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 fields1-5. 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 properties6,7. 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 properties8-10. 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 decades11-17. Among these cluster-based models, Dong’s “cluster-plus-glue-atom” model15 can be used to describe the atomic structure of nearly all materials. Denoted by a uniform cluster formula of [cluster](glue atoms)x18-21, 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 part22-28. Accordingly, all atoms in a given structure belong to three kinds of the central atoms, the shell atoms and the glue atoms29,30, 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 materials31-35. 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 materials36,37. One of the most important corollaries of these electronic theories, is that the stable electronic configuration of common covalent compounds

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and ionic compounds follow the octet rule. 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. Actually, many structural distinctions of metals and alloys can be discussed directly from their electron concentration differences. 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. 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 (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 CP GAMEC rule), by analogy with the octet rule and its extension for common covalent compounds and ionic compounds. 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. 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, like 8 for NaCl, 16 for CO$_2$ and 24 for Al$_2$O$_3$ etc., as presented in Fig. 1 and Supplementary Table S1. 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 CP GAMEC 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. The CP GAMEC rule is described by the valence electrons’ number per unit cluster formula ($N_{eu}$), and expressed as the following form

$$N_{eu} = (e/a) \times Z,$$

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, just as the Hume-Rothery rule 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 CP GAMEC 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 atom)$_x$. While the key point is determination of the principal cluster entering into the cluster formula: [cluster] (glue atom)$_x$. To resolve this problem, an effective method of central force field model has been developed by...
combining interatomic force constants (IFCs)\(^6,^{16,61}\) and atomic close packing principle\(^14,^{22,62}\), 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\(^{63}\). 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 (\(\rho_{\text{max}}\)). 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 (\(N_{\text{ev}}\)), 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\(^{26}\), reflected by the correlations between electron concentration \((e/a)\) and total number of atoms per unit cluster formula \((Z)\), have been investigated by formula (1) upon analysis of their cluster structure and electron concentration information. As the results shown in Fig. 2, the \(N_{\text{ev}}\) 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\(^{19,63–66}\), 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. Thereof, 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 \((N_{\text{ev}})\) 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

\[
e/a = \sum C_i \times (e/a)_i,
\]

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\(^{35,47,48,69}\), 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\(^6\). Besides, we notice that \((e/a)\), 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 \((e/a)\), 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 \(N_{\text{ev}}\) 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 \(N_{\text{ev}}\) value of these ICs is close to a specific constant of eight-multiples and

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**Figure 2. CPGAMEC rule for complex metallic alloys (including the ICs in Zr-/Ti-based systems, Al-based QCs\(^{44}\) 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 \((Z)\).**
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 $e/a$ 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 48, 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

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**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 ($\rho_{ra}$), the red vertical line depicts the cutoff radius of the principal cluster. (b) Atomic clusters present in the structures of Zr-Cu/Al ICs.
are stabilized by the Fermi sphere–Brillouin zone interaction, the cluster-resonance model provides another applicable method to calculate their $e/a$-ratio, as expressed in the following form

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

(3)

where $r_1$ and $\rho_a$ each represents the principal cluster radius and the atomic density, respectively. 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 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, 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, which has been successfully used to explain their experimental compositions (see insets in Fig. 4). This distinction is attributed to the structural differences of these CMAs, as will be discussed in the following part.

