

Cluster formulas of Hume-Rothery phases

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Abstract: Hume-Rothery phases sharing the same e/a (electron concentration, which usually is 1.50(=21/14), 1.62(=21/13), 1.75(=21/12)) crystallize into many different types of structures based on a common Bravais lattice, hence the e/a alone can not be used as the finger print parameter specifying a Hume-Rothery phase. A refined electronic structure parameter is desirable for the classification of Hume-Rothery phases in a more rigorous manner. So the cluster-plus-glue-atom model is used to decipher the structures of Hume-Rothery phases, from which the cluster formula and relative number of electrons per unit formula, e/u , are derived. Hume-Rothery phases with an identical e/a are classified by e/u , so e/u is a new parameter to specify Hume-Rothery phase structures.

Key words: Hume-Rothery phases; electron concentration; cluster-plus-glue-atom model; cluster formula

0 Introduction

Hume-Rothery phases, also known as electron compounds, are formed between metal elements having close atomic radii and electronegativity, such as Cu, Zn and Ag, etc.. In these phases, the effect of the valence electrons on the structure formation is quite pronounced as compared to the phases composed of atoms with large atom radius differences, where geometrical factor plays an important role, or to electrochemical compounds, in which chemical bonding dominates. Hume-Rothery phases have distinct e/a (number of valence electron per

atom), namely, 21/14, 21/13 and 21/12, irrespective of their different chemical species and compositions^[1].

The stabilization mechanism behind the apparent e/a rule lies in the Fermi surface-Brillouin zone (FsBz) effect, due to which the electron density of states (eDOS) reaches the minimum by forming pseudogap across the Fermi level^[2-3]. In Mizutani's work, the first principles calculations are applied to various complex metal alloys including some Hume-Rothery phases, like Cu_5Zn_8 , Al_4Cu_9 , CuZn , AgMg , etc.^[4]. Firstly, they resolved the problem discovered in Pippard's work^[5] that

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Fermi surface at $e/a = 1.0$ for copper is already in contact with Brillouin zone by taking into consideration not only the s- and p- electrons but also the d- electrons forming the eDOS in their calculations. Secondly, the contributions to stability of the FsBz effect and the orbital hybridization effects in complex metallic alloys are separately verified. For most Hume-Rothery phases, the FsBz effect is revealed to be the main factor contributing to phase stability and the e/a for each element in those phases can be deduced. The available e/a is 1 for Cu and Ag, 2 for Zn, and 3 for Al, etc.. While for some phases containing transition metal elements like Fe, Co, Ni, the hybridization effect plays an important part in the formation of the pseudogap, and the e/a for these elements may not remain to be an integer. The phases containing d-band electrons are not considered in this work.

The concept of Hume-Rothery phases has also been extended to quasicrystals and their approximants. Yokiyama and Tsai, *et al.* used $e/a = 1.8$ as a guidance and found a series of stable quasicrystals in Al-Cu-TM (TM = Fe, Ru, Os) and Al-Pd-TM (TM = Mn and Re) system^[6-8]. Dubois and Dong, *et al.* discovered a so-called e/a -constant line in Al-Cu-Fe and pseudo Al-Cu-(Fe, Cr) phase diagrams^[9-10]. The depression of eDOS at Fermi level has been discovered experimentally by Traverse, *et al.* in Al-Mn quasicrystal by soft X-ray emission spectra^[11] and theoretically by Fujiwara in the Al-Mn approximants using first principles calculation^[12].

Based on the Friedel oscillation scheme, Blandin, *et al.* first proposed a real-space interpretation of momentum-based resonance stabilization mechanism^[13]. Nagel, *et al.* pointed out that the stabilization effect of conduction electrons is applicable for amorphous systems^[14]. Haeussler and coworkers first showed that binary amorphous alloys composed of noble metals and polyvalent non-transitional

elements can be regarded as Hume-Rothery phases with amorphous structures of $e/a = 1.8$ ^[15-17]. For systems with short mean free path of conduction electrons, the effective pair potential Φ_{eff} can be written as $\Phi_{\text{eff}} \propto \sin(2k_F \cdot r)/r^3$ ^[18]. The resonance between the Friedel oscillation of valence electrons and the pair correlation function is shown to depress effectively the total energy.

