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Hidden electronic rule in the "cluster-plus-glue-atom" model

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Electrons and their interactions are intrinsic factors to affect the structure and properties of materials. Based on the "cluster-cluster-plus-glue-atom" model, an electron counting rule for complex metallic alloys (CMAs) has been revealed in this work (i. e. the CPGAMEC rule). Our results on the cluster structure and electron concentration of CMAs with apparent cluster features, indicate that the valence electrons' number per unit cluster formula for these CMAs are specific constants of eight-multiples and twelve-multiples. It is thus termed as specific electrons cluster formula. This CPGAMEC rule has been demonstrated as a useful guidance to direct the design of CMAs with desired properties, while its practical applications and underlying mechanism have been illustrated on the basis of CMAs' cluster structural features. Our investigation provides an aggregate picture with intriguing electronic rule and atomic structural features of CMAs.

Composition-structure-properties correlations are important topics with great significance in materials science research fields[1–5]. Crystallographic method describes simple crystalline materials' structure by means of "atomic positions plus space lattice", and usually knowledge of a few atoms within the unitcell is sufficient to deduce their partial properties[6,7]. For complex metallic alloys (CMAs) like some intermetallics, quasicrystals and amorphous alloys, the problem becomes complicated because their structural information is often submerged in a long list of atomic coordinates. In this case, the structural characteristics of CMAs cannot be reflected through the crystallographic method, not to mention their structure-related properties[8–10]. Since the atomic clusters are advocated as primary units to represent materials' structural features, to solve the above problem, various cluster-based models have been developed during the past decades[11–17]. Among these cluster-based models, Dong's "cluster-plus-glue-atom" model[15] can be used to describe the atomic structure of nearly all materials. Denoted by a uniform cluster formula of [cluster](glue atoms)$_x$[18–21], this cluster-plus-glue-atom model regards the atomic structure of any materials, no matter whether crystalline or non-crystalline, to be composed of the clusters part and the glue atoms part[22–28]. Accordingly, all atoms in a given structure belong to three kinds of the central atoms, the shell atoms and the glue atoms[29,30], as the red spheres, the blue spheres and the green spheres shown in Supplementary Figure S1, respectively. In this context, the cluster-plus-glue-atom model contains materials' basic composition information and structure information in its cluster formula, thus it lays the foundation to uncover the connections among composition, structure and properties of materials, especially for those CMAs with complicated atomic configuration.

Electrons and their interactions are believed as the most intrinsic factors to dominate the structure and properties of materials[31–35]. When different atoms gather into molecules, there are electrons transferring and these electrons share or overlap in the bond-making process. Consequently, different materials behave different properties, and for a long time, electron factors have attracted considerable attentions to investigate the composition-structure- properties correlations of materials[36,37]. For example, the exclusive principle proposed by Pauli at the beginning of last century, has been successfully used to extend the formal classification of valence electrons by four quantum numbers[38–41]. Afterwards, the valence bond theory and molecular orbital theory have been developed successively to explore the structure and properties of materials[42,43]. One of the most important corollaries of these electronic theories, is that the stable electronic configuration of common covalent compounds

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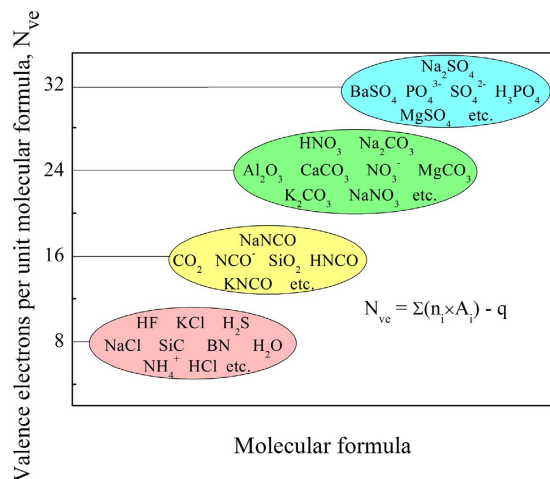
Figure 1. Octet rule and its extension for common covalent compounds and ionic compounds, reflected by the valence electrons' number per unit molecule formula (N_{ve}) being specific constants of eight-multiples. Chemical species related to some covalent compounds and ionic compounds are presented.

and ionic compounds follow the octet rule[44–46]. As for alloy phases, Hume-Rothery points out that electron concentration plays an important role in stabilizing the structure of electron compounds, which is known as the Hume-Rothery rule[47–49]. Actually, many structural distinctions of metals and alloys can be discussed directly from their electron concentration differences[32,47,50]. Furthermore, the structure and structure related properties of CMAs originate from the local atomic bonding inside and between the cluster structural units via electronic interactions[51–53]. Therefore, it becomes necessary to investigate CMAs' composition-structure-property correlations from the electron perspective.

Depending on the cluster-plus-glue-atom model, the cluster formula of CMAs is equivalent to the molecular formula of covalent compounds and ionic compounds. Meanwhile, it is known that a majority of covalent compounds and ionic compounds follow the octet rule. Accordingly, we speculate that CMAs should follow analogous electronic rule as well. In this work, an electron counting rule hidden in the cluster formula for CMAs is revealed. Our analysis on the cluster structure and electron concentration for typical kinds of CMAs[20,22,24,26,54] (including intermetallic compounds, quasicrystals and metallic glasses), indicates that the valence electrons' number per unit cluster formula for these CMAs are close to specific constants of eight-multiples and twelve-multiples. It is thus termed as CMAs' specific electrons cluster formula. This electron counting rule has been demonstrated as a useful guidance to direct the design of CMAs with desired properties, and its practical application has been illustrated accordingly. Furthermore, an underlying mechanism behind this electron counting rule is presented on the basis of CMAs' cluster structural features. The present work will help people to better understand the composition-structure-properties correlations of CMAs.

Proposal of the cluster-plus-glue-atom model electron counting (CPGAMEC) rule

Based on the cluster-plus-glue-atom model, we set the goal of revealing the electron counting scheme for CMAs (i. e. the CPGAMEC rule), by analogy with the octet rule and its extension for common covalent compounds and ionic compounds[55–57]. As is known that atoms in covalent compounds and ionic compounds satisfy the octet rule by means of either sharing electrons with neighbor atoms, or transferring electrons from one atom to another[44–46]. As a consequence, the valence electrons' number per unit molecular formula (N_{ve}) for a majority of covalent compounds and ionic compounds is specific constants of eight-multiples[56,58], like 8 for NaCl, 16 for CO_2 and 24 for Al_2O_3 etc., as presented in Fig. 1 and Supplementary Table SI. Here in our work, this electron counting scheme of the N_{ve} value being constants of eight-multiples, is regarded as an extension of octet rule. Noting that it is only a sufficient condition of the octet rule, rather than its necessary condition. Accordingly, the CPGAMEC rule is proposed to reveal the electron counting scheme for CMAs, since the cluster formula of CMAs is equivalent to the molecular formula of covalent compounds and ionic compounds[15,29]. Analogously, the CPGAMEC rule is described by the valence electrons' number per unit cluster formula ($N_{e/u}$), and expressed as the following form

$$N_{e/u} = (e/a) \times Z, \tag{1}$$

where e/a represents the electron concentration (i. e. the e/a-ratio), and Z represents the total number of atoms per unit cluster formula.

