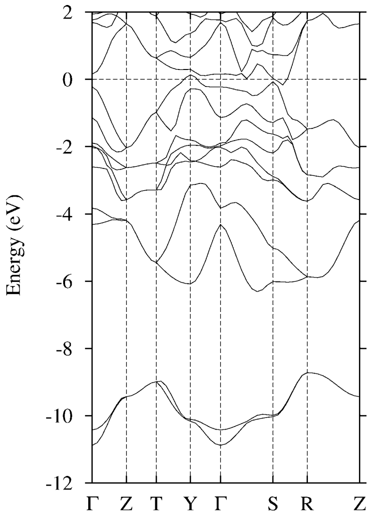


Figure 3. Band structure of YAlC within density functional theory.

However at closer inspection, selected mixing and polarization appears to be crucial. Clearly, yttrium and aluminum cannot be interchanged since they play different roles in bonding. Note for instance, the difference of orbital contributions to the electronic states as shown in Figure 2, giving to yttrium more of a general stabilizing factor to most electronic states, while aluminum shares distinct covalent features with carbon. The partially covalent Al−C interaction is indicated by the shifting (and splitting) of the aluminum partial DOS, which show significant contributions at energies where the carbon states appear. Between −7 and −4 eV, aluminum s-states even provide the dominating contributions to the total DOS. This can be interpreted as a signature of low-oxidation-state aluminum centers according the semipolar description $Y^{3+}[AlC]^{3-}$ model. It should be noted that $[AlC]^{3-}$ might be understood as a Zintl-type polyanion according the Zintl–Klemm concept.[5] However, it is isoelectronic to polyacetylene and it reveals a very similar but undistorted conformation (with H atoms replaced by lone electron pairs) there are the additional out-of-plane Al–Al bonds extending in a one-dimensional zigzag chain (Figure 4b).

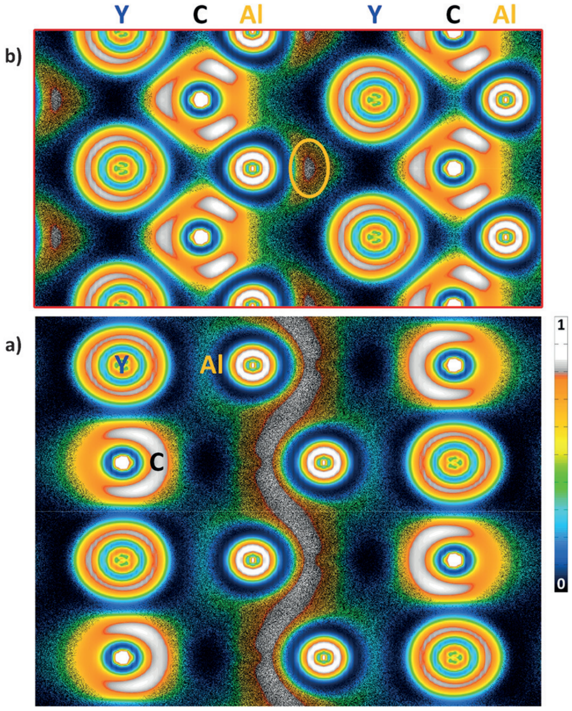


Figure 4. Surface sections of the electron localization function (ELF) of YAlC. a) (001) plane showing the polarization of the carbon shell because of the covalent C–Al interaction. The yellow-orange circle highlights a cross-section of the Y–Al multi-center interaction. b) (100) plane exhibiting the Y-Al ELF stripe, and side-view of carbon lone-pairs. Electron density and ELF are shown simultaneously as density of colored pixels and their color, respectively, over a black background. The color scale is shown in the right-side bar of the figure.

Around the Fermi level, Y d and Al p orbitals mix with dominant contributions by Al p states (Figure 2). The polarization of the carbon valence shell is also visible in the ELF map in Figure 4a. Note the formation of two high-ELF lobes point each of them towards an aluminum atom, and the double lone pair that extends in the interstitial space between yttrium atoms. This type of deformation of the anion shell, when coordinating small and large cations, is commonly found in ternary Zintl phases.[9]

In Figure 4b, tapes of high ELF with low-electron density are found meandering along the Al–Al zigzag chains. The cross-section of one of these tapes is signaled with a yellow oval in Figure 4a. The tapes correspond to the Al–Al half bonds, assisted by Y d states, which can also be addressed as Y–Al multicenter bonds. As a matter of fact, it is not a lack of electrons for an Al–Al bond what makes this interaction special, but rather their (de-)localization involving yttrium. The rather low localization values at the yttrium cores are also a sign of the partial occupation of the 4d orbitals (back-bonding). Note that the ELF is not an additive function, and the occupation of states with higher angular momentum (with more nodes) results in a reduction of the ELF. In other words, a more cation-like yttrium (with emptier 4d states) shows spherical shells with higher ELF values.