For structural description of non-crystalline alloys, such as quasicrystals and amorphous alloys, a structural model focusing on the 1st and 2nd nearest-neighbor local structures has been developed and termed the cluster-plus-glue-atom model^[19-20], in line with the suggestion by Mackay, *et al.*^[21] that the nearest-neighbor coordination polyhedra should be good alternative to the normally used atomic coordinates in the description of non-crystalline structures. In this model, a structure is dissociated into a 1st-neighbor cluster part and a 2nd-neighbor glue atom part, or expressed by cluster formula as $[\text{Cluster}](\text{glue atom})_x$, where x denoting the number of glue atoms matching one cluster. Such a cluster formula provides both the composition and structural information, so that it can be regarded as the basic structural unit in a solid phase. Recently, this model has been extended into a cluster-resonance model^[22], in which the number of valence electrons per unit formula (e/u) is derived to be 24 from the free electron model, irrespective of the alloy systems and compositions. This formula suggests a universal electronic structure feature for ideal metallic glasses. The generation of such cluster formula sheds some light on the possible identification of the structure unit in the Hume-Rothery phases and henceforth on a refined classification of them in terms of e/u , instead of e/a .

1 Analytical methods

The constitution of the cluster formulas of

alloy phases follows the steps described in Chen's work^[23-25]. For different non-equivalent sites in a given crystal structure, their clustering properties are shown by two ways, i. e. the atomic dense packing and least cluster sharing.

Firstly, in order to choose a cluster centered by a non-equivalent site, the cut-off distance is determined in an ambiguous way based on the principle of atomic dense packing. When plotting the radial atomic density (number of atoms enclosed in a given radius r) around a center atom, the density near center atom is usually higher than average density of a phase. The cut-off distance is defined to be the maximum in the plot, or in some cases, very

near the maximum point. Here, Cu_5Zn_8 phase is presented as an example. From its unit cell, the radial atomic densities \bar{D} around Cu1, Zn1, Cu2 and Zn2 non-equivalent sites can be drawn, as shown in Fig. 1 (a), in which the density is divided by the atomic density of the phase. The shells in the radial atomic density distributions where the densities reach their highest points are taken to be the cut-off radii of clusters. The clusters $[\text{Cu}_4\text{Zn}_9]$ at Cu1 site, $[\text{Zn}_7\text{Cu}_6]$ at Zn1, $[\text{Cu}_4\text{Zn}_{10}]$ at Cu2, and $[\text{Zn}_6\text{Cu}_6]$ at Zn2 are shown in Fig. 1 (b)-(e), respectively. Here, the bracketed are atomic clusters and the first constituent element represents the central atom.

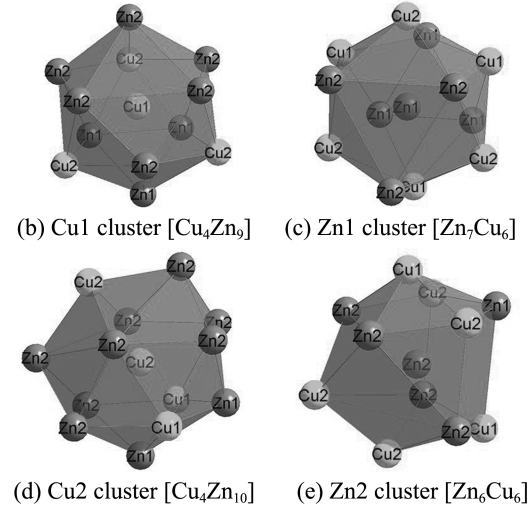
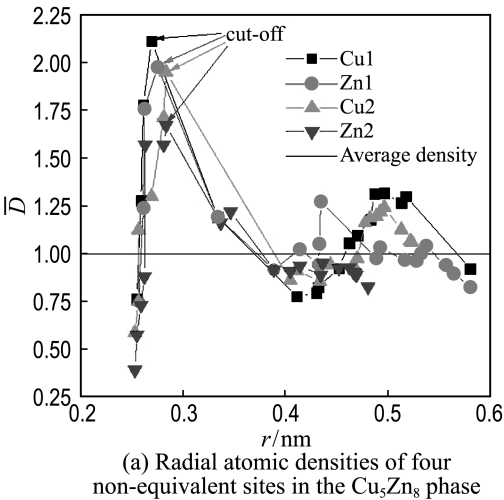


Fig. 1 Radial atomic densities and clusters at different sites

Secondly, according to the least sharing principle, the less overlapped with each other, clustering property will be more prominent. Thus, only clusters centered by non-equivalent sites with the smallest multiplicities are thought to be principal clusters. The unit cell of Cu_5Zn_8 phase has eight Cu1 and one Zn1 atoms, twelve Cu2 atoms and twenty four Zn2 atoms. Cu1 and Zn1 sites have the least multiplicities. So the two sites are taken as the center atoms for cluster formulas.