### 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.

| Alloy system | ICs' composition | Principal cluster | Cluster formula | $e/a$ | $Z$ | $N_{e/u}$ |
|--------------|------------------|-------------------|----------------|-------|-----|---------|
| Zr-Cu/Al     | CN10 Al$_3$Zr$_{9/2}$ cluster | [Al$_3$Zr$_9$](Al$_3$) | 1.625 12.8 20.8 |       |     |         |
|              | CN11 Zr$_{18/5}$Cu$_6$ cluster | [Zr$_{18/5}$Cu$_6$](Zr$_3$) | 1.556 15.75 24.51 |       |     |         |
|              | CN12 Ti$_9$Cu$_4$ cluster | [Ti$_9$Cu$_4$](Cu$_1/2$) | 1.667 15 24 |       |     |         |
| Ti-Al/Cu     | CN12 Ti$_5$Al$_8$ cluster | [Ti$_5$Al$_8$](Ti$_3$) | 1.75 15 25 |       |     |         |
|              | CN14 Ti$_7$Al$_8$ cluster | [Ti$_7$Al$_8$](Ti$_3$) | 1.625 16 20 |       |     |         |
|              | CN11 Ti$_9$Al$_4$ cluster | [Ti$_9$Al$_4$](Al$_3$) | 1.667 15 24 |       |     |         |
|              | CN12 Ti$_{10/3}$Al$_{12/5}$ cluster | [Ti$_{10/3}$Al$_{12/5}$](Al$_3$) | 1.625 16 20 |       |     |         |
|              | CN11 Ti$_{15/4}$Al$_{15/4}$ cluster | [Ti$_{15/4}$Al$_{15/4}$](Al$_3$) | 1.556 15.75 24.51 |       |     |         |
|              | CN10 Al$_3$Zr$_8$ cluster | [Al$_3$Zr$_8$](Al$_3$) | 1.625 12.8 20.8 |       |     |         |
|              | CN11 Zr$_{15/4}$Al$_{15/4}$ cluster | [Zr$_{15/4}$Al$_{15/4}$](Zr$_3$) | 1.556 15.75 24.51 |       |     |         |
|              | CN12 Ti$_{10/3}$Al$_{12/5}$ cluster | [Ti$_{10/3}$Al$_{12/5}$](Al$_3$) | 1.625 16 20 |       |     |         |
|              | CN11 Ti$_{15/4}$Al$_{15/4}$ cluster | [Ti$_{15/4}$Al$_{15/4}$](Al$_3$) | 1.556 15.75 24.51 |       |     |         |
|              | CN12 Ti$_{10/3}$Al$_{12/5}$ cluster | [Ti$_{10/3}$Al$_{12/5}$](Al$_3$) | 1.625 16 20 |       |     |         |
|              | CN11 Ti$_{15/4}$Al$_{15/4}$ cluster | [Ti$_{15/4}$Al$_{15/4}$](Al$_3$) | 1.556 15.75 24.51 |       |     |         |
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) theory\(^{80,82}\) 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\(_8\)Zr\(_5\) icosahedral cluster derived from Zr\(_3\)Cu\(_8\) ICs\(^{29}\), the BMGs compositions can be designed via the known cluster formula of [cluster](glue atoms)\(^{1,2}\) for ideal glassy formers\(^{15,19,21}\). Then the possible cluster formulas are denoted as [Cu\(_{16}\)Zr\(_{28}\)Cu\(_{8}\)], [Cu\(_{16}\)Zr\(_{28}\)Cu\(_{8}\)], [Cu\(_{16}\)Zr\(_{28}\)Cu\(_{8}\)], [Cu\(_{16}\)Zr\(_{28}\)Cu\(_{8}\)]. Under the theoretical guidance of CPGAMEC rule, it has been verified that among these cluster formulas, the specific electrons cluster formula [Cu\(_{16}\)Zr\(_{28}\)Cu\(_{8}\)] with its \(N_{\text{e/u}} = 23.7\) close to the specific constant of eight-multiple and twelve-multiple\(^{24}\), is in good agreement with the experimentally synthesized Cu\(_{16}\)Zr\(_{28}\)BMGs. Likewise, the specific electrons cluster formula [Zr\(_6\)Cu\(_{16}\)]Zr and [Ti\(_6\)Cu\(_{16}\)]Cu\(_{8}\) with \(N_{\text{e/u}} = 24.2\) and 23.6 close to ideal value 24, can be used to explain the composition of Cu\(_{16}\)Zr\(_{28}\) and Cu\(_{16}\)Ti\(_{28}\) BMGs, where the Zr\(_6\)Cu\(_{16}\) and Ti\(_6\)Cu\(_{16}\) 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\(_{16}\)Zr\(_{28}\)] Cu is substituted by one Ti atom with comparable size\(^{15}\), the experimental composition for ternary Cu\(_{14}\)Zr\(_{28}\)Ti\(_{2}\) BMGs can be designed via the specific electrons cluster formula [Cu\(_{14}\)Zr\(_{28}\)Ti\(_{2}\)] Cu = Cu\(_{14}\)Zr\(_{28}\)Ti\(_{2}\), with \(N_{\text{e/u}} = 23.4\) close to the specific constant of eight-multiple and twelve-multiple 24. Likewise, the composition of quaternary
Ti₄₀Cu₄₆.₉₅Zr₁₀Sn₃.₀₅ BMGs can be designed on the basis of binary specific electrons cluster formula: [Ti₉Cu₆]Cu₃ via elements’ substitution method, and its resultant cluster formula is [TiCu₅.₄₅Sn₀.₅₅Ti₆.₂Zr₁.₈]Cu₃ with Ne/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. 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 Ne/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, and most of these clusters are the convex polyhedron with coordination number (CN) of twelve. In particular, the short-range-ordering features induced by the CN12 icosahedral clusters in the structure of BMGs and IQCs, have been verified by many theoretical and experimental investigations. On this ground, we assume the specific electrons cluster formula as an entire CN₁₂ 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 and under the above assumption, it is readily understood that the Ne/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. For instance, the CN₁₂ Cu₈Zr₅ icosahedral cluster represents the primary structural features of Zr₃Cu₈ phase. Figure 6 presents the atomic cluster structures and the charge density distribution of Zr₃Cu₈ phase, it shows that the electrons mainly distribute on the twelve vertex of Cu₈Zr₅ 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 Ne/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 CN₁₂ convex polyhedron. Furthermore, the fact that the Ne 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. Similarly, the fact that the Ne 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 CN₁₂ 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 (Ne/u) for different kinds of CMAs, are close to...
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.

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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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