Given that the e/a-ratio has been proven to be an important concept in the theory of alloys[39,40,45,59], just as the Hume-Rothery rule[47] reflected that the structures of specific intermetallic phases (i. e. electron compounds) are stabilized by specific e/a-ratio (see Supplementary Figure S2). Thus, the e/a-ratio is used as an effective parameter to investigate the CPGAMEC rule in this work, and the methods for its calculation are presented in the following parts. Besides, the total number of atoms per unit cluster formula (Z) is obtained on the basis of [cluster](glue atoms)$_x$. While the key point is determination of the principal cluster entering into the cluster formula: [cluster](glue atoms)$_x$. To resolve this problem, an effective method of central force field model[29,60] has been developed by
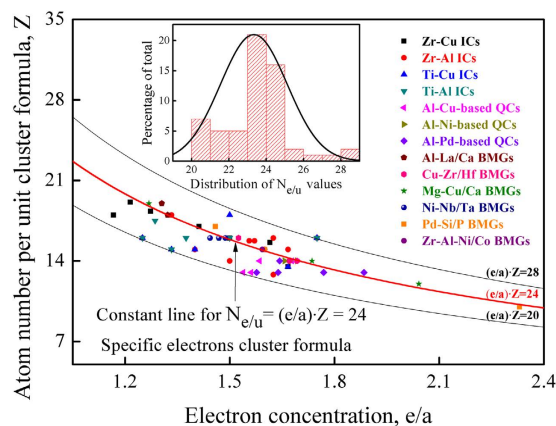
Figure 2. CPGAMEC rule for complex metallic alloys (including the ICs in Zr-/Ti-based systems, Al-based QCs[24] and BMGs in several glass-forming systems[26]), reflected by the correlations between electron concentration (*e/a*) and total number of atoms per unit cluster formula (*Z*).

combining interatomic force constants (*IFCs*)[61,62] and atomic close packing principle[14,22], while its general utility has been validated by different CMAs in numerous alloy systems[27–29]. For a given alloy phase, the central force field model shows that those atoms with the largest *IFCs* act as the central atom of the cluster, those atoms with the smallest *IFCs* act as the glue atoms of the model, while those atoms with the *IFCs* locating between the max. *IFCs* and min. *IFCs* act as either the shell atoms or the glue atoms[29]. Then the cutoff shell of principal cluster is determined by the atomic close-packing principle[14,22], as shown in the inset map (a) of Supplementary Figure S3, the cutoff radius (*r*) of cluster shell corresponds to the maximum radial atomic density (ρ_{ra}). Thereof, the principal cluster and the corresponding cluster formula can be obtained conveniently, and thus the total number of atoms per unit cluster formula (*Z*) can be achieved. Hence, the CPGAMEC rule described by the valence electrons' number per unit cluster formula ($N_{e/u}$), can be obtained via formula (1). In this work, the *IFCs* are computed by performing first-principles calculations within the framework of density functional perturbation theory[61,62], and the computational details are provided in Supplementary Materials.

Confirmation of the CPGAMEC rule

To confirm the existence of the CPGAMEC rule, different kinds of CMAs including Zr-/Ti-based intermetallic compounds (ICs), Al-based quasicrystals (QCs) and bulk metallic glasses (BMGs) in several glass forming systems, have been investigated by formula (1) upon analysis of their cluster structure and electron concentration information. As the results shown in Fig. 2, the $N_{e/u}$ values of these Zr-/Ti-based ICs, Al-based QCs and BMGs, are close to specific constants of eight-multiples and twelve-multiples, verifying the existence of CPGAMEC rule for CMAs. In what follows, we will present the results and discussion about confirmation of this electron counting rule in detail.

Confirmation of the CPGAMEC rule in ICs. The Zr-Cu/Al ICs and Ti-Al/Cu ICs with apparent cluster features have been studied first[27,29,53], and their crystallographic information are listed in Supplementary Table SII. Based on the central force field model[29,63–66], the cluster structure information of these Zr-Cu/Al and Ti-Al/Cu ICs are obtained. The results are collected in Fig. 3, Supplementary Figure S3 and Table SIII, where the first atom represents the central atom of the principal cluster. Therewith, the total number of atoms per unit cluster formula (*Z*) for these Zr-Cu/Al ICs and Ti-Al/Cu ICs can be easily obtained. And thus the valence electrons' number per unit cluster formula ($N_{e/u}$) is computed via formula (1). Here the *e/a*-ratio[32,47] of these Zr-Cu/Al ICs and Ti-Al/Cu ICs is calculated by weight averaging the valence electrons contribution of all constituent elements, as expressed in the following form

$$e/a = \sum C_i \times (e/a)_i, \tag{2}$$

where C_i and $(e/a)_i$ denotes the atomic fraction and the valence electrons contribution of the *i*-th element, respectively. The determination of $(e/a)_i$ in those TM-containing systems, however, is complicated because of sp-d hybridization[35,47,48,59], thus it is still a great challenge to completely obtain the *e/a*-ratio of these ICs. Nevertheless, the extra-nuclear electronic configuration of TMs in the periodic table is definite[67]. Besides, we notice that $(e/a)_i$ assignment for the *e/a*-ratio calculation in Hume-Rothery rule is adopted as the usual valences of the constituent elements[32,47,68]. Therefore, the *e/a*-ratio of these ICs is calculated by adopting the outermost electrons and the common valences[44] as the $(e/a)_i$ assignments, respectively (see Supplementary Table SIV). The detailed discussion on the valence electrons contribution of these constituent elements is provided in Supplementary Materials.

By assigning the outermost electrons as the valence electrons contribution, the *e/a*-ratio of these ICs are calculated via formula (2). The results indicate that the *e/a*-ratio of these Zr-Cu/Al ICs and Ti-Al/Cu ICs lies within the range from 1.2 to 1.8, and it varies with the *i*-element's content (C_i) in a linear manner (see Supplementary Figure S4). Accordingly, the $N_{e/u}$ values for these ICs are obtained via formula (1), and the results are presented in Table 1. It is found that in this case, the $N_{e/u}$ value of these ICs is close to a specific constant of eight-multiples and
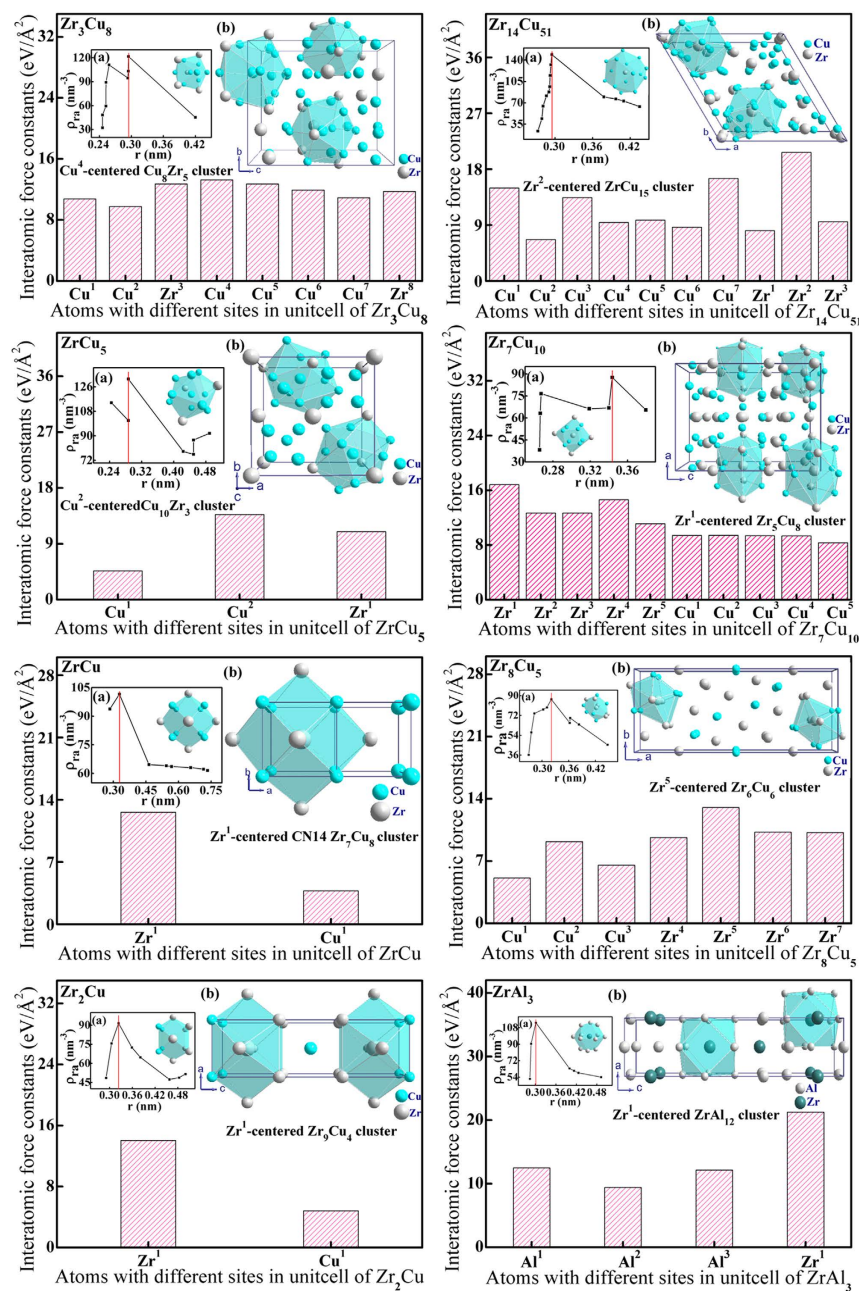
Figure 3. Principal clusters of the Zr-Cu/Al ICs and their interatomic force constants (*IFCs*). (a) Correlation between radial distances (*r*) and radial atomic density (ρ_{ra}), the red vertical line depicts the cutoff radius of the principal cluster. **(b)** Atomic clusters present in the structures of Zr-Cu/Al ICs.

