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Hume-Rothery stabilization mechanism and e/a determination in MI-type Al-Mn, Al-Re, Al-Re-Si, Al-Cu-Fe-Si and Al-Cu-Ru-Si 1/1-1/1-1/1 approximants - a proposal for a new Hume-Rothery electron concentration rule

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Hume-Rothery stabilization mechanism and e/a determination in MI-type Al–Mn, Al–Re, Al–Re–Si, Al–Cu–Fe–Si and Al–Cu–Ru–Si 1/1-1/1-1/1 approximants – a proposal for a new Hume-Rothery electron concentration rule

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Full-potential linearized augmented plane wave (FLAPW) band calculations with subsequent FLAPW-Fourier analyses have been performed for five MI-type Al–TM (transition metal)-based 1/1-1/1-1/1 approximants in order to elucidate the origin of a pseudogap from the point of view of the Fermi surface–Brillouin zone (FsBz) interactions. The square of the Fermi diameter \( (2k_F)^2 \) is determined from the Hume-Rothery plot to be close to 50 without exception in units of \( (2\pi/a)^2 \), where \( a \) is the lattice constant. The FsBz interactions involving several reciprocal lattice vectors are claimed to be responsible for constituting the pseudogap structure across \( E_F \). This is referred to as the multi-zone effect. Among them, the \( |G|^2 = 50 \) wave, in which the Fourier coefficients are most evenly and densely distributed across \( E_F \), is selected as the critical one satisfying the matching condition \( (2k_F)^2 = |G|^2 \). The \( d \)-states-mediated-splitting appears to be absent in spite of substantial occupations of TM-\( d \) states in the valence band. All MI-type approximants studied are found to obey the Hume-Rothery stabilization mechanism. A new Hume-Rothery electron concentration rule linking the number of atoms per unit cell, e/uc, with a critical reciprocal lattice vector \( |G|^2 \) is found to hold well for structurally complex intermetallic compounds obeying the Hume-Rothery stabilization mechanism.

Keywords: MI-type 1/1-1/1-1/1 approximant; pseudogap; FLAPW band calculation

1. Introduction

A quasicrystal is defined as a solid satisfying conditions such that (1) the diffraction intensities consist of an infinite number of \( \delta \)-functions, (2) the number of basis vectors is larger than its dimension, and (3) rotational symmetry forbidden in crystals
is manifest [1]. Structures satisfying the above conditions can be constructed using the so-called cut-and-project method, which involves a projection from a higher-dimensional model space to three- or two-dimensional real space [1]. The atomic structure of icosahedral and decagonal quasicrystals, respectively, can be constructed by decorating three- and two-dimensional quasi-lattices thus generated with atoms. Using a small high-dimensional rotation the cut-and-project method can generate not only a quasi-lattice but also a crystalline counterpart having nearly the same local structure as that of a quasicrystal. The latter is specifically called an approximant to the quasicrystal. Approximants are, therefore, lattice-periodic crystals containing generally more than one hundred atoms in a giant unit cell and are characterized by a local rotational symmetry similar to that existing in quasicrystals. Conversely, quasicrystals can be regarded as highly ordered intermetallic compounds with an infinitely large unit cell.

Icosahedral quasicrystals and their approximants are often classified according to the atomic clusters that their structures are composed of. Three different atomic cluster-types are known to exist: the Mackay icosahedral-type (abbreviated as MI) cluster, the rhombic triacontahedral-type (abbreviated as RT) cluster and the Tsai-type cluster being composed of 54, 44 and 65 to 66 atoms, respectively [2,3]. The MI-type quasicrystals and their approximants are formed by a combination of Al and transition metal (TM) elements, while the RT-type ones by a combination of polyvalent elements like Al, Mg, Zn, etc., and/or noble metals. The Tsai-type ones were more recently discovered in a variety of Cd- and Sc-based alloy systems [2,3].

Particular attention has been focused on understanding why such structurally complex phases with giant unit cells exist in nature. A seminal series of papers which appeared in the late 1980s to 1991 and another influential publication from 1989 are worth mentioning. First of all, Tsai et al. synthesized a series of the MI-type quasicrystals in Al–Cu–TM (TM = Fe, Ru and Os) and Al–Pd–TM (TM = Mn and Re) alloy systems by using the Hume-Rothery electron concentration rule as a guide [4–6], which stimulated researchers to study why the number of electrons per atom ratio, e/a, plays a key role in the stabilization of these quasicrystals. In 1989, Fujiwara made, for the first time, first-principles LMTO (linearized muffin-tin orbital) band calculations for an Al$_{114}$Mn$_{24}$ approximant containing 138 atoms per unit cell and revealed a deep pseudogap at the Fermi level in the density of states (DOS) of its valence band [7]. He suggested that the DOS pseudogap across the Fermi level is responsible for stabilizing such complex phases including quasicrystals. Since then, a large amount of experimental and theoretical studies have been conducted regarding the structure of a pseudogap existing in many quasicrystals and their approximants.

We are now well convinced that the formation of a pseudogap across the Fermi level is characteristic of structurally complex intermetallic compounds including quasicrystals and their approximants and plays an important role in their stabilization. There are two mechanisms for its formation at the Fermi level: (1) Fermi surface–Brillouin zone (abbreviated as FsBz) interactions and (2) orbital hybridization effects [3,8,9]. Here we wish to emphasize that the e/a-dependent phase stabilization inferred from the works by Tsai et al. [4–6] can be pursued only through the former mechanism.
Mott and Jones [10] were the first to point out that the e/a-dependent phase stability or the Hume-Rothery electron concentration rule for noble metal alloys can be interpreted in terms of the FsBz interactions in the framework of the free-electron model. They proposed that the stability of a given phase is enhanced, when the Fermi sphere touches the relevant Brillouin zone planes, leading to the so-called matching condition $2k_F = |G|$, where $2k_F$ is the Fermi diameter and $|G|$ is the magnitude of the reciprocal lattice vector corresponding to the relevant Brillouin zone planes. The e/a dependence is brought into the matching condition through the well-known relation:

$$k_F = \left[ 3\pi^2 \left( \frac{e}{a} \right) \right]^{1/3},$$

where $V_a$ is the volume per atom, which can be calculated for any crystal [3]. Note, however, that it cannot be easily defined for quasicrystals characterized by an infinitely large unit cell. Hence, we limit ourselves only to crystals in the rest of the Introduction. Clearly, the formation of a pseudogap at the Fermi level in crystals including approximants cannot generally be pursued quantitatively within the free electron model. Fortunately, for non-strongly-correlated electron systems, the FsBz interactions and its effect on the formation of a pseudogap can be studied realistically on the basis of first-principles band calculations.

The FsBz interactions can be easily extracted in the context of the nearly-free-electron (NFE) model, in which a periodic ion potential and wave functions are expanded into plane waves in terms of reciprocal lattice vectors allowed to a given lattice [11]. The NFE model is, however, not applicable to systems, where orbital hybridization effects are strong. In such systems, both FsBz interactions and orbital hybridization effects generally coexist and the degree of orbital hybridization effects is strongly system dependent. Mizutani and coworkers [3,12–20] have developed a powerful technique to extract the FsBz interactions, regardless of the degree of orbital hybridization effects involved, based on first-principles FLAPW (full potential linearized augmented plane wave) electronic structure calculations. They have made full use of its formalism, in which the wave functions outside the muffin-tin (MT) spheres are expanded into plane waves over allowed reciprocal lattice vectors.