Thirdly, the cluster formulas are determined by considering sharing between

clusters in a certain structure. The compositions after sharing are the compositions of cluster formulas which comprise the whole crystal structures. Dealing with the sharing between clusters can be difficult if one calculates the sharing of single shell atoms among clusters in phases with multiple non-equivalent sites. The compositions of clusters after sharing are identical to the compositions of the phases because they are the basic units filling up the structure. And an easier way is found to calculate the compositions for cluster formulas by dividing multiplicities of all non-equivalent

sites with multiplicity of center atom and summing up each divided non-equivalent sites the clusters take up. For instance, in the case of Cu_5Zn_8 phase, all non-equivalent sites are included in Cu1 and Zn1 clusters, the cluster formula for Cu1 cluster is $[\text{Cu}_{2.5}\text{Zn}_4]$, calculated from $[\text{Cu}_{1/8/8}-\text{Zn}_{1/8/8}-\text{Cu}_{2/12/8}-\text{Zn}_{2/12/8}]$; the cluster formula for Zn1 cluster is $[\text{Zn}_4\text{Cu}_{2.5}]$, calculated from $[\text{Cu}_{1/8/8}-\text{Zn}_{1/8/8}-\text{Cu}_{2/12/8}-\text{Zn}_{2/12/8}]$.

2 Results and discussion

The above method is applied to typical Hume-Rothery phases, whose structures are available in Pearson's handbook^[26], which includes the phases with $e/a = 21/14$ (AgCd, AgMg, AgZn, AuCd, AuMg, AuZn, BeCu, CaTl, CuZn, MgTl, SrTl, Ag_3In , Au_5Sn), γ -brass ($\bar{1}43\text{m}$) with $e/a = 21/13$ (Ag_5Cd_8 , Ag_5Zn_8 , Au_5Cd_8 , Cu_5Zn_8), γ -brass ($\bar{P}43\text{m}$) with $e/a = 21/13$ (Ag_9In_4 , Al_4Cu_9 , Au_9In_4 , Cu_9Ga_4 , Cu_9In_4), and closely-packed hexagonal phases with $e/a = 21/12$ (AuCd_3 , Cu_3Ge , CuZn_3). The results are shown in Tab. 1. Also, the electron per unit cluster, e/u , of each cluster formula is calculated. When calculating the e/a with the cluster formula, the valence electron of Cu is taken as 0.7 since the occupation number of Cu site in CuZn_3 phase is 0.7^[26]. In the case of phases with symmetry $\bar{P}43\text{m}$ (Ag_9In_4 , Al_4Cu_9 , Au_9In_4 , Cu_9Ga_4 , Cu_9In_4) and AuCd_3 phase, the clusters chosen by atomic dense packing do not cover all non-equivalent sites. The part outside of a cluster is 2nd-neighbor glue atoms, which is put outside of the bracket in the formula.

According to the electron configuration of the elements and the results reported in references^[1, 4], the e/a of the elements involved in these typical Hume-Rothery phase is 1 for Cu, Ag, Au and Tl, 2 for Be, Mg, Ca, Sr, Zn and Cd, 3 for Al, Ga, In, and 4 for Ge and Sn.

It is evident that the e/u for these crystalline Hume-Rothery phases is quite different. At $e/a = 21/14$, the e/u is 3 for

AgCd, AgMg, AgZn, AuCd, AuMg, AuZn, BeCu, CaTl, CuZn, MgTl and SrTl, 6 for Ag_3In and 9 for Au_5Sn , respectively. At $e/a = 21/13$, e/u is 10.5 for the γ -brass phases Ag_5Cd_8 , Ag_5Zn_8 , Au_5Cd_8 , Cu_5Zn_8 associated with space group $\bar{1}43\text{m}$, and 21 for the Ag_9In_4 , Al_4Cu_9 , Au_9In_4 , Cu_9Ga_4 and Cu_9In_4 γ -phases with space group $\bar{P}43\text{m}$. At $e/a = 21/12$, e/u is 21 for AuCd_3 , 7 for Cu_3Ge and 4.7 for CuZn_3 . It is seen that e/u can be used to differentiate Hume-Rothery phases having the same e/a but different structure types.