twelve-multiples 24, as shown in Fig. 2. Meanwhile, in the case when the *e/a*-ratios of these ICs are calculated by assigning the common valences as the valence electrons contribution, the $N_{e/u}$ value for these ICs is again found to approach a specific constant of eight-multiples and twelve-multiples 48 (see Supplementary Table SV). The results indicate that in both cases, the $N_{e/u}$ values of these ICs are close to the specific constants of eight-multiples and twelve-multiples, as shown in Supplementary Figure S5, which confirms the existence of the CPGAMEC rule in alloy compounds, just as the extension of octet rule for covalent compounds and ionic compounds. For convenience, this electron counting scheme for CMAs is termed as the specific electrons cluster formula. For some ICs' $N_{e/u}$ values deviating from the specific constants of eight-multiples and twelve-multiples (see Supplementary Figure S5), it arises from the $(e/a)_i$ assignment in the *e/a*-ratio calculation process.

Confirmation of the CPGAMEC rule in QCs and BMGs. Based on the cluster-resonance model[20,69], it has been found that the valence electrons' number per unit cluster formula ($N_{e/u}$) for typical QCs and BMGs[24,26], is also close to the specific constant of eight-multiples and twelve-multiples 24, as shown in Fig. 4. This coincidence implies that QCs and BMGs follow the CPGAMEC rule as well. As for those QCs and BMGs, whose structures

Alloy system	ICs' composition	Principal cluster	Cluster formula	e/a	Z	$N_{e/u}$
Zr-Cu/Al	$ZrCu_5$	$CN12$ $Cu_{10}Zr_3$ cluster	$[Cu_{10}Zr_3](Cu_5)$	1.167	18	21
	$Zr_{14}Cu_{51}$	$CN15$ $ZrCu_{15}$ cluster	$[ZrCu_{15}](Zr_{159/51})$	1.215	19.12	23.24
	Zr_3Cu_8	$CN12$ Cu_8Zr_5 cluster	$[Cu_8Zr_5](Cu_{16/3})$	1.273	18.33	23.33
	Zr_7Cu_{10}	$CN12$ Zr_5Cu_8 cluster	$[Zr_5Cu_8](Cu_2Zr_2)$	1.412	17	24
	$ZrCu$	$CN14$ Zr_7Cu_8 cluster	$[Zr_7Cu_8](Zr)$	1.5	16	24
	Zr_8Cu_5	$CN11$ Zr_6Cu_6 cluster	$[Zr_6Cu_6](Zr_{18/5})$	1.615	15.6	25.2
	Zr_2Cu	$CN12$ Zr_9Cu_4 cluster	$[Zr_9Cu_4](Cu_{1/2})$	1.667	13.5	22.5
	$ZrAl_3$	$CN12$ $ZrAl_{12}$ cluster	$[ZrAl_{12}](Zr_3)$	1.25	16	20
	$ZrAl_2$	$CN16$ Zr_5Al_{12} cluster	$[Zr_5Al_{12}](Zr)$	1.333	18	24
	Zr_2Al_3	$CN13$ Zr_5Al_9 cluster	$[Zr_5Al_9](Zr)$	1.4	15	21
	$ZrAl$	$CN13$ Zr_7Al_7 cluster	$[Zr_7Al_7]$	1.5	14	21
	Zr_5Al_4	$CN11$ Zr_5Al_7 cluster	$[Zr_5Al_7](Zr_{15/4})$	1.556	15.75	24.51
	Zr_4Al_3	$CN14$ Zr_9Al_6 cluster	$[Zr_9Al_6](Al_{3/4})$	1.571	15.75	24.74
	Zr_3Al_2	$CN14$ Zr_9Al_6 cluster	$[Zr_9Al_6]$	1.6	15	24
	$P6_3/mmc$-Zr_5Al_3	$CN14$ Zr_9Al_6 cluster	$[Zr_9Al_6](Zr)$	1.625	16	26
	$I4/mcm$-Zr_5Al_3	$CN10$ Al_3Zr_8 cluster	$[Al_3Zr_8](Al_{9/5})$	1.625	12.8	20.8
	Zr_2Al	$CN11$ Zr_7Al_5 cluster	$[Zr_7Al_5](Zr_3)$	1.667	15	25
	Zr_3Al	$CN12$ Zr_9Al_4 cluster	$[Zr_9Al_4](Zr_3)$	1.75	16	28
Ti-Al/Cu	$TiAl_3$	$CN12$ $TiAl_{12}$ cluster	$[TiAl_{12}](Ti_3)$	1.25	16	20
	Ti_2Al_5	$CN12$ Ti_5Al_8 cluster	$[Ti_5Al_8](Al_{9/2})$	1.286	17.5	22.5
	$TiAl_2$	$CN12$ Ti_3Al_{10} cluster	$[Ti_3Al_{10}](Ti_2)$	1.333	15	20
	Ti_3Al_5	$CN12$ Ti_3Al_{10} cluster	$[Ti_3Al_{10}](Ti_3)$	1.375	16	22
	$TiAl$	$CN14$ Ti_7Al_8 cluster	$[Ti_7Al_8](Ti)$	1.5	16	24
	Ti_3Al	$CN12$ $AlTi_{12}$ cluster	$[AlTi_{12}](Al_3)$	1.75	16	28
	$TiCu_3$	$CN12$ $TiCu_{12}$ cluster	$[TiCu_{12}](Ti_3)$	1.25	16	20
	$TiCu_2$	$CN14$ Ti_5Cu_{10} cluster	$[Ti_5Cu_{10}]$	1.333	15	20
	Ti_2Cu_3	$CN14$ Ti_6Cu_9 cluster	$[Ti_6Cu_9]$	1.4	15	21
	$TiCu$	$CN14$ Ti_9Cu_6 cluster	$[Ti_9Cu_6](Cu_3)$	1.5	18	27
	Ti_2Cu	$CN12$ Ti_9Cu_4 cluster	$[Ti_9Cu_4](Cu_{1/2})$	1.667	13.5	22.5
	Ti_3Cu	$CN12$ Ti_9Cu_4 cluster	$[Ti_9Cu_4](Ti_3)$	1.75	16	28

Table 1. Cluster information for the Zr-Cu/Al and Ti-Cu/Al ICs, including the principal cluster with its coordination number (CN), cluster formula, total number of atoms per unit cluster formula (Z), electron concentration (e/a) and valence electrons' number per unit cluster formula ($N_{e/u}$), calculated via formula (1) with e/a obtained from formula (2), where the $(e/a)_i$ is assigned as the outermost electrons of the i-element.

are stabilized by the Fermi sphere-Brillouin zone interaction[70–72], the cluster-resonance model provides another applicable method to calculate their e/a-ratio, as expressed in the following form

$$e/a = (1.25^3\pi)/(3\rho_a \times r_1^3), \tag{3}$$

where r_1 and ρ_a each represents the principal cluster radius and the atomic density[15,50]. Accordingly, the e/a-ratio for some Al-based QCs and typical BMGs is calculated. While the Z value is acquired from the cluster formula of these QCs and BMGs, which has been successfully used to explain their experimental compositions (see Supplementary Table SVI and SVII). Hence, the $N_{e/u}$ values for these Al-based QCs and BMGs[24,26] are obtained, and the results are presented in Fig. 4 and Supplementary Figure S6. As reflected that the $N_{e/u}$ values for these QCs and BMGs are close to the specific constant of eight-multiples and twelve-multiples 24, confirming the existence of the CPGAMEC rule in QCs and BMGs. Furthermore, the $N_{e/u}$ values' standard deviation from constant 24 for BMGs is smaller than that for Al-based QCs (see insets in Fig. 4). This distinction is attributed to the structural differences of these CMAs, as will be discussed in the following part.