Briefly, in the FLAPW-Fourier method they developed, one constructs the energy spectrum of the squares of the Fourier coefficients of plane waves specified by the square of the wave vector $|2(k + G)|^2$ for the wave functions outside the MT spheres at selected wave vectors $k$, normally at high-symmetry points like the points $N$ at the center of the $\{110\}$ zone planes of the bcc Brillouin zone, and determines plane waves dominating electronic states at the Fermi level [3]. This is nothing but the extraction of $|G|^2$ satisfying the matching condition. (For the sake of convention, $|2(k + G)|^2$ at particular symmetry points is simply expressed as $|G|^2$.) They also developed a method of determining the square of the Fermi diameter $(2k_F)^2$, another quantity appearing in the matching condition, by constructing the energy dispersion relation for itinerant electrons outside the MT sphere [3]. It is called the Hume-Rothery plot, since the e/a value, which serves as a key parameter in discussing the Hume-Rothery electron concentration rule, can be immediately determined from the Fermi diameter. In this way, we have established a rigorous method to clarify the...
role of the matching condition \((2k_F)^2 = |\mathbf{G}|^2\) in the formation of a pseudogap on the basis of first-principles FLAPW band calculations, which can be reliably performed regardless of the degree of orbital hybridizations involved. For a more detailed account of this method we refer interested readers to [3] or [12–20].

The FLAPW-Fourier analysis was, for the first time, applied to investigate the mechanism of opening a pseudogap at the Fermi level in Cu$_5$Zn$_8$ and Cu$_9$Al$_4$ gamma-brasses containing 52 atoms per unit cell [12]. It was confirmed that the value of \((2k_F)^2\) was determined from the Hume-Rothery plot to be close to 18 or \((e/a)_{\text{total}} = 1.6\) for both Cu$_5$Zn$_8$ and Cu$_9$Al$_4$. In addition, the FLAPW-Fourier spectra revealed that the formation of a pseudogap in both compounds originates from the FsBz interactions involving \(|\mathbf{G}|^2 = 18\) as a critical reciprocal lattice vector. The Hume-Rothery stabilization mechanism is, therefore, meant to be e/a-dependent phase stabilization driven by the FsBz-induced pseudogap [3,20].

The situation in 1/1-1/1-1/1 approximants is not as simple as that in the gamma-brasses described above. Naturally, more frequent zone foldings occur as a result of a larger number of atoms, exceeding one hundred, in the unit cell. Consequently, the dispersion relations in 1/1-1/1-1/1 approximants are always much more densely populated even inside a DOS pseudogap. Inukai et al. [20] discussed the origin of pseudogaps in the RT-type Al$_{48}$Mg$_{64}$Zn$_{48}$ and Al$_{84}$Li$_{52}$Cu$_{24}$ 1/1-1/1-1/1 approximants by performing the FLAPW-Fourier and Hume-Rothery plot analyses and revealed that plane waves specified by not only \(|\mathbf{G}|^2 = 50\) but also its neighboring ones over \(|\mathbf{G}|^2 = 46\) to 54 dominate the Fermi level and contribute to the formation of a DOS pseudogap in these RT-type approximants. The existence of more than two reciprocal lattice vectors around \(|\mathbf{G}|^2 = 50\) is taken as a characteristic feature of the RT-type 1/1-1/1-1/1 approximants and is called the multi-zone effect. This is in sharp contrast to the situation in gamma-brasses, where dispersion relations are less crowded. The value of \((2k_F)^2\) for Al$_{48}$Mg$_{64}$Zn$_{48}$ and Al$_{84}$Li$_{52}$Cu$_{24}$ was determined from the Hume-Rothery plot to be 49.9 ± 0.1 and 47.1 ± 0.4, respectively, which led to the conclusion that the Hume-Rothery stabilization holds true with the fulfillment of the matching condition and that the multi-zone effect is taken as a unique feature present in these 1/1-1/1-1/1 approximants.

The MI-type quasicrystals and their approximants have received much more attention than the RT-type ones discussed above. To the best of our knowledge, however, no one has so far attempted to extract the FsBz interactions in them because of the presence of TM as major constituent elements and a large number of atoms in the unit cell. The e/a determination of the TM element is certainly of crucial importance. It is further worthwhile studying if the multi-zone effect discussed above for the RT-type approximants also applies to MI-type approximants. There is another phenomenon called \(d\)-states-mediated-splitting, which significantly perturbs the FLAPW-Fourier spectrum [3]. It refers to the splitting of \(|\mathbf{G}|^2\)-specified plane waves into bonding and anti-bonding states near the bottom and top of the d-band, respectively, and occurs as if the d-band is avoided. It was revealed, for the first time, in gamma-brasses containing the TM element as a major constituent [14]. One needs to study if the \(d\)-states-mediated-splitting remains substantial and affects the argument on the Hume-Rothery stabilization mechanism in the MI-type approximants.

In the present work, we focused on five MI-type 1/1-1/1-1/1 approximants: Al$_{114}$Mn$_{24}$, Al$_{114}$Re$_{24}$, Al$_{102}$Re$_{24}$Si$_{12}$ and Al$_{108}$Cu$_6$TM$_{24}$Si$_6$ (TM = Fe and Ru),
where the orbital hybridizations are expected to be substantial between Al-$sp$ and TM-$d$ states. In order to clarify the role of the FsBz interactions on the formation of a pseudogap across the Fermi level, we performed FLAPW band calculations with subsequent FLAPW-Fourier analysis and the Hume-Rothery plot by employing the commercially available WIEN2k-FLAPW program package [21]. Special care was taken to optimize various parameters in the WIEN2k code in running the self-consistent field (SCF) cycles as efficiently as possible without any serious loss in accuracy and reliability of resulting data for such large systems.

2. Atomic structure

The successive shell structure of the atomic cluster in the MI-type 1/1-1/1-1/1 approximant is illustrated in Figure 1 [3]. The central atom site is always vacant. Twelve atoms form an icosahedron around the central site. The inner icosahedral (II) shell is surrounded by further twelve TM atoms, which form a larger icosahedron. The 30 mid-edge sites of the larger icosahedron are filled with atoms, which form an icosidodecahedron, whose 30 vertices are divided into six sites MI1 and 24 sites MI2. The resulting 54-atom cluster is called the MI-type cluster and is arranged to form a bcc lattice by locating them at the center and corner of the bcc lattice. Further atoms are added to the space between the neighboring MI-clusters. They are called glue atoms. The total number of atoms in the cubic unit cell amounts to 138 to 144. For all structural models described below the final atomic coordinates were determined through structural relaxation with WIEN2k using 8 $k$-points in the entire Brillouin zone and $R_{MTK_{\text{max}}} = 6.0$ (see Section 3.1). Structural relaxation was continued until all force components were less than $2 \text{mRy}/a_0$, where $a_0$ is the Bohr radius equal to 0.0529 nm.

![Figure 1. Atomic structure model for MI-type 1/1-1/1-1/1 approximants. Solid circles: TM elements like Mn, Re, Fe and Ru. The 54-atom cluster is called an MI-type cluster.](image-url)
2.1. \( Al_{114}Mn_{24} \) 1/1-1/1-1/1 approximant

Cooper and Robinson [22] refined the X-ray diffraction data for an \( Al_9Mn_2Si_{1.8} \) or \( Al_{30.3}Mn_{15.6}Si_{14.0} \) single crystal and determined all 138 atom positions without distinguishing Si from Al. The space group was deduced to be \( Pm\bar{3} \), since glue atoms filled outside the MI-cluster destroy the bcc symmetry and give rise to a simple cubic lattice. The composition for the refined structure was reduced to be \( Al_{114}Mn_{24} \) by filling 24 Mn atoms on vertices of a larger icosahedron and Al atoms onto remaining sites. In the present work, we ignored the presence of Si, as Cooper and Robinson did, and employed atomic coordinates and the lattice constant of \( a = 1.268 \text{ nm} \), which they refined.

2.2. \( Al_{102}Re_{24}Si_{12} \) 1/1-1/1-1/1 approximant

Takeuchi and co-workers [23] determined 138 atom positions including positions of Si atoms in a series of Al-Re-Si 1/1-1/1-1/1 approximants by performing the Rietveld refinement analysis for powder diffraction data taken at SPring-8 synchrotron radiation facility, Japan, and revealed the complete ordering with space group \( Pm\bar{3} \) at the composition \( Al_{102}Re_{24}Si_{12} \). In the present study, their experimentally derived atomic structure with the lattice constant \( a = 1.28603 \text{ nm} \) was employed for the electronic structure calculations.

