Unified cluster-based description of valence bands in AlIr, RuAl₂, RuGa₃ and Al–TM quasicrystalline approximants

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Abstract. Formation of the valence bands in AlIr, RuAl₂ and RuGa₃ was analysed on the basis of Wannier functions. It was sufficient to consider nine (s-, p- and d-like) Wannier functions per cluster centred on each transition metal for describing the valence bands. As in the case of Al–Cu–Ir quasicrystalline approximant, which we reported previously [Kitahara K, Takagiwa Y and Kimura K 2015 J. Phys. Soc. Jpn. 84 014703-1–8], covalent bonds between clusters form where the distance between neighbouring clusters is about 0.3 nm, making conduction states as antibonding functions. sp³d⁵, sp³ and pₓ-like Wannier functions are used for the covalent bonds in AlIr, RuAl₂ and RuGa₃, respectively.

1. Introduction

Formation of pseudogap or narrow bandgap in some of group 13 element–transition metal (TM) intermetallic compounds including Al–TM quasicrystalline approximants had extensively been studied, and importance of hybridisation between sp-functions of group 13 elements (or free electrons in jellium) and d-functions of TM atoms were realised [1]. However the concept of sp–d hybridisation cannot completely explain the formation of bandgap, especially the number of valence bands. For example, in the case of RuAl₂, there are seven valence bands per ruthenium atom without considering spin degeneracy. While five out of the seven bands may be associated with sp–d bonding functions, the origin of the other two bands is unclear.

We studied the electronic band structures in AlIr (CsCl-type), RuAl₂ (TiSi₂-type), RuGa₃ (CoGa₃-type) and Al–Cu–Ir quasicrystalline approximant as typical intermetallic compounds with pseudogap or narrow bandgap. To analyse the band structures, we used maximally localised Wannier functions [2], which are representative functions corresponding to the bands in a specified energy range. We have already reported analysis on the Al–Cu–Ir approximant [3], where we described the valence and a part of the conduction bands on the basis of Wannier functions centred on clusters of 0.2 nm radius, and the number of valence bands (173) was decomposed in terms of the numbers of TMs (t = 23), clusters (c = 16) and covalent bonds between the clusters (b = 6) per primitive unit cell as 5t + 4c − b without considering spin degeneracy. As we shall show, fundamentally the same description can be applicable to the other three intermetallic compounds, AlIr, RuAl₂ and RuGa₃.
2. Methods

Self-consistent ground-state electronic structure calculations were performed using an all-electron full-potential linearised augmented plane-wave code [4] within the local density approximation of the density functional theory [5] for AlIr [CsCl-type, space group Pm3m, Figure 1(a)], RuAl₂ [TiSi₂-type, space group Fddd, Figure 1(b)] and RuGa₃ [CoGa₃-type, space group P4₂/mnm, Figure 1(c)]. We used experimental lattice constants and atomic positions for AlIr [6], RuAl₂ [7] and RuGa₃ [8]. Spin polarisation and spin–orbit coupling were not considered in this study. Unshifted 16 × 16 × 16, 8 × 8 × 8 and 4 × 4 × 4 wave-vector grids were used to construct Wannier functions for AlIr, RuAl₂ and RuGa₃, respectively. We constructed sets of Wannier functions which span the valence and a part of the conduction bands and which are localised around TMs in similar ways as described in [3].

3. Results

We constructed nine Wannier functions per iridium atom for AlIr. As shown in Figure 2(a), these Wannier functions contain all the valence states. While three t₂g-like functions are distributed within the valence bands [Figure 2(b)], the other six (s-, eₓz- and p-like) functions significantly contain conduction states [Figures 2(c)–2(e)]. To analyse how these functions split into valence and conduction states, we constructed sp³d²-like hybrid functions oriented toward ⟨100⟩ directions as linear combinations of the six functions [Figures 2(f) and 2(i)]. Then, we solved partial Hamiltonians between pairs of sp³d²-like functions and obtained pairs of bonding [Figure 2(j)] and antibonding [Figure 2(k)] functions. As shown in Figures 2(g) and 2(h), the bonding and antibonding functions were mainly composed of valence and conduction states, respectively.

We constructed nine Wannier functions per ruthenium atom for each of RuAl₂ and RuGa₃. These Wannier functions completely describe the valence bands in RuAl₂ and RuGa₃, and the nine functions can be classified into one s-like, five d-like and three p-like functions or, strictly speaking, linear combinations of them.

In the case of RuAl₂, d₃gₓ²−ₙᵧ², dₓz-like, pₓ-like and pₜ-like functions significantly contain conduction states, and hence we constructed sp³-like hybrid functions oriented toward ⟨111⟩ directions—we call the functions sp³ instead of pₜdₓ for simplicity as the symmetry is the same, i.e. both belong to the same reducible representation under the point group of the ruthenium site—as linear combinations of the four functions [Figure 3(a)]. Bonding [Figure 3(b)] and antibonding [Figure 3(c)] functions between two sp³-like functions at neighbouring ruthenium sites were mainly composed of valence and conduction states, respectively [see Supplementary Figures S1(a)–S1(m) for the partial densities of states projected on each Wannier function].