YAlC shows indeed a fascinating compromise between the polarized metal (stuffed intermetallic) and the semi-covalent $Y^{3+}[AlC]^{3-}$ model. A key feature is the coexistence of two-center and multi-center bonds. The latter appear as tapes meandering wherever there would be a direct Al–Al or Y–Al contact, and contain the residual electron density after the formation of the Al–C semi-covalent chains.

Experimental Section

Single crystals of YAlC were obtained from pure elements with perylene as C-source in liquid Mg, at elemental ratios Mg/Y/Al/C(/H) of 90:10:10:15(:9). The synthesis was carried out in Nb ampoules under an Ar atmosphere. The reaction took place at 670 °C during 7 days (heating rate of 250 $\mathrm{K\,h^{-1}}$; cooling 2 $\mathrm{K\,h^{-1}}$ to 570 °C within 6 h to room temperature) yielding a regulus that was purified from Mg at 600 °C during 18 h in high vacuum ($<5\times10^{-5}$ mbar), leaving an inhomogeneous and loose solid.

All steps, including PXRD as well as selecting and sealing of single-crystals for diffraction experiments but except weighing of the sample for analysis of the hydrogen content, were done under an Ar atmosphere.

For structure determination, a crystal of YAlC ($0.08\times0.04\times0.02$ mm) was selected under a microscope in inert atmosphere. The data set was collected using a Bruker AXS smart APEX CCD 1 K area detector working with $\mathrm{MoK_{\alpha}}$-radiation (0.73071 Å).

Crystal Data: YAlC, $M=127.90\ \mathrm{g\,mol^{-1}}$, orthorhombic, $a=3.4063(19)$, $b=11.374(6)$, $c=5.037(3)$, $V=195.16(18)$, $T=293.15$ K, space group *Cmcm*, $Z=4$, $\rho_{\mathrm{calc}}=4.353\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{MoK_{\alpha}})=29.80\ \mathrm{mm^{-1}}$, reflections = 1236, individual reflections = 207 ($R_{\mathrm{int}}=0.0209$), $wR_2=0.0351$ (all data), $\Delta\rho=0.79/-0.77$.

Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-425093.

Powder X-ray diffraction data were measured on a STOE Stadi P diffractometer (Debye–Scherrer geometry) with a DECTRIS MYTHEN 1 K solid state detector using a curved Ge(111) monochromator ($\mathrm{CuK_{\alpha1}}=1.54056$ Å) enclosed in capillaries for exclusion of air. The PXRD is in good agreement with a mixture of YAlC, $Y_2Al_2C_3$, and Al_2Y, and further unassignable reflections indicating yet unknown phase(s).

Elemental analysis of the hydrogen content was carried out on a LECO CHN-900 analyzer. The hydrogen content of the synthesis product after distillation was $\omega_{\mathrm{H}}\leq0.05\,\%$. The yttrium, aluminum, and magnesium content was determined on single crystals using a LA-ICP-MS-spectrometer.[10] LA-ICP-MS indicated occlusion of Mg or MgO within YAlC single crystals instead Al substitution.

Further details on the characterization of YAlC and the synthesis product are provided in the Supporting Information.

The electronic structure calculations were performed using three different implementations of DFT, in the order check for consistency, and avoid biased results; for example, bias due to a choice of basis set. We employed CASTEP and DMol^3 packages within Materials studio and the TB-LMTO-ASA code from the Max Plank Institute in Stuttgart.[11] The exchange correlations employed were PBE, POB, and Langreth–Mehl, respectively.[12] Details on the precision of the calculation can be provided if requested. The ELF was obtained with the code implemented by A. Savin in the LMTO package and it was drawn using a code developed in-house.[13] ELF minima separate bonding features and close shells, all from each other.

Keywords: carbides · electronic structure · intermetallic phases · Zintl phases

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