The clusters so chosen are assumed to be the most dominant short-range order in these phases. In phases with $e/a = 21/14$, the clusters of CuZn (the same type for AgCd, AgMg, AgZn, AuCd, AuMg, AuZn, BeCu, CaTl, CuZn, MgTl and SrTl) are CN14 dodecahedra, while Ag_3In and Au_5Sn phases have CN12 cuboctahedron and CN12 twinned cuboctahedron clusters, respectively. In $e/a = 21/13$ phases, the clusters of Cu_5Zn_8 (the same type for Ag_5Cd_8 , Ag_5Zn_8 and Au_5Cd_8) and Al_4Cu_9 (the same for Ag_9In_4 , Au_9In_4 , Cu_9Ga_4 and Cu_9In_4) phases are mostly CN12 icosahedron, except for Ga1 site in Cu_9Ga_4 , which is CN13 cluster. In $e/a = 21/12$ phases, the clusters appear to be quite different. For AuCd_3 phase, Cd1 cluster is a CN12 icosahedron. For Cu_3Ge phase, its Cu1 cluster is a CN9 three-capped trigonal prism and its Ge1 cluster is a CN11 five-capped trigonal prism. For CuZn_3 phase, its Zn1 cluster is a CN12 elongated hexagonal bipyramid; its Cu1 cluster and Zn2 cluster are CN11 five-capped trigonal prisms, respectively.

In general, unit cell is thought to be a suitable building block to represent a structure. From the cluster-plus-glue-atom model, cluster formulas can be obtained and the clusters chosen may offer the dominant short-range information of a specific phase. The cluster formulas also give the compositions after sharing, which are proportional to the phase compositions. In this way, a Hume-Rothery phase is envisaged to be