In the case of RuGa₃, only pₓ-like function [Figure 4(a)] contains conduction states. Bonding [Figure 4(b)] and antibonding [Figure 4(c)] functions between two pₓ-like functions at neighbouring ruthenium sites were mainly composed of valence and conduction states, respectively [see Supplementary Figures S2(a)–S2(l) for the partial densities of states projected on each Wannier function].

Figure 1. Crystalline structures of (a) AlIr, (b) RuAl₂ and (c) RuGa₃.
Figure 2. (colour online) Integrated partial densities of states in AlIr projected on (a) all the Wannier functions, (b) $t_{2g}$-like, (c) $s$-like, (d) $e_g$-like, (e) $p$-like, (f) $sp^3d^2$-like hybrid, (g) $sp^3d^2$–$sp^3d^2$ bonding and (h) $sp^3d^2$–$sp^3d^2$ antibonding functions (solid lines, black). In each graph, partial density of states is shown in an arbitrary unit (filled area, light red), and the corresponding functions are visualised (insets). In Figure (a), integrated total density of states (dashed line, grey) and corresponding density of states (in an arbitrary unit, filled area, light grey) are also shown. Figures (i), (j) and (k) show magnified images of a pair of $sp^3d^2$–$sp^3d^2$ hybrid, an $sp^3d^2$–$sp^3d^2$ bonding and an $sp^3d^2$–$sp^3d^2$ antibonding functions, respectively.

Figure 3. (colour online) Visualised images of (a) a pair of $sp^3$-like hybrid, (b) an $sp^3$–$sp^3$ bonding and (c) an $sp^3$–$sp^3$ antibonding functions in RuAl$_2$.

Figure 4. (colour online) Visualised images of (a) a pair of $p_y$-like, (b) a $p_y$–$p_y$ bonding and (c) a $p_y$–$p_y$ antibonding functions in RuGa$_3$.

4. Discussion

To summarise our results, it is convenient to consider clusters of which centres are the same as those of the constructed Wannier functions. In the cases of AlIr, RuAl$_2$ and RuGa$_3$, the centres of such clusters are the sites of TMs; therefore, the numbers of TMs ($t$) and clusters ($c$) per primitive unit cell are $t = c = 1$ for AlIr, $t = c = 2$ for RuAl$_2$ and $t = c = 4$ for RuGa$_3$. For each cluster, we constructed one $s$-, three $p$- and five $d$-like Wannier functions as candidates of valence states. It corresponds to a part of our counting rule $5t + 4c$, i.e. five $d$-like functions per TM and one $s$- and three $p$-like functions per cluster. Formation of pairs of bonding and antibonding functions between Wannier functions at neighbouring sites can be considered as covalent bonds between the clusters. Such covalent bonds form where the distance between two clusters is about 0.3 nm as discussed in [3]. Six $sp^3d^2$, four $sp^3$- and one $p_y$-like functions per cluster are used for the covalent bonds in AlIr, RuAl$_2$ and RuGa$_3$, respectively, making a conduction state as an antibonding function per pair of clusters. Thus, the number of covalent bonds between the clusters ($b$) per primitive unit cell is $b = 3$ for AlIr, $b = 4$ for RuAl$_2$ and $b = 2$ for RuGa$_3$, and then the number of valence bands is correctly evaluated on the basis of $5t + 4c - b$ rule as
5 × 1 + 4 × 1 − 3 = 6 for AlIr, 5 × 2 + 4 × 2 − 4 = 14 for RuAl₂ and 5 × 4 + 4 × 4 − 2 = 34 for RuGa₃.

We should note that, Yannello and Fredrickson proposed 18 − n rule for the number of valence electrons per TM in TM–main group intermetallic phases [9], where n is the number of electrons in bonding functions between TMs. This rule is a special case of our 5t + 4c − b rule, which reduces to 18 − n rule when t = c; in such case, 2b = tn, and therefore 2(5t + 4t − b) = t(18 − n).

In the present cases, we do not need to consider TMs and clusters separately, and therefore 18 − n rule is sufficient. However, in some cases (at least in the case of Al–Cu–Ir quasicrystalline approximant [3]), the numbers of TMs and clusters can differ, and 5t + 4c − b rule is required.

To associate all the valence states with TMs implies that formal charges of iridium in AlIr, ruthenium in RuAl₂ and ruthenium in RuGa₃ are −3, −6 and −9, respectively. Öğüt and Rabe [10] calculated the Born effective charge tensor of ruthenium in RuAl₂, and the directional average of the tensor was about −6.2. This fact supports the formal charge of ruthenium in RuAl₂. To examine the role of aluminium or gallium in formation of the electronic structures, we also calculated the electronic band structures in TMs-in-jellium models, where each aluminium or gallium in AlIr, RuAl₂ and RuGa₃ are replaced with homogeneous charges of 3+ and three free electrons. In Figures 5(a)−(c), the densities of states in these approximated models are compared with those of the original models. In the cases of AlIr and RuAl₂, the densities of states of both the original and the approximated models are almost the same. Even in the case of RuGa₃, where 75% of atoms are replaced with jellium in the approximated model, overall structure of the density of states is not drastically changed, and gap-like structure remains around 1 eV above the Fermi energy. It indicates that the role of aluminium or gallium is, as a first approximation, just to offer free electrons to the system.

Finally, as our description is based on a short-range mechanism, it is very interesting whether it can be applicable to quasicrystals or higher order approximants, too; if not, there is a room to consider a long-range mechanism.

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