2.3. \( Al_{114}Re_{24} \) 1/1-1/1-1/1 approximant

All Si atoms in the atomic structure of the \( Al_{108}Cu_6(TM_{1-x}Ru_x)_{24}Si_{6} \) \( (TM = Fe \text{ or } Ru) \) 1/1-1/1-1/1 approximants was experimentally determined by analyzing powder diffraction spectra taken by using synchrotron radiations at SPring-8, Japan, by means of the Rietveld method [24,25]. Space group is reduced to \( Im\bar{3} \) as a result of random distributions of different chemical species in most equivalent sites in the unit cell. The exception is that the TM element Fe or Ru is exclusively filled into twelve sites on the larger icosahedron for both \( Al_{108}Cu_6Fe_{24}Si_{6} \) and \( Al_{108}Cu_6Ru_{24}Si_{6} \). The lattice constants were found to be 1.248 and 1.26832 nm, respectively. The experimentally derived total number of atoms per unit cell was deduced to be 139 in both cases [3].

2.4. \( Al_{108}Cu_6TM_{24}Si_{6} \) (\( TM = Fe \text{ or } Ru \)) 1/1-1/1-1/1 approximants

The atomic structure of \( Al_{108}Cu_6(Fe_{1-x}Ru_x)_{24}Si_{6} \) \( (x = 0, 0.5 \text{ and } 1) \) 1/1-1/1-1/1 approximants was experimentally determined by analyzing powder diffraction spectra taken by using synchrotron radiations at SPring-8, Japan, by means of the Rietveld method [24,25]. Space group is reduced to \( Im\bar{3} \) as a result of random distributions of different chemical species in most equivalent sites in the unit cell. The exception is that the TM element Fe or Ru is exclusively filled into twelve sites on the larger icosahedron for both \( Al_{108}Cu_6Fe_{24}Si_{6} \) and \( Al_{108}Cu_6Ru_{24}Si_{6} \). The lattice constants were found to be 1.248 and 1.26832 nm, respectively. The experimentally derived total number of atoms per unit cell was deduced to be 139 in both cases [3].

To allow first-principles electronic structure calculations, we need to construct a model structure free from chemical disorder by a slight modification of the experimentally determined atomic structure discussed above [3,16,25]. Briefly, the presence of Cu atoms with occupancies less than about 10% on sites II, MI1 and
MI2 is fully ignored. These sites together with glue sites G3 are filled with Al atoms. To compensate for the deficient Cu, the model assumes Cu atoms to fill into glue sites G1. Space group \( Pm\bar{3} \) is intentionally employed to put six Cu atoms on glue sites G1 in one of the MI-type cluster and six Si atoms on G1 in the other one. We obtain the chemical formula \( \text{Al}_{108}\text{Cu}_6\text{TM}_{24}\text{Si}_6 \) (\( \text{TM} = \text{Fe} \) and \( \text{Ru} \)) for the model structure with the total number of atoms per unit cell equal to 144.

3. Electronic structure calculations

3.1. WIEN2k-FLAPW band calculations

First-principles electronic structure calculations for MI-type 1/1-1/1-1/1 approximants have been extensively made in the past: \( \text{Al}_{114}\text{Mn}_{24} \) [7, 26], \( \text{Al}_{102}\text{Re}_{24}\text{Si}_{12} \) [23] and \( \text{Al}_{108}\text{Cu}_6\text{Ru}_{24}\text{Si}_6 \) [25]. All of these calculations were conducted in the LMTO-ASA method and were found to be consistent with the finding of a deep DOS pseudogap across the Fermi level. The origin of the pseudogap was largely discussed from the viewpoint of orbital hybridization effects [3, 9]. As noted in the introduction, any attempts to extract the FsBz interactions have not been so far reported for the MI-type 1/1-1/1-1/1 approximants. (Mizutani et al. [16] reported both \( (2k_F)^2 \) and \( c/a \) values deduced from the Hume-Rothery plot for \( \text{Al}_{108}\text{Cu}_6\text{TM}_{24}\text{Si}_6 \) (\( \text{TM} = \text{Fe} \) and \( \text{Ru} \)) 1/1-1/1-1/1 approximants. But the FLAPW-Fourier analyses were not attempted to extract a critical reciprocal lattice vector.)

Present FLAPW band calculations were conducted for the five MI-type 1/1-1/1-1/1 approximants described above, using the WIEN2k program package [21]. The WIEN2k-FLAPW method employs a mixed “LAPW” and “APW + lo” basis, where “lo” stands for local orbitals. This code converges to results identical to the LAPW method with an effective reduction in the cut-off parameter \( R_{\text{MT}}K_{\text{max}} \) by one, leading to significantly smaller basis sets so that the computational time is drastically reduced. Here \( R_{\text{MT}} \) refers to the smallest MT sphere radius and \( K_{\text{max}} \) is the magnitude of the largest \( \mathbf{K} \) vector equal to \( \mathbf{k} + \mathbf{G} \), where \( \mathbf{k} \) is a wave vector inside the first Brillouin zone and \( \mathbf{G} \) is an allowed reciprocal lattice vector. The exchange-correlation energy is calculated within the local density approximation of Perdew and Wang.

As discussed in [20], we need to carefully determine three important parameters in order to perform FLAPW band calculations with subsequent FLAPW-Fourier analysis in an efficient but reliable way for systems with giant unit cells: the radii of the muffin-tin spheres \( R_{\text{MT}} \) for constituent elements, the cut-off parameter \( R_{\text{MT}}K_{\text{max}} \), which determines the number of basis functions or size of the matrices, and the number of \( \mathbf{k} \)-points in the first Brillouin zone, \( N_{\mathbf{k}} \). They are listed in Table 1 for the present five 1/1-1/1-1/1 approximants. The value of \( N_{\mathbf{k}} \) was fixed to be 1000 for all cases, since it was found to be large enough to extract reliably the FsBz interactions as well as \( (2k_F)^2 \) and \( c/a \) from the Hume-Rothery plot for systems containing 138 to 144 atoms per unit cell. To facilitate the FLAPW-Fourier analysis, we had to intentionally lower the value of \( R_{\text{MT}}K_{\text{max}} \) below 6.0 employed for the RT-type 1/1-1/1-1/1 approximants [20]. After careful repeated checks, we chose the value over the range 5.41 to 5.60 for the present MI-type approximants, which appeared not to lead to a significant loss of accuracy for the electronic structure data used in the
FLAPW-Fourier method. The need to reduce the size of the basis set used in the FLAPW-Fourier method and for the Hume-Rothery plot arose, because the number of independent atom coordinates is increased to 138 and 144 in the present MI-type approximants with space group $Pm\bar{3}$ compared to 80 in the RT-type approximants with space group $Im\bar{3}$. As noted in Section 2, however, the higher value of $R_{MT}K_{max} = 6.0$ was invariably employed for the structural relaxations.

