Molecule-like chemical units in metallic alloys

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ABSTRACT Each conventional alloy has its own specific compositions but the compositional origin is largely unknown due to our insufficient understanding about chemical short-range ordering in the alloy, in particular, in the solid-solution state. In the present paper, the compositions of metallic alloys are discussed and formulated, by unveiling the basic molecule-like structural units in solid solutions. Friedel oscillation theory, which describes the partial charge screening behavior in solid solutions, and henceforth the origin of short-range ordering, is applied to pin down the ideal chemical compositions of conventional metallic alloys. We propose that, at a specific composition, atoms self-assemble into an ideally ordered structure consisting of atoms residing in the nearest-neighbor shell (denoted as cluster) plus those in the next outer shell (denoted as glue atoms), which can be formulated as [cluster](glue atoms). This simplified version of short-range-order structure represents the smallest charge-neutral and mean-density zone (termed as "chemical units") and can be regarded as the 'molecules' of solid solutions. Accordingly, the chemical units and the corresponding molecule-like formulas for face-centered-cubic (FCC), hexagonal close-packed (HCP), and body-centered cubic (BCC) structures are analyzed and equations are obtained to identify the chemical formulas for FCC solid solutions. For instance, well-known α-brass Cu-30Zn alloy is formulated as $[Zn-Cu_{12}]Zn_4$. Examples of aluminum alloys, superalloys and stainless steels are also illustrated, demonstrating the versatility of the present model to interpret chemically complex alloys.

Keywords: metallic alloys, chemical unit, solid solution, short-range order, cluster-plus-glue-atom model

INTRODUCTION

The development and application of metallic alloys have historically relied heavily on experiences and tedious engineering practices. These alloys have specific chemical compositions and are accordingly classified into industrial standards. However, it is well known that properties of a metallic alloy are determined not only by its composition but also by its complex microstructures, which are, in turn, affected by its fabrication processes. Consequently, it is difficult to directly correlate an alloy's performance with its chemical constituents.

Up to date, there is essentially no reliable theoretical tool, analytical or computational, allowing the explanation of compositional range of commercially available metallic alloys for daily usage. Commercial alloys usually contain multi-elements, multi-phases and, sometimes, even multi-scaled structures. The exploration of their chemical compositions is also largely hindered by the fact that the concept of chemical molecules in metallic alloys does not exist, considering the continuous chemical bonding in metals, where the absence of weak intermolecule forces prohibits the identification of their chemical identities. However, industrially important alloys do have specific compositions, which strongly suggests the possible existence of some molecule-like "chemical units", which determine the final compositions of the alloys. These chemical units mimic the molecules in chemical substances but generally differ from crystallographic structural units in periodic Bravais lattices. The possibility of having these fundamental units has been apparently overlooked because of the lack of structural models to properly address the chemical states of solid solutions.

A solid-solution structure is characterized by self-

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organization of atoms, known as short-range order (SRO). Because of the disordering feature, SRO is at most described by statistical parameters, such as the widely-used Cowley SRO α-parameter [1], which describes the chemical deviation from the average composition at each concentric shell centered around a certain atom. However, this α-parameter only reveals solute distribution in an oscillating fashion over a certain radial distance range, but is unable to provide information on the chemical composition. In fact, the SRO feature makes a solid solution structurally heterogeneous, rather than randomly homogeneous [2]. To unveil the structural units responsible for the composition, it is necessary to re-examine the mechanism for the SRO formation.