All of the results reveal the fact that the $N_{e/u}$ values of Zr-/Ti-based ICs, Al-based QCs and typical BMGs are close to the specific constants of eight-multiples and twelve-multiples (see Fig. 2), which confirms the existence of CPGAMEC rule for CMAs. Moreover, the CPGAMEC rule signifies that CMAs' cluster formula is superior to the customary stoichiometric formula[54]. Meanwhile, the eight-multiples' characteristic of the $N_{e/u}$ values for CMAs suggests that CMAs follow the extension of octet rule as well. Besides, the cluster formula of CMAs may differ from the molecular formula of covalent compounds and ionic compounds only by the linkage between the primary units[44], which retains the basic features of interatomic interaction instead of inter-molecular forces. As for some CMAs deviating from the CPGAMEC rule, it is attributed to the e/a-ratios involving in the $N_{e/u}$ calculated process, this can be readily understood since the e/a-ratio is only an effective one because of TMs' hybridized effects[15,20]. The situation is similar to the exception of octet rule, where special terminology like hyper-/hypo-valence has been developed to describe those chemical species that do not follow the octet rule[46,57].
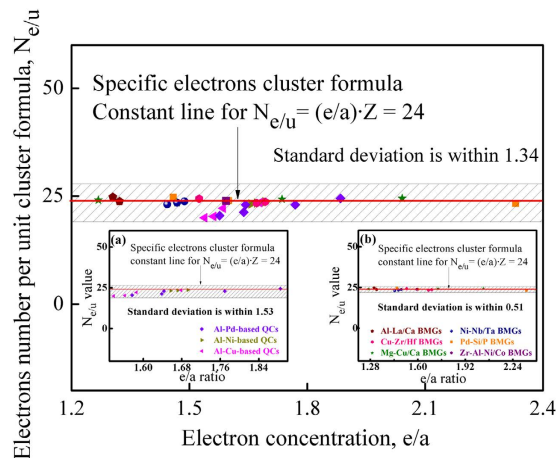
Figure 4. Correlation between electron concentration (*e/a*) and valence electrons' number per unit cluster formula (*$N_{e/u}$*) for typical Al-based QCs and BMGs in several glass-forming systems[28,29], reflecting the CPGAMEC rule of specific electrons cluster formula for CMAs and their *$N_{e/u}$* values' deviation from the specific constant.

Furthermore, the CPGAMEC rule is fairly well followed by those CMAs with apparent cluster features, just as the octet rule is strictly followed by element atoms in the period two, while element atoms in other periods may obey this rule but not necessarily in all molecules[11,12,57]. Especially, the electron counting rules followed by a large number of condensed matters (including CMAs, covalent compounds and ionic compounds), imply that the valence electrons' number per unit molecular formula is close to specific constants, which are firmly related with materials' atomic structure. Besides, the existence of the CPGAMEC rule in ICs, QCs and BMGs further reveals the close relationship between structure and properties of these CMAs[15,29,73,74].

During the past decades, some other electron counting schemes have been developed to explore the interrelationship between the structure and properties of materials[75–99]. For example, the skeletal electron pair (SEP) rule[76–79] used to describe the cluster structural features of complex polynuclear molecules with varied skeletal atoms[85,86], the topology electron counting (TEC)[80,82] theory used to estimate the electron counts of polyhedral metal clusters with varying nuclearity[79,81,84,87]. Both SEP and TEC theories assume that each vertex atom contributes three orbitals to the cluster bonding[75,77,88]. Nevertheless, this assumption is true for the main-group elements but not necessarily true for the transition metals[87]. Besides, the hypervalent electron counting scheme and the Zintl-Klemm electron counting rule[92,93], provide a route for understanding the bonding in ICs containing heavy main group elements. While the 14 electron rule[94,95] indicates that the total valence electrons' number per transition metal atom in Nowotny chimney ladder phases is 14. Compared with these electron counting schemes[75–99], the CPGAMEC rule pay much attention on those CMAs with apparent cluster structural features, like some ICs, QCs and BMGs. All of these electron counting rules made significant progress in our better understanding of the close connections among the valence electrons number, the cluster stereochemistry and the atomic cluster geometries.

Application of the CPGAMEC rule

The CPGAMEC rule can be applied to guide the composition design of CMAs with desired properties. Based on the cluster-plus-glue-atom model and the CPGAMEC rule, it is clear that this electron counting scheme endows the cluster formula of CMAs with apparent molecular features, just like the molecular formula of common covalent and ionic compounds. In this context, the cluster formula corresponding to cluster-plus-glue-atom model brings with itself the basic information on CMAs' composition, atomic structure and electronic unit. Accordingly, the composition-structure-property correlations of CMAs can be investigated further. In the present work, we take BMGs in the ZrCu-based system as an example to explain the correlations reflected by the CPGAMEC rule, and to illustrate its practical applications in CMAs' composition designing process.

As shown in Fig. 5, based on the Cu_8Zr_5 icosahedral cluster derived from Zr_3Cu_8 ICs[29], the BMGs compositions can be designed via the known cluster formula of [cluster](glue atoms)$_{1or3}$ for ideal glassy formers[15,19,21]. Then the possible cluster formulas are denoted as $[Cu_8Zr_5]Cu$, $[Cu_8Zr_5]Zr$, $[Cu_8Zr_5]Zr_2Cu$, $[Cu_8Zr_5]Cu_3$, $[Cu_8Zr_5]Cu_2Zr$ and $[Cu_8Zr_5]Zr_3$. Under the theoretical guidance of CPGAMEC rule, it has been verified that among these cluster formulas, the specific electrons cluster formula $[Cu_8Zr_5]Cu = Cu_{64.3}Zr_{35.7}$ with its $N_{e/u} = 23.7$ close to the specific constant of eight-multiple and twelve multiple 24, is in good agreement with the experimentally synthesized $Cu_{64}Zr_{36}$ BMGs. Likewise, the specific electrons cluster formula $[Zr_7Cu_8]Zr$ and $[Ti_9Cu_6]Cu_3$, with $N_{e/u} = 24.2$ and 23.6 close to ideal value 24, can be used to explain the composition of $Cu_{50}Zr_{50}$ and $Cu_{50}Ti_{50}$ BMGs, where the Zr_7Cu_8 and Ti_9Cu_6 principal clusters are derived from ZrCu ICs and TiCu ICs, respectively[29,65]. By combination with the micro-alloying mechanism, multi-components BMGs' compositions can be achieved via element substitution method[15]. For instance, when one of the shell atoms Zr in binary cluster formula $[Cu_8Zr_5]$ Cu is substituted by one Ti atom with comparable size[21], the experimental composition for ternary $Cu_{64}Zr_{28.5}Ti_{7.5}$ BMGs can be designed via the specific electrons cluster formula $[Cu_8Zr_4Ti]Cu = Cu_{64.3}Zr_{28.6}Ti_{7.1}$, with $N_{e/u} = 23.4$ close to the specific constant of eight-multiple and twelve-multiple 24. Likewise, the composition of quaternary
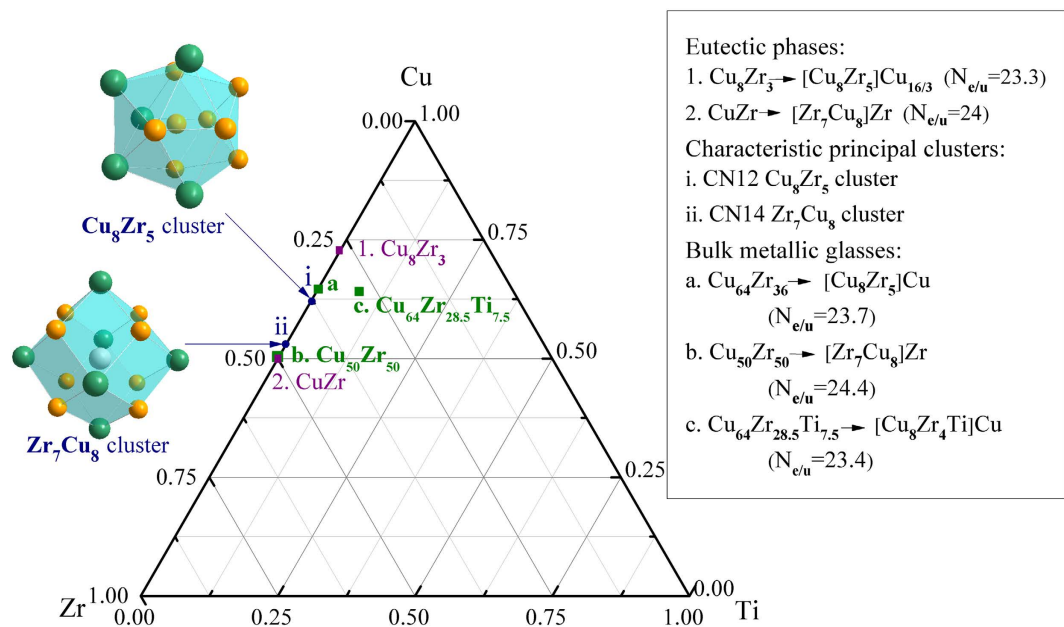
Figure 5. Illustration for the application of the CPGAMEC rule: Specific electrons cluster formula of CuZr-based bulk metallic glasses, and the principal clusters derived from relevant eutectic phases in Cu-Zr alloy system, reflected in ternary Cu-Zr-Ti phase diagram. (In this and subsequent figures, the orange spheres and olive green spheres denote the copper atoms and zirconium atoms, respectively).

