

The complex energy landscape of $\text{Al}_{13}\text{TM}_4$ quasicrystalline approximant surfaces: application to catalysis

É. Gaudry

Université de Lorraine, CNRS, IJL, F-54000 Nancy, France

Emilie.Gaudry@univ-lorraine.fr

A wide range of intermetallic crystal structures are based on polyhedral entities, often called “clusters”, as first introduced by F.A. Cotton in the early 1960’s to describe compounds containing metal-metal bonds. This approach is also largely used to describe more complex intermetallic phases, like intermetallic clathrates, quasicrystals and their approximants.

Termed four-layer decagonal approximants, the structures of the $\text{Al}_{13}\text{TM}_4$ compounds (TM = transition metal, like Co, Fe, Ru, Os for the experimentally grown compounds) have been initially understood as a periodic stacking of pseudo-10-fold symmetric atomic layers. A three-dimensional description of these phases was first introduced by Henley based on geometric entities identified in the bulk structure (pentagonal bi-pyramid clusters) [1]. A visualization of the structure as a cage-compound was then proposed, based on quantum chemical calculations, each cage containing one TM-Al-TM molecular group (Fig. 1) [2].

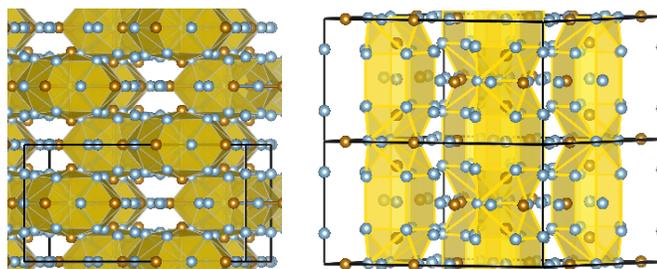


Figure 1. Description of the $\text{Al}_{13}\text{Fe}_4$ bulk structure as a stacking of clusters, as first introduced by Henley (left) or based on quantum chemical calculations (right).

While the bulk atomic arrangements of the $\text{Al}_{13}\text{TM}_4$ compounds are very similar, the structures of their pseudo-10fold surfaces differ. The cluster substructure is preserved up to the $\text{Al}_{13}\text{Fe}_4(010)$ surface, but $\text{Al}_{13}\text{Co}_4(100)$ presents an Al-rich dense termination [3,4]. The situation is even more complex for $\text{Al}_{13}\text{Ru}_4(010)$, since a surface reconstruction is observed experimentally [5]. Such structural differences lead to contrasted catalytic performances.

A systematic determination of the bulk electronic structure and chemical bonding network in the $\text{Al}_{13}\text{TM}_4$ series (TM= Fe, Co, Ru, Rh, Os, Ir) is an essential step in the scope of understanding the experimental pseudo-10fold surface structures of $\text{Al}_{13}\text{TM}_4$ compounds. This is achieved here using a theoretical approach based on Density Functional Theory (plane-wave implementation). The projected Crystal Orbital Hamilton Population (pCOHP) has been used to analyze the chemical bonding network [7]. This method re-extract Hamilton-weighted populations from plane-wave electronic structure calculations to develop a tool analogous to the crystal orbital Hamilton population method. The bonding strengths result from the pCOHP integration to the Fermi level.

According to the pCOHP analysis, the Al-Al and TM-TM bonds with the strongest covalent character are located in between the Henley clusters, while the strongest Al-TM ones are those of the molecular group already identified by quantum chemical calculations [2], part of the Henley-type cluster. In the latter case,

the Fe-Al-Fe molecular group is bonded more strongly than the Co-Al-Co molecular group, which could explain the different surface structures of $\text{Al}_{13}\text{Fe}_4(010)$ and $\text{Al}_{13}\text{Co}_4(100)$. Indeed, Henley-type clusters are intact at the $\text{Al}_{13}\text{Fe}_4(010)$ surface, leading to a highly corrugated surface, while the $\text{Al}_{13}\text{Co}_4(100)$ surface structure is deduced from the selection of the Al-rich atomic plane as surface termination, without any protruding surface Co atoms, the Co-Al-Co bond being broken at the surface (Fig. 2).