Early structural description for solid solutions was based upon electronic structure [3–5]. A solid solution is considered as being stabilized by Fermi sphere-Brillouin zone interaction [4]. A rigorous treatment has been given by Friedel [5], who solved the electronic potential function when a charge disturbance is introduced into a pool of valence electrons in the jellium model. It is noted that, in the so-called Friedel oscillation, the charge disturbance is neutralized over a relatively long radial range, being quite different from the complete neutralization within the nearest neighbors in covalent-bonded molecules. Thus, the molecule concept was not perceived for solid solutions. However, a modified version of Friedel oscillation to account for charge neutralization in short range appears feasible to describe solid solutions. It is conceivable that a modified version of SRO structure based on Friedel oscillation may exist, from which the chemical composition of the alloy can be deduced. We hereafter call this structural entity "chemical units" since they are responsible for the final alloy chemistry. The main reason for our emphasis on solid-solution alloys is based upon the fact that, although metallic alloys have complex in-service microstructures, they are usually in the single-phase solid solution state at high temperatures, such as, the austenitic state of steels. Furthermore, high-temperature thermomechanical processes, such as extrusion and forging, are typically performed in this homogenized state. Therefore, it is reasonable to envision that compositions of metallic alloys are rooted in SROs in single-phase solid solutions.

In this paper, we first present the molecule-like concept of chemical units in solid solutions derived from Friedel oscillation theory. Structural model and mathematical equations are subsequently developed to precisely calculate the formulas of these chemical units. Finally, chemical compositions of several face-centered-cubic (FCC)

alloys are analyzed and identified using these equations. It is shown that the compositions of the most-widely utilized Cu-based binary alloys match well with the theoretical predictions. Successful application of the molecule-like concept to alloys with more complex microstructures and chemistries is demonstrated, and examples of Al-based alloys, Ni-based superalloys, and Fe-based stainless steels are given.

CHEMICAL UNITS RESULTED FROM PARTIAL CHARGE SCREENING

Friedel oscillation describes the partial screening of the electron cloud against localized perturbations in a pool of valence electrons of the jellium model for metals [6]. The effective pair potential around an impurity (or solute atom) as shown in Fig. 1b is expressed as $\Phi(r) \propto -\sin(2k_F r)/r^3$, where k_F is the Fermi wave vector [7] and r is the radial distance. Metal atoms, being positively charged after losing their valence electrons, tend to fill preferentially the negative potential zones, with their mid-points at $r_n = (1/4 + n)\lambda_{Fr}$, $n = 1, 2, 3\ldots$, where $\lambda_{Fr} = \pi/k_F$ is the Friedel wavelength and r_n defines the so-called spherical periodicity order (the inter-shell distance is λ_{Fr}). We hereafter denote this local structure, contained within the r_1 zone (mid-point at $1.25\lambda_{Fr}$), as the cluster (the nearest-neighbor polyhedron). The mid-points of the positive potential zones are located at $r_{n+0.5} = r_n + \lambda_{Fr}/2 = (3/4 + n)\lambda_{Fr}$. The pair distribution function and the corresponding effective pair potential function of Friedel
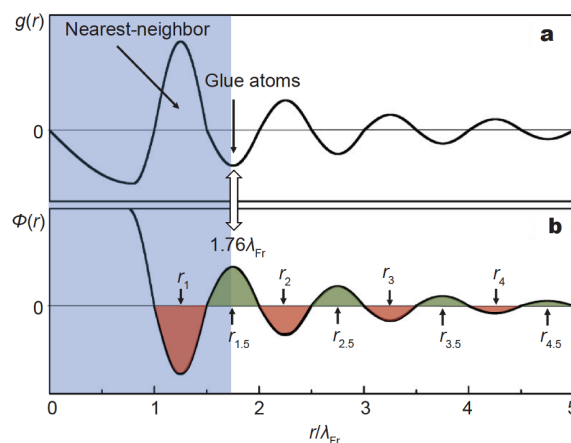
Figure 1 (a) Pair distribution function and (b) corresponding effective electronic potential $\Phi(r) \propto -\sin(2k_F r)/r^3$ arising from Friedel oscillation. The central positions of the negative (red-shaded) and positive (green shaded) potential zones are labeled with r_n and $r_{n+0.5}$, respectively. The radial distance r is scaled with Friedel wavelength λ_{Fr}. The smallest charge-neutral and mean density local zone (shaded), enclosed within radius $1.76\lambda_{Fr}$, makes a molecule-like chemical unit.

oscillation are schematically illustrated in Fig. 1, in which the negative potential zones are labeled by their central locations r_n and the positive potential zones residing between two consecutive negative potential zones are marked by $r_{n+0.5}$.