$Ti_{40}Cu_{46.95}Zr_{10}Sn_{3.05}$ BMGs can be designed on the basis of binary specific electrons cluster formula: $[Ti_9Cu_6]Cu_3$ via elements' substitution method, and its resultant cluster formula is $[TiCu_{5.45}Sn_{0.55}Ti_{6.2}Zr_{1.8}]Cu_3$ with $N_{e/u} = 24.5$ close to the specific constant of eight-multiple and twelve-multiple 24. Relevant experimental studies indicate this quaternary BMGs have good glass forming ability and high strength[65]. Therefore, the CPGAMEC rule provides an innovative theoretical guidance to direct the design of CMAs with desired properties.

Interpretation of the CPGAMEC rule

To make further progress, a possible interpretation for understanding the CPGAMEC rule has been presented on the basis of CMAs' cluster structural characteristics. As mentioned above, the $N_{e/u}$ values for these CMAs are close to the specific constants of twelve-multiples. Meanwhile, the local atomic structures of CMAs are characterized by numerous polyhedral clusters[4,13–15], and most of these clusters are the convex polyhedron with coordination number (*CN*) of twelve[100–103]. In particular, the short-range-ordering features induced by the *CN*12 icosahedral clusters in the structure of BMGs and IQCs, have been verified by many theoretical and experimental investigations[104–113]. On this ground, we assume the specific electrons cluster formula as an entire *CN*12 convex polyhedron, while this polyhedron contains the basic information on composition, structure and electrons of CMAs. According to the charge distribution of Gauss's law[114–116] and under the above assumption, it is readily to understand that the $N_{e/u}$ values for these CMAs are close to the specific constants of twelve-multiples. Meanwhile, the principal cluster in the cluster formula represents CMAs' main structural features, while the glue atoms is only a small part and can be averaged into the cluster part[15,20]. For instance, the *CN*12 Cu_8Zr_5 icosahedral cluster represents the primary structural features of Zr_3Cu_8 phase[15,29]. Figure 6 presents the atomic cluster structures and the charge density distribution of Zr_3Cu_8 phase, it shows that the electrons mainly distribute on the twelve vertex of Cu_8Zr_5 clusters, which further demonstrates the rationality of this interpretation for the CPGAMEC rule. Our understanding on the CPGAMEC rule further implies that the electron counting schemes of materials are closely related to their microscopic atomic structures.

From the viewpoint of CMAs' atomic cluster structures, the above interpretation for the specific electrons cluster formula provides an underlying mechanism behind the CPGAMEC rule. Accordingly, the $N_{e/u}$ values' deviation from the specific constants of twelve-multiples for some CMAs (see the inset in Fig. 2), can be understood as distortions of the *CN*12 convex polyhedron[4,74]. Furthermore, the fact that the N_{ve} values for some covalent compounds and ionic compounds are specific constants of eight-multiples, is regarded as an extension of the octet rule. This can be understood as the valence electrons distribute in successive shells at the corners of a cube[38,57]. Similarly, the fact that the $N_{e/u}$ values for these CMAs are specific constants of twelve-multiples, can be understood as the valence electrons distribute in successive shells at the vertexes of the *CN*12 convex polyhedron. Therefore, the CPGAMEC rule of the specific electrons cluster formula, provides an aggregate picture with intriguing electronic rule and structural features of CMAs. It is worthwhile to mention that there are other underlying mechanisms behind this CPGAMEC rule, and our studies along this direction are still underway.

In conclusion, an electron counting rule for CMAs (i. e. CPGAMEC rule) has been presented in this work, by analogy with the extension of octet rule for common covalent compounds and ionic compounds. It has been found that the valence electrons' number per unit cluster formula ($N_{e/u}$) for different kinds of CMAs, are close to
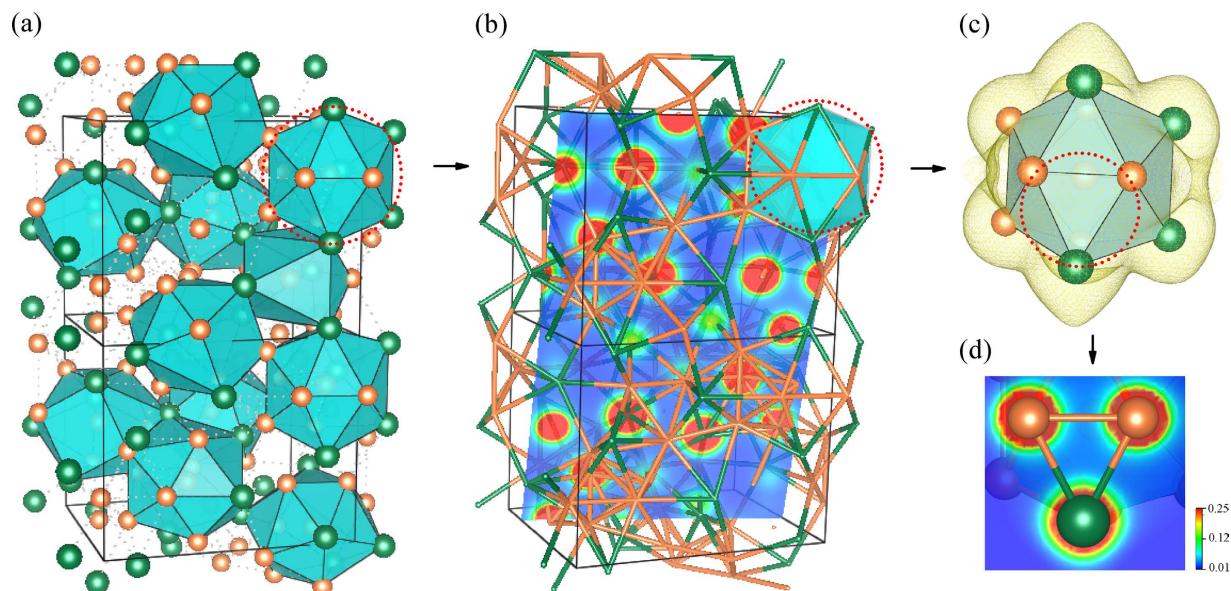
Figure 6. General view of the interpretation for the CPGAMEC rule, based on the charge distribution of Gauss's law and the cluster structural features of CMAs: (**a**) Atomic clusters existed in the structure of Zr_3Cu_8 ICs, (**b**) Charge density distribution of Zr_3Cu_8 ICs, (**c**) Charge density of the $CN12$ Cu_8Zr_5 icosahedral cluster presented in the structure of Zr_3Cu_8 ICs (the isosurface is 0.02 e/Bohr³), (**d**) Color-contour maps on the Cu-Zr-Cu triangle plane of $CN12$ Cu_8Zr_5 cluster in Zr_3Cu_8 ICs.