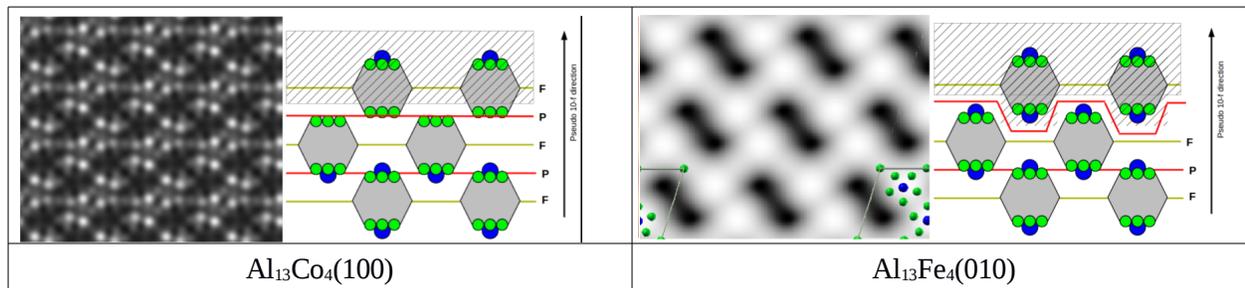


Figure 2. Schematic view describing the interaction between the 2D pseudo-10fold surface and the 3D cluster substructure for $\text{Al}_{13}\text{TM}_4$ compounds (TM=Fe,Co), along with simulated STM (Scanning Tunneling Microscopy) images. Hatched area = zone above the surface. Al and TM atoms are represented in green and blue, respectively.

The broken bonds at the surface lead to complex energy landscapes, meaningful as template for further complex molecular ordering or for their unique surface properties, at least when compared to conventional alloys (low friction and low adhesion, corrosion resistance, catalytic activity, etc). In a second step, the adsorption properties of the pseudo-10f $\text{Al}_{13}\text{Co}_4(100)$ and $\text{Al}_{13}\text{Fe}_4(010)$ surfaces towards atomic hydrogen and small C_xH_y molecules (acetylene, butadiene, butene) are determined [6,8,9]. The influence of the operating conditions (Temperature, Pressure) is considered, using a simple thermodynamic model, for the co-adsorption of atomic hydrogen and butadiene. It highlights that when covered with atomic hydrogen (7 at./surf. cell), at $P_{\text{H}_2}=5\text{mbar}$ and $T=300\text{ K}$, contrasted behaviors are calculated for the butadiene and butene adsorption on the $\text{Al}_{13}\text{Co}_4(100)$ and $\text{Al}_{13}\text{Fe}_4(010)$ surfaces. This provides insights into the different catalytic activities of these two pseudo-10fold surfaces towards the semi-hydrogenation of butadiene.

[1] C. L. Henley, *J. Non-Cryst. Solids*, **153-154** (1993) 172-176.

[2] M. Armbrüster, K. Kovnir, Y. Grin, R. Schögl, *chapter 10 in Complex Metallic Alloys*, edited by J.-M. Dubois and E. Belin-Ferré (2011)

[3] É. Gaudry, C. Chatelier, G. McGuirk, L. Serkovic Loli, M.-C. DeWeerd, J. Ledieu, V. Fournée, R. Felici, J. Drnec, G. Beutier, M. de Boissieu, *Physical Review B* **94** (2016) 165406

[4] J. Ledieu, É. Gaudry, L.N. Serkovic Loli, S. Alarcón Villaseca, M.-C. de Weerd, P. Gille, Y. Grin, J.-M. Dubois and V. Fournée, *Physical Review Letters*, **110** (2013) 076102

[5] J. Ledieu, É. Gaudry, K. Pussi, T. Jarrin, Ph. Scheid, P. Gille, V. Fournée, *J. Phys. Chem. C*, **121** (2017) 22067

[6] L. Piccolo, É. Gaudry, J. Ledieu, V. Fournée, L. Kibis, talk presented at the ECOSS conference (August 2017)

[7] S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.*, **37** (2016) 1030

[8] Kandaskalov, V. Fournée, J. Ledieu, É. Gaudry, *J. Phys. Chem. C*, **121** (2017) 18738

[9] D. Kandaskalov, V. Fournée, J. Ledieu, and É. Gaudry, *Journal of Physical Chemistry C*, **118** (2014) 23032