Friedel oscillation function decays with the third power of the radial distance r. In principle, within a finite distance from the central impurity, the electrical charge disturbance is not fully neutralized; global electrical neutrality can be reached only after the oscillation is completely attenuated. However, since each alloy has a particular chemistry as specified by industrial standards, there must be a small structural unit, within which atoms assemble themselves effectively to achieve the charge neutrality. Knowing that the charge and the relevant density distribution functions are all identical to the pair potential function, it is easy to obtain such distances by integrating the function $-\sin(2k_F r)/r^3$ from any radial distance r to infinity. The first charge neutral (at the same time mean density) position is subsequently determined to be $1.76\lambda_{Fr}$, falling closely to the mid-point $1.75\lambda_{Fr}$ in the $r_{1+0.5}$ zone, where the potential is positive and is unfavorable for the positive ions. It is therefore concluded that, in the scenario of partial charge screening, the central charge cannot be fully neutralized within the nearest neighbors (denoted as the cluster) like in most covalent molecules, rather it must be balanced by some additional atoms from the next outer shell (called herein glue atoms). Consequently, the smallest neutral zone consists of the nearest-neighbor cluster plus some glue atoms. The number of atoms contained with this zone can be simply obtained by multiplying the zone volume with the mean density of the alloy. We denote such a zone as "chemical unit", which refers to the charge-neutral and mean-density zone consisting of a nearest-neighbor-shell cluster plus next outer-shell glue atoms. Since it is the smallest unit that possesses charge-neutrality and mean density, it is essentially molecule-like. In fact, the only difference from the conventional molecular concept is the absence of inter-molecule forces in metals. The idea of chemical units in terms of the nearest neighbors plus a few outer-shell atoms actually agrees with our previously proposed cluster-plus-glue-atom model [8], which was based on experiences. Next, we will demonstrate how to deduce the units in solid-solution alloys with various crystal structures using the spherical volume of radius $1.76\lambda_{Fr}$.

We use a pure FCC-metal as the first trial. In this case, the nearest-neighbor distance is $r_1 = (1/2,1/2,0)a = a/\sqrt{2}$, a being the lattice constant. It is reasonable to assume that this distance falls at the most favorable position, i.e., the mid-point within the r_1 zone, $r_1 = (5/4)\lambda_{Fr} = 1.25\lambda_{Fr}$. Then, a is related to λ_{Fr} by $a = 1.25\sqrt{2}\lambda_{Fr}$. The mean density of FCC metals is $4/a^3$, i.e., 4 atoms in each unit cell of edge length a. The smallest charge-neutral and mean-density zone has a volume of $(4\pi/3)(1.76\lambda_{Fr})^3$ and contains the number of atoms $Z_{FCC} = (4\pi/3)(1.76\lambda_{Fr})^3 \times (4/a^3) \approx 16.65$. This means that for an FCC structure consisting of a single element M, the smallest chemical unit contains 16 atoms. The corresponding spherical volume has to be cut by a reduced radius of $1.74\lambda_{Fr}$. In the following, $1.74\lambda_{Fr}$ is adopted in calculating cluster formulas of different alloys. Since the cluster itself is a cuboctahedron of coordination number 12 (Fig. 2a), the cluster-plus-glue-atom formula is then $[M\text{-}M_{12}]M_3$, where inside the square-brackets is the cuboctahedral cluster and the three glue atoms reside outside.