specific constants of eight-multiples and twelve-multiples, as exemplified by Zr-/Ti-based ICs, Al-based QCs and BMGs in several glass-forming systems. Thus we termed it as CMAs' specific electrons cluster formula. It has been demonstrated that the CPGAMEC rule is a useful guidance to direct the design of CMAs with desired properties. Meanwhile, the cluster formula can be regarded as not only CMAs' composition unit and structural unit, but also their electronic unit and molecular formula. Furthermore, the CPGAMEC rule for CMAs imply that the electron counting schemes of materials are closely related to their atomic structure features. The present work provides an aggregate picture with intriguing electronic rule and structural features of CMAs, and hence offers a significant theoretical guidance for researchers to further investigate the composition-structure-properties correlations of CMAs.

References

1. Maisel, S. B., Hofler, M. & Muller, S. A canonical stability-elasticity relationship verified for one million face-centred-cubic structures. *Nature* **491,** 740–743 (2012).
2. Seitz, F. & Johnson, R. P. Modern Theory of Solids. II. *Journal of Applied Physics* **8,** 186 (1937).
3. Greaves, G. N., Greer, A. L., Lakes, R. S. & Rouxel, T. Poisson's ratio and modern materials. *Nature Materials* **10,** 823–837 (2011).
4. Cheng, Y. Q. & Ma, E. Atomic-level structure and structure-property relationship in metallic glasses. *Progress in Materials Science* **56,** 379–473 (2011).
5. Miller, G. J. The "Color Problem" in Solids: How It Affects Structure, Composition and Properties, *European Journal of Inorganic Chemistry* **5,** 523–536 (1998).
6. Ubbelohde, A. R. Crystallography and the phase rule. *Journal of Applied Physics* **7,** 313–321 (1956).
7. Mackay, A. L. Generalised crystallography. *Journal of Molecular Structure* (*Theochem*) **336,** 293–303 (1995).
8. Louzguine-Luzgin, D. V. & Inoue, A. Formation and Properties of Quasicrystals. *Annual Review of Materials Research* **38,** 403–423 (2008).
9. Chen, M. Mechanical Behavior of Metallic Glasses: Microscopic Understanding of Strength and Ductility. *Annual Review of Materials Research* **38,** 445–469 (2008).
10. Cheng, Y. Q., Ma, E. & Sheng, H. W. Atomic Level Structure in Multicomponent Bulk Metallic Glass. *Physical Review Letters* **102,** 245501 (2009).
11. Castleman, A. W., Jr. & Jena, P. Clusters: a bridge across the disciplines of environment, materials science, and biology. *Proceedings of the National Academy of Sciences of the United States of America* **103,** 10554–10559 (2006).
12. Jena, P. Beyond the Periodic Table of Elements: The Role of Superatoms. *The Journal of Physical Chemistry Letters* **4,** 1432–1442 (2013).
13. Miracle, D. B. A structural model for metallic glasses. *Nature Materials* **3,** 697–702 (2004).
14. Miracle, D. B. The efficient cluster packing model–An atomic structural model for metallic glasses. *Acta Materialia* **54,** 4317–4336 (2006).
15. Dong, C. *et al.* From clusters to phase diagrams: composition rules of quasicrystals and bulk metallic glasses. *Journal of Physics D: Applied Physics* **40,** R273–R291 (2007).
16. Boudreaux, D. S. Theoretical studies on structural models of metallic glass alloys. *Physical Review B* **18,** 4039–4047 (1978).
17. Jones, T. E., Miorelli, J. & Eberhart, M. E. Reactive cluster model of metallic glasses. *Journal of Chemical Physics* **140,** 084501 (2014).
18. Dong, C. *et al.* Cluster-based composition rule for stable ternary quasicrystals in Al-(Cu, Pd, Ni)-TM systems. *Philosophical Magazine* **86,** 263–274 (2006).
19. Yang, L. *et al.* Design of Cu_8Zr_5-based bulk metallic glasses. *Applied Physics Letters* **88,** 241913 (2006).
20. Han, G. *et al.* The e/a values of ideal metallic glasses in relation to cluster formulae. *Acta Materialia* **59,** 5917–5923 (2011).