### Table 1. Key parameters in WIEN2k-FLAPW band calculations for MI-type 1/1-1/1-1/1 approximants.

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{MT}$ (a.u.)</th>
<th>$R_{MT}K_{max}$</th>
<th>$N_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{114}$Mn$</em>{24}$</td>
<td>$r_{Al} = 2.06$, $r_{Mn} = 2.29$</td>
<td>5.52</td>
<td>1000</td>
</tr>
<tr>
<td>Al$<em>{102}$Re$</em>{24}$Si$_{12}$</td>
<td>$r_{Al} = 2.06$, $r_{Re} = 2.63$, $r_{Si} = 2.05$</td>
<td>5.41</td>
<td>1000</td>
</tr>
<tr>
<td>Al$<em>{114}$Re$</em>{24}$</td>
<td>$r_{Al} = 2.06$, $r_{Re} = 2.50$</td>
<td>5.44</td>
<td>1000</td>
</tr>
<tr>
<td>Al$<em>{108}$Cu$</em>{6}$Fe$<em>{24}$Si$</em>{6}$</td>
<td>$r_{Al} = 2.06$, $r_{Cu} = 2.12$, $r_{Fe} = 2.34$, $r_{Si} = 2.10$</td>
<td>5.60</td>
<td>1000</td>
</tr>
<tr>
<td>Al$<em>{108}$Cu$</em>{6}$Ru$<em>{24}$Si$</em>{6}$</td>
<td>$r_{Al} = 2.06$, $r_{Cu} = 2.16$, $r_{Ru} = 2.50$, $r_{Si} = 2.12$</td>
<td>5.50</td>
<td>1000</td>
</tr>
</tbody>
</table>

3.2. **FLAPW-Fourier analysis and Hume-Rothery plot**

The principle of the FLAPW-Fourier analysis was described elsewhere [3]. In short, it is performed by summing the squared sum of real and imaginary parts of the Fourier coefficient outside the MT sphere over equivalent zone planes, which is hereafter denoted as $\sum_G |C_{k+G}|^2$, at a given energy eigenvalue $E$ and electronic state $k$ in the Brillouin zone and subsequently plotting the Fourier coefficient thus obtained as a function of $\{2|k+G|\}^2_E$, where $k$ is fixed as $k = (1/2 \ 1/2 \ 0)$, $k = (1 \ 0 \ 0)$ and $k = (0 \ 0 \ 0)$ corresponding to high symmetry points $N$ and $H$, and point $\Gamma$ of the bcc Brillouin zone, respectively [3,12–20]. As noted in the Introduction, $\{2|k+G|\}^2_E$ is rewritten as $|G|^2$ at high symmetry points. The ‘case.output1’ file generated upon execution of the task ‘Band Structure’ provides this information in WIEN2k [19,20]. The energy dependence of $\sum_G |C_{k+G}|^2$ for representative $|G|^2$ values at symmetry points like $N$ and $H$, and point $\Gamma$ of the bcc lattice is called the FLAPW-Fourier spectrum.

The Hume-Rothery plot uses the ‘case.output1’ file, which is generated after the SCF cycles and the following task ‘DOS’ [20]. It lists the real and imaginary parts of the Fourier coefficient $C_{k+G}$ of the plane wave $k+G$ outside the MT sphere over
allowed \( \mathbf{G} \) values as functions of the energy eigenvalues \( E \) and all wave vectors \( \mathbf{k} \), which are automatically specified in WIEN2k, once the value of \( N_k \) is fixed. For given \( E_j \) and \( \mathbf{k}_i \), the set of linearized augmented plane waves (LAPWs) \( \{2|\mathbf{k}_i + \mathbf{G}|\}^2_E \) having the largest \( \sum \mathbf{G} |C_{\mathbf{k}+\mathbf{G}}|^2 \) is extracted. This is done for all \( \mathbf{k} \) values in the first Brillouin zone in an energy interval \( E_j \leq E < E_j + \Delta E \). Here the Brillouin zone is partitioned into \( N_k \) meshes and \( \mathbf{k}_i \) runs over \( i = 1 \) to \( N_k \), whereas \( E_j \) runs from the bottom of the valence band up to \(+30 \) eV above the Fermi level. The increment \( \Delta E \) is set to be 0.05 eV for all approximants studied in the present work.

The average value of \( \{2|\mathbf{k}_i + \mathbf{G}|\}^2_E \) over meshes \( i = 1 \) to \( N_k \) is then calculated by using the relation:

\[
\langle \{2|\mathbf{k} + \mathbf{G}|\}^2 \rangle_E = \frac{\sum_{i=1}^{N_k} \omega_i \{2|\mathbf{k}_i + \mathbf{G}|\}^2_E}{\sum_{i=1}^{N_k} \omega_i},
\]

where \( \omega_i \) represents degeneracies, including zero, of the selected electronic states \( \{2|\mathbf{k}_i + \mathbf{G}|\}^2_E \) in a given energy interval and a subscript "j" in \( E_j \) is omitted. This gives rise to a single-valued energy dispersion relation, which describes the motion of itinerant electrons outside the MT sphere.

The \( E \) versus \( \langle \{2|\mathbf{k} + \mathbf{G}|\}^2 \rangle_E \) data points would fall on a straight line passing through the origin, provided that the free electron model holds well. However, a deviation certainly occurs in the energy range, where the free electron model breaks down and the electronic structure becomes anisotropic like inside the d-band. This is because the reciprocal lattice vector \( \mathbf{G} \) in \( \{2|\mathbf{k}_i + \mathbf{G}|\}^2_E \) selected as the electronic state having the maximum Fourier coefficient, would not be uniquely fixed but diversified from a mesh to mesh. Now the variance defined in [3] would become large and an averaged quantity given by Equation (2) would lose its physical meaning. Hence, we should ignore the data points having large variances. For this purpose, we draw a straight line by hand to fit only the data points with small variances in the \( E \) versus \( \langle \{2|\mathbf{k} + \mathbf{G}|\}^2 \rangle_E \) plot [3]. The value of \( \langle \{2|\mathbf{k} + \mathbf{G}|\}^2 \rangle_E \) at the Fermi level obviously provides the square of the diameter of the resulting effective Fermi sphere, \( (2k_F)^2 \). The effective \( (e/a)_{\text{total}} \), which plays a key role in the Hume-Rothery electron concentration rule, is immediately calculated from \( (2k_F)^2 \) and Equation (1). This is the reason why the method is called the Hume-Rothery plot.

As revealed in [20], both FLAPW-Fourier spectrum and the Hume-Rothery plot are insensitive to subtle changes in parameters \( R_{\text{MT}} \), \( R_{\text{MT}K_{\text{max}}} \) and \( N_k \). We have employed the ‘case.output1’ file data obtained under the choice of the parameters listed in Table 1 for the five MI-type approximants studied in the present work.

4. Results and discussion

4.1. Electronic structure of \( \text{Al}_{114}\text{Mn}_{24}, \text{Al}_{102}\text{Re}_{24}\text{Si}_{12}, \text{Al}_{114}\text{Re}_{24}, \text{Al}_{108}\text{Cu}_6\text{Fe}_{24}\text{Si}_{6} \)

and \( \text{Al}_{106}\text{Cu}_6\text{Ru}_{24}\text{Si}_{6} \) [1/1-1/1-1/1/1 approximants]

The DOSs for the five MI-type 1/1-1/1-1/1-1/1 approximants are shown in Figure 2. The Fermi level is located in a deep pseudogap for all approximants studied. This is consistent with those reported in literature [7,23,26]. A comparison of DOSs between \( \text{Al}_{102}\text{Re}_{24}\text{Si}_{12} \) and \( \text{Al}_{114}\text{Re}_{24} \) tells us that Si serves as shifting the Fermi level to a...
higher energy as a result of an increase in electron concentration. This suggests that the replacement of some Al atoms by Si atoms brings the Fermi level closer to the bottom of the pseudogap, contributing to the enhancement of the stability of this phase.

Figure 3 allows comparison of Al- and TM-partial DOSs in both Al\textsubscript{114}Mn\textsubscript{24} and Al\textsubscript{114}Re\textsubscript{24} approximants. It is clear that the Mn and Re d-bands are split into bonding and anti-bonding sub-bands across the Fermi level. Similar splitting is also found in Al-s and Al-p partial DOSs. The same argument has been already made for Al\textsubscript{114}Mn\textsubscript{24} [7], Al\textsubscript{102}Re\textsubscript{24}Si\textsubscript{12} [23], Al\textsubscript{108}Cu\textsubscript{6}Fe\textsubscript{24}Si\textsubscript{6} and Al\textsubscript{108}Cu\textsubscript{6}Ru\textsubscript{24}Si\textsubscript{6} \textsubscript{1/1-1/1-1/1} approximants [3,16]. Hence, we can safely take this as evidence that a pseudogap originates from orbital hybridization effects between Al-sp and TM-d states in all MI-type approximants containing Al and TM as major constituent elements. In the following sections, we will study the origin of the pseudogap in these five systems from the viewpoint of FsBz interactions by making full use of the FLAPW-Fourier analysis.