For hexagonal close-packed (HCP) lattice, it can be treated in a similar way, as its atomic density is basically the same as the FCC one (both are densely packed). The corresponding twinned cuboctahedral cluster (Fig. 2b)
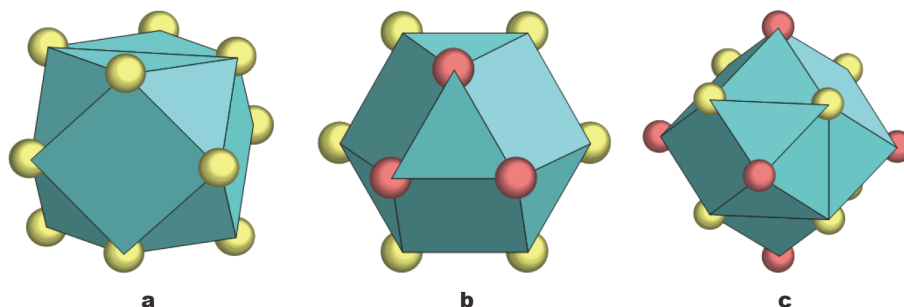
Figure 2 Clusters in typical solid-solution structures: (a) CN12 cuboctahedron in FCC lattice, (b) CN12 twinned octahedron in HCP, and (c) CN14 rhombidodecahedron in BCC. Among the three clusters, only cuboctahedron from FCC (a) is mono-shelled and the cluster radius (nearest-neighbor distance) r_1 can be simply treated as the atomic radius sum of the center and the shell atoms. The HCP and BCC clusters have two sub-shells, denoted by different colors.

also has a coordination number of 12, so that the cluster-plus-glue-atom formula of mono-element HCP structure is $[M-M_{12}]M_3$, with $Z_{HCP} = 16$.

For body-centered cubic (BCC) lattice, the atomic density is $2/a^3$ (2 atoms per unit cell) and the cluster is of rhombidodecahedral type of 15 atoms (Fig. 2c). The nearest neighbor now consists of two separated sub-shells, occupied by eight atoms at $(0.5, 0.5, 0.5)a$ and six atoms at $(1, 0, 0)a$, respectively. Due to the nearest-neighbor separation, it is not possible to accurately obtain the nearest-neighbor distance corresponding to $r_1 = 1.25\lambda_{Fr}$. An approximate estimation can be done by averaging the radial distances of the two sub-shells: $r_1 = (8 \times \sqrt{3}/2 + 6 \times 1)a/14 \approx 0.923a$. Multiplying the spherical volume of radius $1.76\lambda_{Fr}$, we obtain $Z_{BCC} = (4\pi/3)(1.76\lambda_{Fr})^3 \times (2/a^3) \approx 18.51$. Therefore, the smallest unit for mono-element BCC structure contains $Z_{BCC} = 18$ atoms, formulated as $[M-M_8M_6]M_3$. The spherical volume that encloses 18 atoms has a radius of $1.75\lambda_{Fr}$. It should be noted that, the cluster-based chemical unit, containing only a small number of atoms (16 for FCC or HCP, 18 for BCC), would not be able to deal with alloys of complex structure. Further work is necessary to extend the model to cover more atoms so that larger structural unit is identified. The solution should lie in the way the clusters are packed in space.

In the following, we demonstrate the calculation of chemical units in FCC metals, as it is reliable to assume that $r_1 = 1.25\lambda_{Fr}$ corresponds to the nearest-neighbor distance of $a/\sqrt{2}$.

IDENTIFICATION OF CHEMICAL UNITS IN SUBSTITUTION-TYPE FCC METALS

It is particularly noted that, for solid solutions, calculations are not straightforward since the cluster radius r_1 is dependent on the actual location of solute atoms within the chemical unit. It is especially complicated to deal with r_1 in clusters of multiple nearest-neighbor shells such as the twinned cuboctahedron for HCP and rhombidodecahedron for BCC. At the present moment, calculations can be precisely performed only in FCC solid structures, for r_1 can be treated as the atomic radius summation of the central atom and the mono-shell atom. The formulation depends upon the interactions between the solute (marked as A) and solvent atoms (marked as B), as discussed in the following.

(1) Attractive interaction ($\Delta H < 0$)

For a binary concentrated FCC solid-solution alloy, solute A prefers to occupy the center of the cluster to allow a maximum interaction between its surrounding solvent atoms B to form an A-centered and B-shelled cluster, $[A-B_{12}]$. The cluster radius is $r_1 = R_A + R_B$, R_A and R_B being the atomic radii of the central solute A and shell solvent B. In the case of having excessive A atoms for the cluster center, extra A atoms also go to the glue sites. The general chemical unit formula is then $[A-B_{12}](A_xB_y)$, where A represents the solute element with an atomic radius R_A, B represents the solvent element with an atomic radius R_B, and $x + y \geq 1$ is the number of glue atoms.