21. Xia, J. *et al.* Ternary bulk metallic glasses formed by minor alloying of Cu_8Zr_5 icosahedron. *Applied Physics Letters* **88,** 101907 (2006).
22. Chen, H. *et al.* A Cluster-Resonance Criterion for Al-TM Quasicrystal Compositions. *Israel Journal of Chemistry* **51,** 1226–1234 (2011).
23. Li, B. *et al.* Cluster formula of Fe-containing Monel alloys with high corrosion-resistance. *Materials Characterization* **68,** 94–101 (2012).
24. Chen, H., Qiang, J. B., Wang, Y. M. & C., Dong. Compositions of Al-Based quasicrystals interpreted by cluster formulae. *Acta Physica Polonica A* **126,** 446–446 (2014).
25. Li, Z. *et al.* Composition design of superhigh strength maraging stainless steels using a cluster model. *Progress in Natural Science: Materials International* **24,** 35–41 (2014).
26. Luo, L. J. *et al.* 24 electron cluster formulas as the 'molecular' units of ideal metallic glasses. *Philosophical Magazine* **94,** 2520–2540 (2014).
27. Du, J. L., Wen, B., Melnik, R. & Kawazoe, Y. Cluster characteristics and physical properties of binary Al–Zr intermetallic compounds from first principles studies. *Computational Materials Science* **103,** 170–178 (2015).
28. Chen, H. *et al.* Hardness of Al-based quasicrystals evaluated via cluster-plus-glue-atom model. *Philosophical Magazine* **94,** 1463–1477 (2014).
29. Du, J. L., Wen, B., Melnik, R. & Kawazoe, Y. Determining characteristic principal clusters in the "cluster-plus-glue-atom" model. *Acta Materialia* **75,** 113–121 (2014).
30. Hong, H. L., Wang, Q., Dong, C. & Liaw, P. K. Understanding the Cu-Zn brass alloys using a short-range-order cluster model: significance of specific compositions of industrial alloys. *Scientific Reports* **4,** 7065 (2014).
31. Condon, E. U. & Mack, J. E. An Interpretation of Pauli's Exclusion Principle. *Physical Review* **35,** 579–582 (1930).
32. Pauling, L. & Ewing, F. J. The Ratio of Valence Electrons to Atoms in Metals and Intermetallic Compounds. *Reviews of Modern Physics* **20,** 112–122 (1948).
33. Pauling, L. The metallic state. *Nature* **161,** 1019–1020 (1948).
34. Prodan, E. & Kohn, W. Nearsightedness of electronic matter. *Proceedings of the National Academy of Sciences of the United States of America* **102,** 11635–11638 (2005).
35. Pauling, L. The Nature of the Interatomic Forces in Metals. *Physical Review* **54,** 899–904 (1938).
36. Sudbery, T. Exclusion principle still interact. *Nature* **348,** 193 (1990).
37. Pauling, L. Electron Transfer and the Valence States of Cerium and Platinum in Cubic Friauf-Laves Compounds with the Platinum Metals. *Physical Review Letters* **47,** 277–281 (1981).
38. Pauli, W. Remarks on the History of the Exclusion Principle. *Science* **103,** 213 (1946).
39. Pauling, L. Early Work on Chemical Bonding in Relation to Solid State Physics. *Proceedings of the Royal Society of London A* **378,** 207–218 (1981).
40. Pauling, L. The Metallic Orbital and the Nature of Metals. *Journal of Solid State Chemistry* **54,** 297–307 (1984).
41. Kaplan, I. G. The Pauli Exclusion Principle. Can It Be Proved? *Foundations of Physics* **43,** 1233–1251 (2013).
42. Pauling, L. A Resonating-Valence-Bond Theory of Metals and Intermetallic Compounds. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **196,** 343–362 (1949).
43. Pauling, L. Nature of the Metallic Orbital. *Nature* **189,** 656 (1961).
44. Lewis, G. N.The Atom and the Molecule. *Journal of the American Chemical Society* **38,** 762 (1916).
45. Pauling, L. Influence of valence, electronegativity, atomic radii, and crest-trough interaction with phonons on the high-temperature copper oxide superconductors. *Physical Review Letters* **59,** 225–227 (1987).
46. Halgren, T. A., Brown, L. D., Kleier, D. A. & Lipscomb, W. N. Polarization and Hybridization Functions in Chemical Bonding. *Journal of the American Chemical Society* **99,** 6793 (1977).
47. Raynor, G. V. Progress in the Theory of Alloys. *Progress in Metal Physics* **1,** 1–76 (1949).
48. Trambly de Laissardière, G. *et al.* Electronic structure and hybridization effects in Hume-Rothery alloys containing transition elements. *Physical Review B* **52,** 7920–7933 (1995).
49. Sato, H., Takeuchi, T. & Mizutani, U. Identification of the Brillouin zone planes in the Hume-Rothery matching rule and their role in the formation of the pseudogap from ab initio band calculations for the Al-Mg-Zn1/1-1/1-1/1 approximant. *Physical Review B* **64,** 094207 (2001).
50. Stiehler, M., Rauchhaupt, J., Giegengack, U. & Häussler, P. On modifications of the well-known Hume-Rothery rules: Amorphous alloys as model systems. *Journal of Non-Crystalline Solids* **353,** 1886–1891 (2007).
51. Trambly de Laissardiere, G. & Mayou, D. Clusters and localization of electrons in quasicrystals. *Physical Review B* **55,** 2890–2893 (1997).
52. Tamura, R., Asao, T. & Takeuchi, S. Composition-Dependent Electrical Resistivity in an Al-Re-Si 1/1-Cubic Approximant Phase: An Indication of Electron Confinement in Clusters. *Physical Review Letters* **86,** 3104–3107 (2001).
53. Takeuchi, T. & Mizutani, U. Electronic structure, electron transport properties, and relative stability of icosahedral quasicrystals and their 1/1 and 2/1 approximants in the Al-Mg-Zn alloy system. *Physical Review B* **52,** 9300–9309 (1995).
54. Villars, P. & Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; ASM International: Materials Park, OH, (1997).
55. Linnett, J. W. A Modification of the Lewis-Langmuir Octet Rule. *Journal of the American Chemical Society* **83,** 2643–2653 (1961).
56. Kjekshus, A. The general 8-N rule and its relationship to the Octet rule. *Acta Chemica Scandinavica* **18,** 2379–2384 (1964).
57. Gillespie, R. J., Robinson, E. A. & Gilbert, N. Lewis and the chemical bond: the electron pair and the octet rule from 1916 to the present day. *Journal of Computational Chemistry* **28,** 87–97 (2007).
58. Lever, A. B. P. Lewis Structures and the Octet Rule. *Journal of Chemical Education* **49,** 819–821 (1972).
59. Massalski, T. B. & King, H. W. Alloy Phases of the Noble Metals. *Progress in Materials Science* **10,** 3–78 (1963).
60. Miracle, D. B. Efficient local packing in metallic glasses. *Journal of Non-Crystalline Solids* **342,** 89–96 (2004).
61. Gonze, X. & Lee, C. Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Physical Review B* **55,** 10355 (1997).
62. Gonze, X., Allan, D. C. & Teter, M. P. Dielectric tensor, effective charges, and phonons in α-quartz by variational density-functional perturbation theory. *Physical Review Letters* **68,** 3603–3606 (1992).
63. Du, J. L. *et al.* Electrochemical potential derived from the atomic cluster structures. *The Journal of Physical Chemistry Letters* **7,** 567–571 (2016).
64. Ma, Y. *et al.* Composition formulas of binary eutectics. *Scientific Reports* **5,** 17880 (2015).
65. Wang, Z. *et al.* Composition design procedures of Ti-based bulk metallic glasses using the cluster-plus-glue-atom model, *Acta Materialia* **111,** 366–376 (2016).
66. Du, J. L., Wen, B., Melnik, R. & Kawazoe, Y. Phase stability, elastic and electronic properties of Cu-Zr binary system intermetallic compounds: A first-principles study. *Journal of Alloys and Compounds* **588,** 96–102 (2014).
67. Schaeffer, B. IUPAC Periodic Table Quantum Mechanics Consistent. *Journal of Modern Physics* **05,** 117–122 (2014).
68. Hoistad, L. & Lee, S. The Hume-Rothery electron concentration rules and second moment scaling. *Journal of the American Chemical Society* **113,** 8216–8220 (1991).