4.2. Determination of the square of the Fermi diameter \((2k_F)^2\)

Figure 4 shows the energy dependence of \(\langle |2(k + G)|^2 \rangle_F\) and its variance in units of \((2\pi/a)^2\) for the Al\textsubscript{114}Mn\textsubscript{24} and Al\textsubscript{114}Re\textsubscript{24} \textsubscript{1/1-1/1-1/1} approximants. As discussed in Section 3.2, the former represents the dispersion relation of itinerant electrons outside the MT sphere. The variance is large over the energy range, where the Mn and Re d-bands extend, respectively. Hence, we drew a straight line passing the data points, as marked with red in color, while ignoring those with large variances. We consider the straight line to represent well the dispersion relation for the motion of itinerant electrons outside the MT sphere. In other words, we effectively cast the
realistic electronic structure onto the free electron model without losing its basic features.

The value of \((2k_F)^2\) for Al\(_{114}\)Mn\(_{24}\) and Al\(_{114}\)Re\(_{24}\) 1/1-1/1-1/1 approximants can be determined to be 48.9 ± 0.5 and 48.6 ± 0.5 from the intercepts at the Fermi level, respectively. The effective \((e/a)_{\text{total}}\) value enclosed by the resulting Fermi sphere, can be easily calculated by inserting the value of \((2k_F)^2\) thus obtained and \(N = 138\) into Equation (1). The value turned out to be 2.59 and 2.57 for the Al\(_{114}\)Mn\(_{24}\) and Al\(_{114}\)Re\(_{24}\) 1/1-1/1-1/1 approximants, respectively. The Hume-Rothery plot was equally made for the Al\(_{102}\)Re\(_{24}\)Si\(_{12}\), Al\(_{108}\)Cu\(_{6}\)Fe\(_{24}\)Si\(_{6}\) and Al\(_{108}\)Cu\(_{6}\)Ru\(_{24}\)Si\(_{6}\) 1/1-1/1-1/1 approximants. In the case of Al\(_{102}\)Re\(_{24}\)Si\(_{12}\), \((2k_F)^2\) is increased to 51.0 ± 0.5 owing to the replacement of some trivalent Al atoms by quadrivalent Si. The resulting \((2k_F)^2\) and \((e/a)_{\text{total}}\) values for all MI-type 1/1-1/1-1/1 approximants are listed in Table 2.

It is of great interest at this stage to consider if we can estimate the value of \((e/a)\) of constituent TM elements Mn, Fe, Ru and Re in the periodic table. We can evaluate from the Hume-Rothery plot not only \((e/a)_{\text{element}}\) of elements in the periodic table but also \((e/a)_{\text{total}}\) in intermetallic compounds existing in various binary alloy systems such as Al-TM alloy systems. The resulting values of \((e/a)_{\text{total}}\) for both pure elements and individual compounds are then plotted as a function of composition in

![Figure 3. Al- and TM-partial DOSs for Al\(_{114}\)Mn\(_{24}\) and Al\(_{114}\)Re\(_{24}\) 1/1-1/1-1/1 approximants. A deep pseudogap can be attributed to orbital hybridization effects between Al-\(sp\) and TM-\(d\) states.](Figure 3. Al- and TM-partial DOSs for Al\(_{114}\)Mn\(_{24}\) and Al\(_{114}\)Re\(_{24}\) 1/1-1/1-1/1 approximants. A deep pseudogap can be attributed to orbital hybridization effects between Al-\(sp\) and TM-\(d\) states.)
Figure 4. Hume-Rothery plot for (a) Al$_{114}$Mn$_{24}$ and (b) Al$_{114}$Re$_{24}$ 1/1-1/1-1/1 approximants. The energy dependence of the variance $\sigma^2(E)$ is shown as gray in color. A straight line passing data points, where $\sigma^2(E)$ is small, is drawn as a guide. The value of $(2k_F)^2$ can be directly read off from the intercept at the Fermi level. Numerical values for the five MI-type approximants studied in the present work are listed in Table 2.

Table 2. Square of the Fermi diameter, $e/a$, $e/uc$ and square of critical reciprocal lattice vectors in MI-type 1/1-1/1-1/1 approximants.

| System          | $N$ (atoms per unit cell) | $(2k_F)^2$ [ $\times (2\pi/a)^2$] | $e/a$ | $e/uc$ | critical $|G|^2$ [ $\times (2\pi/a)^2$] |
|-----------------|---------------------------|-----------------------------------|-------|--------|----------------------------------|
| Al$_{114}$Mn$_{24}$ | 138                        | 48.9 $\pm$ 0.5                    | 2.59  | 357    | 50                               |
| Al$_{102}$Re$_{24}$Si$_{12}$ | 138                        | 51.0 $\pm$ 0.5                    | 2.76  | 381    | 50                               |
| Al$_{114}$Re$_{24}$     | 138                        | 48.6 $\pm$ 0.5                    | 2.57  | 355    | 50                               |
| Al$_{108}$Cu$_6$Fe$_{24}$Si$_6$ | 144                        | 51.6 $\pm$ 0.5                    | 2.70  | 389    | 50                               |
| Al$_{108}$Cu$_6$Ru$_{24}$Si$_6$ | 144                        | 51.7 $\pm$ 0.5                    | 2.70  | 389    | 50                               |
| Al$_{48}$Mg$_{64}$Zn$_{48}$ | 160                        | 49.9 $\pm$ 0.1                    | 2.30  | 368    | 50                               |

Note: For comparison, the data for RT-type Al$_{48}$Mg$_{64}$Zn$_{48}$ 1/1-1/1-1/1 approximant [20] are added in the last row.
a given alloy system. As explained in the Appendix, we could determine the e/a values of relevant constituent elements as follows: \((e/a)_{Al} = 3.0\), \((e/a)_{Cu} = 1.0\), \((e/a)_{Si} = 4.0\), \((e/a)_{Mn} = 1.0\), \((e/a)_{Re} = 1.0\), \((e/a)_{Fe} = 1.1\) and \((e/a)_{Ru} = 1.0\). It is important to note that \((e/a)_{TM}\) is always positive in sign and distributed in the neighborhood of unity for all TM elements so far studied.

Using these figures, we can easily calculate \((e/a)_{\text{total}}\) for \(Al_{114}Mn_{24}\), \(Al_{114}Re_{24}\), \(Al_{102}Re_{24}Si_{12}\), \(Al_{108}Cu_{6}Fe_{24}Si_{6}\) and \(Al_{108}Cu_{6}Ru_{24}Si_{6}\) 1/1-1/1-1/1 approximants to be 2.67, 2.67, 2.75, 2.66 and 2.64, respectively. This is evidently the confirmation of the presence of the multi-zone effect discussed in the Introduction. Among them, the \((e/a)_{\text{total}}\) for the \(Al–Cu–TM (TM = Fe, Ru and Os)\) and \(Al–Pd–TM (Mn and Re)\) quasicrystals they discovered are stabilized at \((e/a)_{\text{total}} = 1.8\), the value of which was derived by employing negative \((e/a)_{TM}\) values for TM elements Raynor proposed in 1949 [27]. The present work does not support the \((e/a)_{\text{total}} = 1.8\) rule for the MI-type quasicrystals and, instead, proposes the \((e/a)_{\text{total}} = 2.7\) rule for the MI-type 1/1-1/1-1/1 approximants.