Tab. 1 Clusters in Hume-Rothery phases and cluster formulas

| Structure Type and e/a | Phase | Center atom | Clusters | Cluster formulas | e/u |
|----------------------------------|---------------------------------|-------------|-------------------------------------|--|-------|
| BCC, 21/14 | AgCd | Ag | [Ag ₇ Cd ₈] | [Ag ₁ Cd ₁] | 3 |
| | | Cd | [Cd ₇ Ag ₈] | [Cd ₁ Ag ₁] | 3 |
| | AgMg | Ag | [Ag ₇ Mg ₈] | [Ag ₁ Mg ₁] | 3 |
| | | Mg | [Mg ₇ Ag ₈] | [Mg ₁ Ag ₁] | 3 |
| | AgZn | Ag | [Ag ₇ Zn ₈] | [Ag ₁ Zn ₁] | 3 |
| | | Zn | [Zn ₇ Ag ₈] | [Zn ₁ Ag ₁] | 3 |
| | AuCd | Au | [Au ₇ Cd ₈] | [Au ₁ Cd ₁] | 3 |
| | | Cd | [Cd ₇ Au ₈] | [Cd ₁ Au ₁] | 3 |
| | AuMg | Au | [Au ₇ Mg ₈] | [Au ₁ Mg ₁] | 3 |
| | | Mg | [Mg ₇ Au ₈] | [Mg ₁ Au ₁] | 3 |
| | AuZn | Au | [Au ₇ Zn ₈] | [Au ₁ Zn ₁] | 3 |
| | | Zn | [Zn ₇ Au ₈] | [Zn ₁ Au ₁] | 3 |
| | BeCu | Be | [Be ₇ Cu ₈] | [Be ₁ Cu ₁] | 3 |
| | | Cu | [Cu ₇ Be ₈] | [Cu ₁ Be ₁] | 3 |
| | CaTl | Ca | [Ca ₇ Tl ₈] | [Ca ₁ Tl ₁] | 3 |
| | | Tl | [Tl ₇ Ca ₈] | [Tl ₁ Ca ₁] | 3 |
| | CuZn | Cu | [Cu ₇ Zn ₈] | [Cu ₁ Zn ₁] | 3 |
| | | Zn | [Zn ₇ Cu ₈] | [Zn ₁ Cu ₁] | 3 |
| | MgTl | Mg | [Mg ₇ Tl ₈] | [Mg ₁ Tl ₁] | 3 |
| | | Tl | [Tl ₇ Mg ₈] | [Tl ₁ Mg ₁] | 3 |
| | SrTl | Sr | [Sr ₇ Tl ₈] | [Sr ₁ Tl ₁] | 3 |
| | | Tl | [Tl ₇ Sr ₈] | [Tl ₁ Sr ₁] | 3 |
| | Ag ₃ In | In | [In ₁ Ag ₁₂] | [In ₁ Ag ₃] | 6 |
| | Au ₅ Sn | Au1 | [Au ₁₀ Sn ₃] | [Au ₅ Sn ₁] | 9 |
| | | Au2 | [Au ₁₀ Sn ₃] | [Au ₅ Sn ₁] | 9 |
| | | Sn | [Sn ₁ Au ₁₂] | [Sn ₁ Au ₅] | 9 |
| γ -Brass, 21/13 | Ag ₅ Cd ₈ | Ag1 | [Ag ₄ Cd ₉] | [Ag _{2.5} Cd ₄] | 10.5 |
| | | Cd1 | [Cd ₇ Ag ₆] | [Cd ₄ Ag _{2.5}] | 10.5 |
| | Ag ₅ Zn ₈ | Ag1 | [Ag ₄ Zn ₉] | [Ag _{2.5} Zn ₄] | 10.5 |
| | | Zn1 | [Zn ₇ Ag ₆] | [Zn ₄ Ag _{2.5}] | 10.5 |
| | Au ₅ Cd ₈ | Au1 | [Au ₄ Cd ₉] | [Au _{2.5} Cd ₄] | 10.5 |
| | | Cd1 | [Cd ₇ Au ₆] | [Cd ₄ Au _{2.5}] | 10.5 |
| | Cu ₅ Zn ₈ | Cu1 | [Cu ₄ Zn ₉] | [Cu _{2.5} Zn ₄] | 10.5 |
| | | Zn1 | [Zn ₇ Cu ₆] | [Zn ₄ Cu _{2.5}] | 10.5 |
| | Ag ₉ In ₄ | Ag1 | [Ag ₁₀ In ₃] | [Ag _{3.5} In ₃] _{Ag_{5.5}In₁} | 21 |
| | | Ag2 | [Ag ₇ In ₆] | [Ag _{5.5} In ₄] _{Ag_{3.5}} | 21 |
| | | Ag3 | [Ag ₁₀ In ₃] | [Ag _{6.5} In ₃] _{Ag_{2.5}In₁} | 21 |
| | | In1 | [In ₄ Ag ₁₀] | [In ₁ Ag _{6.5}] _{Ag_{2.5}In₃} | 21 |
| | Al ₄ Cu ₉ | Al1 | [Al ₄ Cu ₉] | [Al ₁ Cu _{5.5}] _{Al₃Cu_{3.5}} | 21 |
| | | Cu1 | [Cu ₁₀ Al ₃] | [Cu _{3.5} Al ₃] _{Al₁Cu_{5.5}} | 21 |
| | | Cu2 | [Cu ₇ Al ₆] | [Cu _{5.5} Al ₄] _{Cu_{3.5}} | 21 |
| | | Cu3 | [Cu ₁₀ Al ₃] | [Cu _{6.5} Al ₃] _{Al₁Cu_{2.5}} | 21 |
| | Au ₉ In ₄ | Au1 | [Au ₇ In ₆] | [Au _{5.5} In ₄] _{Au_{3.5}} | 21 |
| | | Au2 | [Au ₁₀ In ₃] | [Au _{6.5} In ₃] _{Au_{2.5}In₁} | 21 |
| | | Au3 | [Au ₁₀ In ₃] | [Au _{3.5} In ₃] _{Au_{5.5}In₁} | 21 |
| | | In1 | [In ₄ Au ₉] | [In ₁ Au _{5.5}] _{Au_{3.5}In₃} | 21 |
| | Cu ₉ Ga ₄ | Ga1 | [Ga ₄ Cu ₉] | [Ga ₁ Cu _{5.5}] _{Cu_{3.5}Ga₃} | 21 |
| | | Cu1 | [Cu ₁₀ Ga ₃] | [Cu _{3.5} Ga ₃] _{Cu_{5.5}Ga₁} | 21 |
| | | Cu2 | [Cu ₇ Ga ₆] | [Cu _{5.5} Ga ₄] _{Cu_{3.5}} | 21 |
| | | Cu3 | [Cu ₁₀ Ga ₃] | [Cu _{6.5} Ga ₃] _{Cu_{2.5}Ga₁} | 21 |
| | Cu ₉ In ₄ | Cu1 | [Cu ₁₀ In ₃] | [Cu _{6.5} In ₃] _{Cu_{2.5}In₁} | 21 |
| | | Cu2 | [Cu ₁₀ In ₃] | [Cu _{3.5} In ₃] _{Cu_{5.5}In₁} | 21 |
| | | Cu3 | [Cu ₇ In ₆] | [Cu _{5.5} In ₄] _{Cu_{3.5}} | 21 |
| | | In1 | [In ₄ Cu ₉] | [In ₁ Cu _{5.5}] _{Cu_{3.5}In₃} | 21 |
| Close-packed hexagonal, 21/12 | AuCd ₃ | Cd1 | [Cd ₁₀ Au ₃] | [Cd ₇ Au ₃] _{Cd₂} | 21 |
| | Cu ₃ Ge | Cu1 | [Cu ₇ Ge ₃] | [Cu ₃ Ge ₁] | 7 |
| | | Ge | [Ge ₁ Cu ₁₁] | [Ge ₁ Cu ₃] | 7 |
| | CuZn ₃ | Zn1 | [Zn ₉ Cu ₆] | [Zn ₂ Cu ₁] | 4.7 |
| | | Cu | [Cu ₃ Zn ₉] | [Cu ₁ Zn ₂] | 4.7 |
| | | Zn2 | [Zn ₉ Cu ₃] | [Zn ₂ Cu ₁] | 4.7 |

