Poster

The impact of orbitals interactions on the stability of ZnMgSc approximant crystal

I. Buganski, R. Strzalka, J. Wolny

AGH University of Krakow, Faculty of Physics and Applied Computer Science, Krakow, Poland
Ireneusz.buganski@fis.agh.edu.pl

Tsai and Bergman clusters represent distinct structural motifs found within icosahedral quasicrystals. The dominance of one cluster type over the other determines the classification of the quasicrystal. However, research has shown that structures initially attributed to one cluster type can alternatively be interpreted in terms of the other. For instance, in 2008, the proposed structure solution for the Ag- In-Yb 2/1 periodic approximant crystal suggested the presence of pseudo-Bergman clusters instead of the traditionally assumed Tsai clusters [1]. Notably, the Bergman cluster's arrangement was imperfect, requiring either distortion or the presence of vacant sites within its concentric shells to achieve optimal packing. Recent investigations have delved deeper into the modifications necessary to attain ideal Tsai or Bergman cluster structures. This analysis unveiled that Tsai and Bergman clusters can indeed be interchangeable, given a certain level of flexibility in shell occupancy and atomic displacement within the clusters [2]. These deviations follow systematic patterns and appear to hold true across various types of quasicrystals and approximant crystals. The key question thus arises: what are the fundamental disparities between Tsai and Bergman phases, and what factors influence the formation of each phase?

To explore the structural preference for Tsai cluster geometry, we employ Density Functional Theory with plane waves for electronic structure analysis. Our selection of the $Zn_{84.79}Mg_{0.86}Sc_{14.35}$ [3] (Figure 1 .) phase for these calculations is driven by its diamagnetic nature and the inclusion of relatively light elements. To investigate the impact of electron, we systematically shift atoms from ideal Tsai positions to ideal Bergman positions in five steps. At each step, we analyze the density of states and Löwdin charges. Two distinct calculation approaches are employed: one focuses on the isolated molecule, while the other involves band structure calculations for a bulk material with periodic boundary conditions. The rationale behind this dual approach is two-fold. Firstly, the isolated molecule analysis aims to unveil the nature of additional sites absent in Bergman structures of both quasicrystals and periodic approximants. Since quasicrystals lack periodicity, we opt out of periodic boundary conditions for this part of the study. However, due to the limited number of atoms in the isolated molecule model, electronic structure behavior can only be qualitatively analyzed. For quantitative analysis, we utilize the full unit cell with periodic boundary conditions, leveraging the full extent of periodicity in the system.

Calculations revealed that certain sites are strictly reserved for electronegative or electropositive atoms. Upon structural transformation, the interaction between neighboring orbitals, especially between p orbitals of Zn leads to the increase of the total energy and destroys the dispersion relation and lead to flat bands. The p character of orbitals prevails as the density of d states coming from Sc decreases below Fermi energy. Löwdin charges analysis confirms the transfer from s to p states of Zn what suggests Bergman phases are more dependent on p orbitals. Because the density of Sc-3d states decreases, it can be concluded that the absence of the sp- d hybridization in molecular orbitals of the structure after transformation is the main reason of the structure instability. That confirms the role of sp-d hybridization in this phase as confirmed to also be the factor in other Tsai-type structures.

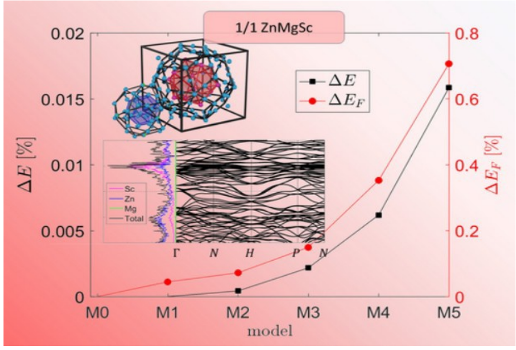

Figure 1. The increase of total energy and Fermi Energy upon transformation to Bergman-type structure. The atomic model and the band structure are shown in the inset.

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[2] Buganski, I., Wolny, J. (2023). *J. Alloy. Compd.* **939**, 168823.

[3] Buganski, I., Strzalka, R., Wolny, J. (2024). Isr. J. Chem., https://doi.org/10.1002/ijch.202300139