4.3. Extraction of sets of lattice planes interfering with electrons near \(E_F\)

The FLAPW-Fourier spectra were constructed at symmetry points \(M\) and \(X\), and point \(\Gamma\) of a simple cubic lattice, since all the MI-type 1/1-1/1-1/1 approximants studied in the present work are characterized by the space group \(Pm\bar{3}\). Attention is now directed to only plane waves specified by \(|G|^2\), whose Fourier coefficient \(\sum_{G} |C_{k+G}|^2\) is sizable in the vicinity of the Fermi level. This is nothing but the way to extract the FsBz interactions involved [20].

The FLAPW-Fourier spectra, i.e. energy dependences of \(\sum_{G} |C_{k+G}|^2\) with \(|G|^2\) in the range 41 to 56 for \(Al_{114}Mn_{24}\) 1/1-1/1-1/1 approximant. are shown at symmetry points \(M\) and \(X\), and point \(\Gamma\) along with its DOS in Figure 5. It can immediately be seen that all plane waves over \(|G|^2 = 41\) to 56 possess sizable Fourier coefficients across the Fermi level. This is evidently the confirmation of the presence of the multi-zone effect discussed in the Introduction. Among them, the \(|G|^2 = 50\) waves interfering with the set of \(\{543\} + \{550\} + \{710\}\) lattice planes are most evenly and densely distributed across the Fermi level. Indeed, \(|G|^2 = 50\) agrees well with the square of the Fermi diameter \((2k_F)^2\) of 48.9, proving that the matching condition \((2k_F)^2 = |G|^2\) holds for the \(Al_{114}Mn_{24}\) 1/1-1/1-1/1 approximant. Similar FLAPW-Fourier spectra were also obtained for the \(Al_{114}Re_{24}\) and \(Al_{102}Re_{24}Si_{12}\). We could confirm not only the presence of the multi-zone effect involving \(|G|^2\) from 41 to 56 at the Fermi level, but also identify \(|G|^2 = 50\) to be the most critical. It is of interest to note that the matching condition is best satisfied in \(Al_{102}Re_{24}Si_{12}\), for which \((2k_F)^2 = 51.0 \pm 0.5\) was derived.

We show in Figure 6 the FLAPW-Fourier spectra in the vicinity of the Fermi level only at symmetry points \(M\) for the \(Al_{108}Cu_{6}Fe_{24}Si_{6}\) and \(Al_{108}Cu_{6}Ru_{24}Si_{6}\) 1/1-1/1-1/1 approximants. The sizable Fourier coefficients are found at the Fermi level over the range \(38 \leq |G|^2 \leq 58\). Among them, the \(|G|^2 = 50\) waves are again most evenly and densely distributed around the Fermi level for both approximants. As discussed in the preceding section, \((2k_F)^2\) is found to be 51.6 \(\pm 0.5\) and 51.7 \(\pm 0.5\) for
Figure 5. The FLAPW-Fourier spectra at (a) symmetry points $M$, (b) symmetry points $X$ and (c) symmetry point $\Gamma$ for $Al_{114}Mn_{24}$ $1/1-1/1-1/1$ approximants. Only plane waves, whose Fourier coefficients are sizable across the Fermi level, are shown. The DOS is shown at the uppermost location to envisage the pseudogap structure in this compound. The most critical waves of $|G|^2 = 50$ are marked with bold and red in color.

Figure 6. The FLAPW-Fourier spectra at symmetry points $M$ for (a) $Al_{108}Cu_6Fe_{24}Si_6$ and (b) $Al_{108}Cu_6Ru_{24}Si_6$ $1/1-1/1-1/1$ approximants, along with the corresponding DOSs. Only plane waves, whose Fourier coefficients are sizable across the Fermi level, are shown. The most critical waves of $|G|^2 = 50$ are marked with bold and red in color.
these two approximants. Therefore, we can safely take the results as a proof for the presence of the multi-zone effect and the validity of the matching condition \((2k_F)^2 = |G|^2\) for the Al–Cu–TM (TM = Fe and Ru)-based approximants. The most critical \(|G|^2\) thus obtained for all MI-type approximants studied is listed in Table 2.

4.4. FsBz-induced pseudogap in MI-type 1/1-1/1-1/1 approximants

In the case of Cu₅Zn₈ gamma-brass, the DOS pseudogap of 1.2 eV in width is comparable to an energy separation across the Fermi level at symmetry points \(N\) in its energy dispersion relation. As noted in the Introduction, this simplicity allowed us to perform the FLAPW-Fourier analysis only for wave functions at the highest occupied and the lowest unoccupied states at symmetry points \(N\) in its energy dispersion relations corresponding to the bottom and top of the DOS pseudogap, respectively [3]. As emphasized in [20], however, the situation in the 1/1-1/1-1/1 approximant is entirely different. The width of the DOS pseudogap across the Fermi level in RT-type 1/1-1/1-1/1 approximants is 2 to 3 eV, which is more than 10 times as large as an average energy separation of the order of 0.1 eV, say, at symmetry points \(N\) in energy dispersion relations. Inukai et al. [20] demonstrated how the multi-zone effect creates the DOS pseudogap from extremely crowded energy dispersions by making use of the NFE (nearly free electron) model for the Al-Mg-Zn 1/1-1/1-1/1 approximant. We consider that the multi-zone effect plays a key role in the MI-type 1/1-1/1-1/1 approximants as well, though the NFE model is difficult to apply for systems containing a large amount of TM elements.

Figure 7 allows comparison of the energy dependence of the most critical waves of \(|G|^2 = 50\) at symmetry points \(N\) (or \(M\)) for RT- and MI-type 1/1-1/1-1/1 approximants so far studied, respectively. A full-width of half-maximum (FWHM) of the distribution is read off from Figures 7a and b, as marked by arrows. Numerical data are listed in Table 3. The FWHM values in the two RT-type approximants range from 2.0 to 3.2 eV, while those in the five MI-type approximants range over 5.0 to 7.1 eV. Such wide energy distributions of the Fourier coefficients are also found at \(|G|^2\)s other than 50 (see Figures 5 and 6). It means that the wave functions outside the MT spheres, say, at the Fermi level are composed of many plane waves having sizable Fourier coefficients over the range \(40 < |G|^2 < 60\). We consider this as evidence that the multi-zone effect is essential in discussing a DOS pseudogap in terms of plane waves specified by \(|G|^2\) in not only RT- but also MI-type approximants, when its formation is regarded from the FsBz interactions.

As indicated in Figure 7, the FWHM values of 5.0–7.1 eV in the MI-type 1/1-1/1-1/1 approximants are two to three times as wide as those in the RT-type 1/1-1/1-1/1 approximants. We have pointed out in Section 4.1 that the pseudogap across the Fermi level in the MI-type approximants can be explained simply in terms of orbital hybridization effects. This is in sharp contrast to the RT-type approximants, where the orbital hybridization effects are essentially negligible [20]. The stronger the orbital hybridizations among constituent elements, the less dispersive is the energy distribution of valence electrons and the more plane waves specified by \(|G|^2\) are needed to construct the wave functions outside the MT spheres. Hence, a wider energy distribution of the critical \(|G|^2 = 50\) and its neighboring plane waves in the
MI-type approximants is simply attributed to the fact that a spatially more localized wave function at a given energy eigenvalue yields a broader FLAPW-Fourier spectrum as a function of $|G|^2$ at high symmetry points of the Brillouin zone.

Before ending this section, we need to discuss whether the $d$-states-mediated splitting affects the formation of a DOS pseudogap in the MI-type approximants. Figure 8 shows the partial $d$-DOS for the MI-type approximants studied. A comparison with Figure 7b immediately tells us that the critical $|G|^2 = 50$ waves are not substantially swept out from the $d$-band to cause bonding and anti-bonding states near the bottom and top of the $d$-band, respectively. Instead, they are rather uniformly distributed over $-4$ to $+3$ eV except for the manifestation of a concave structure due to the formation of a pseudogap. Hence, we conclude that the $d$-states-mediated splitting is essentially absent in the MI-type approximants. This is in sharp contrast to that in TM-based gamma-brasses, where the $d$-states-mediated splitting is significant and is attributed to the orthogonality condition of the $sp$-like wave function with the $d$-like ones [3,14]. Its absence in the MI-type approximants means that energy dispersion relations are so flat that the orthogonality condition phases out and that $d$- and $sp$-electrons may be treated without serious discrimination. It was rather surprising to find that the deviation from a straight line fitting in the energy range, where the $d$-bands exist, in the Hume-Rothery plot in Figure 4 is well suppressed. This indicates that the electronic structure of the MI-type approximants becomes fairly isotropic even inside the $d$-bands. This is in sharp contrast to the occurrence of a much larger deviation from a straight line fitting in compounds like
Table 3. FWHM of $|\mathbf{G}|^2 = 50$ plane wave in RT- and MI-type 1/1-1/1-1/1 approximants.