69. Han, G. *et al.* Composition formulae of ideal metallic glasses and their relevant eutectics established by a cluster-resonance model. *Philosophical Magazine* **91**, 2404–2418 (2011).
70. Mizutani, U., Takeuchi, T. & Sato, H. Interpretation of the Hume–Rothery rule in complex electron compounds: g-phase Cu_5Zn_8 Alloy, FK-type $Al_{30}Mg_{40}Zn_{30}$ and MI-type $Al_{68}Cu_7Ru_{17}Si_8$ 1/1–1/1–1/1 approximants. *Progress in Materials Science* **49**, 227–261 (2004).
71. Mizutani, U., Inukai, M. & Sato, H. Hume-Rothery stabilisation mechanism and d-states-mediated Fermi surface-Brillouin zone interactions in structurally complex metallic alloys. *Philosophical Magazine* **91**, 2536–2254 (2011).
72. Hafner, J. & Krajčí, M. Electronic structure and stability of quasicrystals: Quasiperiodic dispersion relations and pseudogaps. *Physical Review Letters* **68**, 2321–2324 (1992).
73. Pierce, F. S., Poon, S. J. & Biggs, B. D. Band-structure gap and electron transport in metallic quasicrystals and crystals. *Physical Review Letters* **70**, 3919–3922 (1993).
74. Cheng, Y. Q., Sheng, H. W. & Ma, E. Relationship between structure, dynamics, and mechanical properties in metallic glass-forming alloys. *Physical Review B* **78**, 014207 (2008).
75. Wade, K. Structural Significance of the Number of Skeletal Bonding Electron-pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-metal Carbonyl Cluster Compounds. *Chemical Communications* 792–793, doi: 10.1039/C29710000792 (1971).
76. Wade, K. Skeletal Electron Counting in Cluster and Ring Compounds. *Nature Physial Science* **240**, 71 (1972).
77. Mingos, D. M. P. A general theory for cluster and ring compounds of the main group and transition elements. *Nature Physial Science* **236**, 99–102 (1972).
78. Mingos, D. M. P. Polyhedral Skeletal Electron Pair Approach. *Accounts of Chemical Research* **17**, 311–319 (1984).
79. Teo, B. K. New Topological Electron-Counting Theory. *Inorganic Chemistry* **23**, 1251–1266 (1984).
80. Stone, A. & Alderton, M. A New Model of Structure and Bonding in the Boron Hydrides. *Inorganic Chemistry* **21**, 2297–2302 (1982).
81. Teo, B. K. A simple electron counting rule for close-packed high nuclearity metal clusters. *Journal of the Chemial Society, Chemical Communications* **22**, 1362–1364 (1983).
82. Lee, S. & Hoistad, L. Second moment scaling, metallic and covalent structure rationalization and electron counting rules. *Journal of Alloys and Compounds* **229**, 66–79 (1995).
83. Teo, B. K. & Zhang, H. Counting electrons and rationalizing structures of clusters and clusters of clusters. *Polyhedron* **9**, 1985–1999 (1990).
84. K., Wade Skeletal electron counting in cluster species. Applications to metal-hydrocarbon π–complexes. *Inorgnic and Nuclear Chemistry Letters* **8**, 563–566 (1972).
85. Wade, K. Skeletal Bond Orders in Borane Anions $B_nH_n^{2-}$ and Related Closo-Cluster Species. *Inorgnic and Nuclear Chemistry Letters* **8**, 823–827 (1972).
86. Teo, B. K. TEC and SEP Electron-Counting Rules for Polyhedral Cluster Systems: Similarities and Differences, Strengths and Weaknesses. *Inorganic Chemistry* **24**, 115–116 (1985).
87. Teo, B. K. Generalization of the topological electron counting rules. *Inorganic Chemistry* **24**, 4209–4213 (1985).
88. Mingos, D. M. P. Theoretical Analyses and Electron Counting Rules for High Nuclearity Clusters. *Journal of the Chemial Society, Chemical Communications* 1352–1354, doi: 10.1039/C39850001352 (1985).
89. Firman, T. K. & Landis, C. R. Structure and electron counting in ternary transition metal hydrides. *Journal of the American Chemical Society* **120**, 12650–12656 (1998).
90. Vajenine, G. V. & Hoffmann, R. Magic electron counts for networks of condensed clusters: Vertex-sharing aluminum octahedral. *Journal of the American Chemical Society* **120**, 4200–4208 (1998).
91. Lee, C. S. & Miller, G. J. Where Are the Elements in Complex Aluminides? An Experimental and Theoretical Investigation of the Quasicrystalline Approximants, $Mg_{2-y}(ZnxAl_{1-x})_{3+y}$. *Journal of the American Chemical Society* **122**, 4937–4947 (2000).
92. Papoian, G. A. & Hoffmann, R. Hypervalent bonding in one, two, and three dimensions: extending the Zintl-Klemm concept to nonclassical electron-rich networks. *Angewandte Chemie International Edition* **39**, 2408–2448 (2000).
93. Papoian, G. A. & Hoffmann, R. Electron-rich rods as building blocks for Sb strips and Te sheets. *Journal of the American Chemical Society* **123**, 6600–6608 (2001).
94. Fredrickson, D. C., Lee, S., Hoffmann, R. & Lin, J. H. The Nowotny Chimney Ladder Phases: Following the c_{pseudo} Clue toward an Explanation of the 14 Electron Rule. *Inorganic Chemistry* **43**, 6151–6158 (2004).
95. Fredrickson, D. C., Lee, S. & Hoffmann, R. The Nowotny chimney ladder phases: Whence the 14 electron rule? *Inorganic Chemistry* **43**, 6159–6167 (2004).
96. Whangbo, M.-H., Lee, C. & Kohler, J. Transition-Metal Anions in Solids and Their Implications on Bonding. *Angewandte Chemie International Edition* **45**, 7465–7469 (2006).
97. Kohler, J. & Whangbo, M.-H. Electronic Structure Study of the $[Ag-Ag]^{4-}$, $[Au-Au]^{4-}$, and $[Hg-Hg]^{2-}$ Zintl Anions in the Intermetallic Compounds Yb_3Ag_2, Ca_5Au_4, and Ca_3Hg_2: Transition Metal Anions As p-Metal Elements. *Chemistry Materials* **20**, 2751–2756 (2008).
98. Kiran, B. *et al.* Magic Rule for AlnHm Magic Clusters. *Physical Review Letters* **98**, 256802 (2007).
99. Yannello, V. J. & Fredrickson, D. C. Orbital Origins of Helices and Magic Electron Counts in the Nowotny Chimney Ladders: the 18–n Rule and a Path to Incommensurability. *Inorganic Chemistry* **53**, 10627–10631 (2014).
100. Sha, Z. D. *et al.* The basic polyhedral clusters, the optimum glass formers, and the composition-structure-property (glass-forming ability) correlation in Cu-Zr metallic glasses. *Journal of Applied Physics* **107**, 063508 (2010).
101. Kaban, I. *et al.* Local atomic arrangements and their topology in Ni-Zr and Cu-Zr glassy and crystalline alloys. *Acta Materialia* **61**, 2509–2520 (2013).
102. Ward, L. *et al.* Structural evolution and kinetics in Cu-Zr metallic liquids from molecular dynamics simulations. *Physical Review B* **88**, 134205 (2013).
103. Liu, A. C. Y. *et al.* Systematic Mapping of Icosahedral Short-Range Order in a Melt-Spun $Zr_{36}Cu_{64}$ Metallic Glass. *Physical Review Letters* **110**, 205505 (2013).
104. Mechler, S. *et al.* Local structure and site substitution in amorphous and quasicrystalline Zr-Ti-Ni-(Cu) alloys. *Applied Physics Letters* **97**, 041914 (2010).
105. Tian, H. *et al.* Ab initio molecular dynamics simulation of binary $Cu_{64}Zr_{36}$ bulk metallic glass: Validation of the cluster-plus-glue-atom model. *Journal of Applied Physics* **109**, 123520 (2011).
106. Saida, J. *et al.* Local structure characterization in quasicrystal-forming $Zr_{80}Pt_{20}$ binary amorphous alloy. *Applied Physics Letters* **91**, 111901 (2007).
107. Luo, W. K. *et al.* Icosahedral Short-Range Order in Amorphous Alloys. *Physical Review Letters* **92**, 145502 (2004).
108. Hadler, A. B., Harris, N. A. & Fredrickson, D. C. New Roles for Icosahedral Clusters in Intermetallic Phases: Micelle-like Segregation of Ca-Cd and Cu-Cd Interactions in $Ca_{10}Cd_{27}Cu_2$. *Journal of the American Chemical Society* **135**, 17369–17378 (2013).
109. Nordell, K. J. & Miller, G. J. Linking Intermetallics and Zintl Compounds: An Investigation of Ternary Trielides (Al, Ga, In) Forming the $NaZn_{13}$ Structure Type. *Inorganic Chemistry* **38**, 579–590 (1999).

110. Tillard-Charbonnel, M., Belin, C., Manteghetti, A. P. & Flot, D. M. Heteroatomic Centering of Icosahedral Clusters. Crystal and Electronic Structure of the $K_6(NaCd)_2Tl_{12}Cd$ Compound Containing the Not-So-Naked $Tl_{12}Cd_{12}$- Polyanion. *Inorganic Chemistry* **35,** 2583–2589 (1996).

111. King, R. B., Silaghi-Dumitrescu, I. & Lupan, A. Density Functional Study of 8- and 11-Vertex Polyhedral Borane Structures: Comparison with Bare Germanium Clusters. *Inorganic Chemistry* **44,** 7819–7824 (2005).

112. Tillard-Charbonnel, M., Manteghetti, A., Belin & C. Icosahedron Oligomerization and Condensation in Intermetallic Compounds. Bonding and Electronic Requirements. *Inorganic Chemistry* **39,** 1684–1696 (2000).

113. Hirata, A. *et al.* Geometric frustration of icosahedron in metallic glasses. *Science* **341,** 376–379 (2013).

114. Standler, R. B. & Winn, W. P. Effects of coronae on electric fields beneath thunderstorms. *Quarterly Journal of the Royal Meteorological Society* **105,** 285–302 (1979).

115. Schneider, M. B. Discovery-based Gauss's law. *American Journal of Physics* **72,** 1272 (2004).

116. Singh, C. Student understanding of symmetry and Gauss's law of electricity. *American Journal of Physics* **74,** 923 (2006).

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Author Contributions

B.W. conducted the project, J.D. and B.W. performed the first principles calculations and analyzed the data, J.D., B.W., C.D., R.M. and Y.K. discussed the results and wrote the paper. All authors contributed to the manuscript.

Additional Information

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