built with the molecular unit instead of a unit cell. Chemical formulas can offer structural and composition information when describing chemical compounds, and here the cluster formulas exhibit the similar function when used to describe Hume-Rothery phases. It is also expected that the cluster formulas will make it possible to establish in a certain degree the structure-property correlation, and this will be studied in the future work.

On the other hand, chemical formulas usually obey octet rule because chemical bonding is dominant effect in chemical compounds. Hume-Rothery phases, however, are dominated by metallic bonding. Therewith, the cluster formulas of metals and alloys are thought to maintain electric neutrality instead of obeying octet rule. Moreover, they can be thought of as basic units containing both chemical and electronic information. Based on the cluster formulas of these phases, the parameter e/u can offer the short-range information that is concealed by e/a ratios.

3 Conclusion

By applying cluster-plus-glue-atom model to Hume-Rothery phases, cluster formulas are obtained, which contain both geometrical and chemical information of structures. By calculating the e/u , it is found that the Hume-Rothery phases with the same e/a but with different structure types can be distinguished. A refined parameter for classification of Hume-Rothery phases with the same e/a is obtained. In the Hume-Rothery phase stabilization mechanism, e/a is calculated from the FsBz effect in reciprocal space. Since the present results give explicit short-range and mediate-range order in an alloy phase, the real space pair correlation function can be derived, and its resonance with the Friedel oscillation can be considered. Therefore, e/u appears to be a promising parameter for studying the structural stability of alloy phases.

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Hume-Rothery 相的团簇式

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摘要: Hume-Rothery 相的电子浓度(e/a)一般为特定值 1.50($=21/14$)、1.62($=21/13$)或 1.75($=21/12$),但相同电子浓度的相常基于布拉维格呈现不同晶体结构,因此, e/a 并不能作为准确区分 Hume-Rothery 相结构类型的特征参数.为此需要一个更精细的结构参数对 Hume-Rothery 相进行更严谨的划分.运用团簇加连接原子模型分析常见的 Hume-Rothery 相,得到了各类 Hume-Rothery 相的团簇式和相关单位团簇电子数 e/u ,发现 e/u 能有效对具有相同 e/a 的 Hume-Rothery 相进行归类,是区分 Hume-Rothery 相结构类型的新参数.

关键词: Hume-Rothery 相;电子浓度;团簇加连接原子模型;团簇式

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