<table>
<thead>
<tr>
<th>System</th>
<th>RT-type 1/1-1/1-1/1 approximants</th>
<th>MI-type 1/1-1/1-1/1 approximants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Al}<em>{48}\text{Mg}</em>{64}\text{Zn}_{48}$</td>
<td>$\text{Al}<em>{114}\text{Mn}</em>{24}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Al}<em>{84}\text{Li}</em>{52}\text{Cu}_{24}$</td>
<td>$\text{Al}<em>{114}\text{Re}</em>{24}$</td>
</tr>
<tr>
<td></td>
<td>$\text{Al}<em>{102}\text{Re}</em>{24}\text{Si}_{12}$</td>
<td>$\text{Al}<em>{108}\text{Cu}</em>{6}\text{Fe}<em>{24}\text{Si}</em>{6}$</td>
</tr>
<tr>
<td>FWHM (eV)</td>
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<td>5.0</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>
gamma-brasses with $N = 52$, where the $d$-states-mediated splitting is substantial [3,14]. We are, therefore, led to conclude that the effect of the $d$-states-mediated splitting on the FLAPW-Fourier spectrum is essentially lost, when the dispersion relations become so crowded, flat and isotropic as a result of repeated zone foldings, particularly, inside the $d$-band, as is the case in the MI-type 1/1-1/1-1/1 approximants ($N = 138–144$).

4.5. New Hume-Rothery electron concentration rule

As was clear from Figure 7, $|\mathbf{G}|^2 = 50$ can be universally designated as a critical reciprocal lattice vector for both RT- and MI-type 1/1-1/1-1/1 approximants. Instead, there exists sizable discrepancy in $e/a$ between the RT- and MI-type approximants: $e/a = 2.05–2.30$ for the RT-type 1/1-1/1-1/1 approximants, while $e/a = 2.7–2.8$ for MI-type ones. Figure 9 shows the $e/a$ dependence of the number of atoms per unit cell, $N$, for a variety of 1/1-1/1-1/1 approximants including the data for Cd$_6$Ca [28], to which $e/a = 2.0$ may be safely assigned, since it consists of the two divalent elements Cd and Ca. A decrease in $N$ is observed with increasing $e/a$. From this we can expect the product of $e/a$ and $N$, i.e. $e/uc$, the number of atoms per unit cell, to be kept almost constant for all 1/1-1/1-1/1 approximants, regardless of the atomic cluster types involved. We are encouraged to propose that $e/uc$, the value of

![Graph showing $d$-electron partial DOSs for the five MI-type approximants studied in the present work.](image)
which is listed in Table 2, may be better correlated with the critical reciprocal lattice vector $|\mathbf{G}|^2$ for a given family of intermetallic compounds characterized by the possession of a deep pseudogap at the Fermi level.

Both $e/uc$ and critical $|\mathbf{G}|^2$ can be rigorously determined from the Hume-Rothery plot and the FLAPW-Fourier analysis, respectively, for many structurally complex intermetallic compounds including RT- and MI-type 1/1-1/1-1/1 approximants ($N = 138–144$), gamma-brasses ($N = 52$) [3] and gamma-phase Mg$_{17}$Al$_{12}$ compound ($N = 58$) [17] so far studied. In addition, the data for Al$_6$Mn and Al$_6$Re compounds are newly added to strengthen our arguments on $e/uc$ versus $|\mathbf{G}|^2$ correlation.

The WIEN2k-FLAPW band calculations were conducted along with the FLAPW-Fourier analysis and the Hume-Rothery plot for Al$_6$TM (TM = Mn and Re). Both compounds possess 28 atoms per orthorhombic unit cell and are characterized by a deep pseudogap at the Fermi level. The $e/a$ value of 2.7 was commonly deduced from the Hume-Rothery plot, while $|\mathbf{G}|^2 = 16$ and 18 were found to be equally critical as satisfying the matching condition. The critical reciprocal vector $|\mathbf{G}|^2 = 17$ on average is only slightly lower than $|\mathbf{G}|^2 = 18$ for gamma-brasses in spite of a large difference in $e/a$ between Al$_6$TM (TM = Mn and Re) ($e/a = 2.7$) and gamma-brasses ($e/a = 1.6$). However, a correlation emerges in $e/uc$ and $|\mathbf{G}|^2$, since $e/uc$ reaches the value of 76 ($= 2.7 \times 28$) slightly lower than $e/uc = 84$ for gamma-brasses mentioned above.

Figure 10 shows $e/uc$ thus obtained as a function of critical reciprocal lattice vector $|\mathbf{G}|^2$ for many structurally complex intermetallic compounds so far studied. The data for Al$_{13}$Mg$_{43}$Zn$_{42}$ (N = 676–692) [3] and beta-phase Al$_3$Mg$_2$ compound ($N = 1178$) [17], the latter of which has been often referred to as Samson compound, were also included, though FLAPW-Fourier analysis and Hume-Rothery plot have not yet been made. Nevertheless, the value of $e/uc$ may be reliably determined, since $e/a$ is easily calculated from nominal valences of
constituent elements \((e/a)_{Al} = 3.0, (e/a)_{Mg} = (e/a)_{Zn} = 2.0\) and the number of atoms per unit cell is available in the literature [3,17]. The critical \(|G|^2\) is less clear but is estimated to be 125 and 200 from the diffraction peak satisfying the matching condition in powder X-ray diffraction spectra for \(Al_{15}Mg_{43}Zn_{42}\) \(2/1-2/1-2/1\) approximant [3] and beta-phase \(Al_{3}Mg_{2}\) compound [3], respectively. The set of 24-fold \{11 20\}, 24-fold \{10 50\}, 48-fold \{10 43\} and 48-fold \{865\} lattice planes with \(|G|^2 = 125\) is deduced to be critical in \(Al_{15}Mg_{43}Zn_{42}\) \(2/1-2/1-2/1\) approximant. In the case of \(Al_{3}Mg_{2}\) Samson compound, the set of 12-fold \{10 10 0\}, 48-fold \{10 86\} and 24-fold \{14 20\} lattice planes with \(|G|^2 = 200\) were selected. An almost spherical Brillouin zone net would be formed in such compounds with a giant unit cell to effectively encompass its Fermi surface in reciprocal space.

All the \(e/uc\) versus critical \(|G|^2\) data are found to fall on a straight line with a slope of 3/2 on a log–log scale, being consistent with the relation:

\[
(e/uc) = \left[\frac{\pi}{3} (2k_F)^2\right]^{3/2} = \left[\frac{\pi}{3} |G|^2\right]^{3/2}
\]

which is derived by inserting the matching condition \((2k_F)^2 = |G|^2\) into Equation (1).

We propose that Figure 10 can be taken as a new Hume-Rothery electron concentration rule established on the basis of first-principles FLAPW band calculations coupled with the FLAPW-Fourier analysis and the Hume-Rothery plot. It clearly links the electron concentration parameter \(e/uc\), instead of \(e/a\), and a
crystal structure through critical $|G|^2$. We confirmed, for the first time, that the Hume-Rothery electron concentration rule holds true even for strongly orbital-hybridizing systems as represented by the MI-type 1/1-1/1-1/1 approximants and Al$_6$TM (TM = Mn and Re). This means that all the compounds falling onto the fitted line do obey the Hume-Rothery stabilization mechanism. Therefore, the new Hume-Rothery electron concentration rule can cover a wider range of alloys than the empirical Hume-Rothery rule, which was validated only for noble metal alloys.

