Electron counting in 1/1 approximant of Al–Cu–Li quasicrystal

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The electron count is a key to understand the stability of quasicrystals and has been extensively used to find new quasicrystals. Three popular classes of stable icosahedral quasicrystals (iQCs), i.e., Mackay-type, Bergman-type, and Tsai-type iQCs have been discovered around the electron counts per atom of ~1.8, ~2.1, and ~2.0, respectively [1]. We have recently concentrated on revealing orbital origins of these counts. Through analyzing the valence electrons in an Al–Cu–Ir approximant of the Mackay-type iQCs [2] and other related intermetallic compounds (AlIr, $RuAl_2$, and $RuGa_3$) [3] by means of first-principles band-structure calculations and Wannier-functions analyses, a universal counting rule for the number of the valence bands (valence states per primitive cell) was developed. The rule is a general variant of the well-known 18 - n rule [4], and molecular-like bonding between small clusters (mainly centered on transition-metal elements) plays a crucial role in the formation of the valence bands. Since only local structural information is required to apply the rule, we tried evaluating the number of the valence states in an ideal structural model of the Mackay-type iQCs and derived the number of the valence states per atom of ~1.8 + $10x_T$, where x_T is the mole fraction of transition-metal elements [5]. This value (excluding $10x_T$ term) is comparable with the above-mentioned electron count per atom for the Mackay-type iQCs.

In this paper, we focus on 1/1 Al–Cu–Li approximant of the Bergman-type iQCs. Nozawa and Ishii theoretically studied valence electrons and bonding in this system, emphasizing similarities between the approximant and NaTl-type LiAl Zintl phase [6]. In the case of the LiAl phase, the aluminum sublattice can be regarded as a diamond structure, and the origin of four valence states per LiAl unit can be easily understood as sp^3–sp^3 bonding orbitals between aluminum atoms. On the other hand, orbital origins of the valence states and their count in the approximant were unclear. We analyzed the valence states in $Al_{54}Li_{26}$ model, which Nozawa and Ishii had used for the approximant, by using maximally-localized Wannier functions [7]. There is one Bergman cluster per the formula unit, and the valence bands contain ~176 states per cluster. We constructed 88 Wannier functions for the valence bands per spin. After the localization process, 25 functions were found around the $Al_{12}@Li_{20}@Al_{12}$ inner shells of the cluster, and the other 63 functions were found at every mid-edge position of the fullerene-like shell. Because each cluster shares six edges and eight six-membered rings of the fullerene-like shell with neighboring clusters, 54 Wannier functions are shared with neighboring clusters. This is why the number of the Wannier functions found at the edges (=63) differs from that of the edges of the shell (=90) by 27. Generalization of this counting for Al–Cu–Li iQC is under way. The latest progress will also be presented.

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