The extension of the present approach to the family of quasicrystals may not be straightforward. Obviously, the data points on the diagram would move up along the 3/2-power law line in Figure 10, as the order of approximants increases. The data for quasicrystals, where the size of the unit cell is infinitely large, would be infinitely diverged. As noted in the Introduction, experimentalists have employed the $e/a$, instead of $e/uc$, and related it to the reciprocal lattice vector corresponding to one of the major diffraction lines to discuss the matching condition. This looks convenient, since $e/a$ is a quantity independent of the size of the unit cell. However, the discussion along this line will break down, as soon as one attempts to calculate, for instance, the Fermi diameter $2k_F$ by inserting $e/a$ into Equation (1). This is because an infinitely large unit cell prevents us to define the volume per atom $V_a$. We consider the basic difficulty in handling quasicrystals to stem from the breakdown of the Bloch theorem, on which the electron theory of metals, including first-principles FLAPW band calculations, totally relies. We are still too remote from establishing the electron theory of quasicrystals in order to describe the motions of electrons in a quasi-periodic lattice.

Finally, we wish to briefly discuss the effect of the $d$-states-mediated splitting on the $e/uc$ versus $|G|^2$ diagram. As emphasized earlier, it plays a significant effect on the FLAPW-Fourier spectrum when the number of atoms per unit cell, $N$, is in the neighborhood of 50 like in the TM-based gamma-brasses but becomes less important in the MI-type 1/1-1/1-1/1 approximants, where $N$ is increased to 138 to 144. The FLAPW-Fourier spectra are displayed in Figure 11 for Al$_8$V$_5$ gamma-brass ($N = 52$) [14] and Al$_6$Mn ($N = 28$), along with the corresponding 3$d$ partial DOSs, respectively. Clearly, plane waves specified by $|G|^2$ tend to avoid the $d$-band and split into bonding and anti-bonding states near the bottom and top of the $d$-band, respectively. This is we have called the $d$-states-mediated splitting [3]. A small deviation from the straight line is observed, as in the data points for Al$_8$V$_5$ and Al$_6$TM (TM = Mn and Re) in Figure 10. But its effect may well be ignored in the $e/uc$ versus $|G|^2$ diagram on a log–log scale. Hence, the diagram can be validated for structurally complex compounds characterized by a pseudogap at the Fermi level, even when the number of atoms per unit cell, $N$, is reduced to 52 to 28 and the $d$-states-mediated splitting becomes significant.

### 5. Conclusions

WIEN2k-FLAPW band calculations were performed for the five MI-type Al$_{114}$Mn$_{24}$, Al$_{102}$Re$_{24}$Si$_{12}$, Al$_{114}$Re$_{24}$, Al$_{108}$Cu$_6$Fe$_{24}$Si$_6$ and Al$_{108}$Cu$_6$Ru$_{24}$Si$_6$ 1/1-1/1-1/1 approximants, all of them being characterized by the possession of 138–144 atoms per unit cell and a deep pseudogap at the Fermi level. The origin of the
pseudogap was analyzed from the point of view of FsBz interactions by performing the FLAPW-Fourier analysis and the Hume-Rothery plot. The square of the Fermi diameter \( (2k_F)^2 \) is deduced to be close to 50 for all approximants studied. It is confirmed that the origin of the pseudogap can be attributed to the FsBz-interactions involving several reciprocal lattice vectors centered at \( |G|^2 = 50 \) satisfying the matching condition \( (2k_F)^2 = |G|^2 \). The multi-zone effect, whose role was claimed to be crucial in RT-type 1/1-1/1-1/1 approximants, is found to serve as a key role in MI-type approximants as well. However, the effect due to \( d \)-states-mediated splitting essentially disappears in MI-type approximants in spite of the substantial occupation of TM-\( d \) states in the valence band. A new Hume-Rothery electron concentration rule linking \( e/uc \) with critical \( |G|^2 \) has been proposed for structurally complex intermetallic compounds characterized by a deep pseudogap at the Fermi level. Finally, the MI-type 1/1-1/1-1/1 approximants can be said to obey the Hume-Rothery stabilization mechanism and the Hume-Rothery electron concentration rule with \( e/a = 2.7 \).

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References

Appendix. Determination of \((e/a)_{TM}\) for transition metal elements

Figure A1 shows the Hume-Rothery plots for Al, \(\alpha\)-Mn and Re metals, which crystallize into fcc with \(N = 4\), simple cubic with \(N = 58\) and hcp with \(N = 2\), respectively. The smaller the number of atoms per unit cell, \(N\), the larger the number of \(k\)-points in the Brillouin zone, \(N_k\), is needed to reduce the scatter of the data points in WIEN2k-FLAPW-Hume-Rothery plot. The determination of \((2k_F)^2\) and \(e/a\) values in both Mn and Re is certainly less accurate than that in Al because of the existence of the \(d\)-band across the Fermi level in these TM elements.

In order to enhance the reliability to determine the values of \((e/a)_{TM}\) for TM elements, we performed the FLAPW band calculations with subsequent Hume-Rothery plot for intermetallic compounds existing in Al–TM (TM = Mn, Fe, Ru and Re) binary alloy systems.

Figure A1. The Hume-Rothery plots for (a) fcc Al \((N = 4)\), (b) \(\alpha\)-Mn \((N = 58)\) and (c) hcp Re \((N = 2)\). The value of \(N_k\) is selected to be 8000, 1000 and 30,000, respectively.
The resulting \((e/a)_{total}\) values for the compounds, including the data for pure elements discussed above, are plotted in Figure A2 as a function of concentration for both Al–Mn and Al–Re alloy systems. Among them, \(\text{Al}_{114}\text{Mn}_{24}\) and \(\text{Al}_{114}\text{Re}_{24}\) compounds referred to in the text as the model structure for Al–TM–Si (TM = Mn and Re) 1/1-1/1-1/1 approximants, do not exist as a stable phase in the respective equilibrium phase diagrams. As shown in Figure A2, we consider it reasonable to draw a straight line to fit all the data points for Al–Mn alloy systems. In the case of the Al–Re alloy system, the data points in Al-rich alloys are found to fall on the line identical to that for Al–Mn alloy systems, while those in Re-rich alloys to deviate systematically upward, as shown by dotted line. The composition dependence of \((e/a)_{total}\) can be used to judge not only an appropriate determination of \((e/a)_{TM}\) for the TM element involved but also the environmental effect on \((e/a)_{total}\) such as the size of the unit cell and crystal structure in individual compounds. The latter is apparently negligibly small in both Al–Mn and Al–Re alloy systems.

All structurally complex alloy phases including 1/1-1/1-1/1 approximants are located in Al-rich composition range. Thus, the values of \((e/a)_{\text{Mn}}\) and \((e/a)_{\text{Re}}\) are deduced to be equally 1.0 from the intercept of the solid straight line, as shown in Figure A2. Similarly, the values of \((e/a)_{\text{Fe}} = 1.1, (e/a)_{\text{Ru}} = 1.0\) and \((e/a)_{\text{Cu}} = 1.0\) discussed in the text have been also determined by plotting the composition dependence of \((e/a)_{total}\) for existing intermetallic compounds in the respective Al-based binary alloy systems. We consider the e/a values thus deduced for the relevant TM elements to reflect their valences embedded in Al-rich matrices like in the present 1/1-1/1-1/1 approximants.

Figure A2. The composition dependence of \((e/a)_{total}\) for intermetallic compounds and pure elements in (a) Al–Mn and (b) Al–Re alloy systems. A solid line was drawn by passing data points for Al-rich alloys, while a dotted line for Al–Re alloy system was drawn by passing data points for Re-rich alloys.