The total atomic volume of the chemical unit can be evaluated using $(1 + x)[(4\pi/3)R_A^3]/0.74 + (12 + y)[(4\pi/3)R_B^3]/0.74$, where 0.74 is the packing efficiency of FCC structure. This volume is made equal to the spherical volume of $(4\pi/3)(1.74\lambda_{Fr})^3 = (4\pi/3)(1.74 \times (R_A + R_B)/1.25)^3$, where $r_1 = 1.25\lambda_{Fr}$ is assumed to be the nearest neighbor distance $R_A + R_B$. The following equation for an FCC alloy formulated by $[A-B_{12}](A_xB_y)$ is then obtained:

$$x R_{A/B}^3 + y = R_{A/B}^3 + 6R_{A/B}^2 + 6R_{A/B} - 10. \tag{1}$$

In principle, a close-integer (x, y) solution for the above equation gives the final chemical formula that best fits Friedel oscillation. The only variable in the above equation is the atomic radius ratio of the solute over the solvent, $R_{A/B}$. When the atomic radius ratio $R_{A/B} = 1$ (equal radius substitution or single-element FCC phase), $x + y = 3$, which leads to $[A-B_{12}](A_xB_{3-x})$. This is precisely the formula previously obtained for mono-element FCC structure.

(2) Repulsive interaction ($\Delta H \geq 0$)

In this case, the solvent B atoms prefer to form the solvent cluster $[B-B_{12}]$ and the solute atoms move to the glue sites. The cluster radius is the same as that of the solvent atom, $r_1 = 2R_B$. The general chemical unit formula is then $[B-B_{12}](A_xB_y)$.

The total atomic volume of the chemical unit is evaluated as $x[(4\pi/3)R_A^3]/0.74 + (13 + y)[(4\pi/3)R_B^3]/0.74$.

The expression for (x, y) is $xR_{A/B}^3 + y = 2.97$. When $R_{A/B} = 1$, the integer solution must satisfy $x + y = 3$. Therefore, the equation becomes simply

$$x R_{A/B}^3 + y = 3. \tag{2}$$

The close-packed HCP structure, whose nearest neighbors in twinned cuboctahedron configuration also fall closely within a single shell, can be dealt with similarly. However, it is difficult to deal with r_1 in clusters of multiple nearest-neighbor shells such as rhombidodecahedron for BCC. At present, the calculations can be reliably performed only in FCC and HCP solid solutions,

for r_1 can be treated as the atomic radius summation of the central atom and the mono-shell atom, $r_1 = R_A + R_B$.

CHEMICAL UNITS AND THEIR COMPOSITIONS FOR FCC SOLID-SOLUTION ALLOYS

In this section, we describe the procedures to deduce the chemical formula (or composition) of solid-solution alloys. It will be demonstrated that compositions of commonly used industrial alloys are remarkably close to the model predictions, validating the presence of simple chemical units in metallic alloys.

Cu-based binary alloys

We first used binary Cu-Zn to illustrate our model. Copper can dissolve a maximum of about 39 wt% Zn at high temperatures [9]. According to the ASM handbook [10], FCC α-brass specifications cover the entire solid solubility range but the most widely used one is the cartridge alloy Cu-30Zn (the wt% is placed before the solute element). SROs in α brasses have been carefully measured on a single-crystal sample [11], which confirmed the Zn-Cu-type nearest-neighbor order (α_{110} = -0.1373) and Zn-Zn-type next-shell order (α_{200} = 0.1490), as expected from the negative enthalpy of mixing between Zn and Cu. For alloys containing sufficient amounts of Zn, the general chemical formula can thus be written as $[\text{Zn-Cu}_{12}](\text{Zn}_x\text{Cu}_y)$. In accordance with the measured positive α_{200}, the glue atoms should be enriched with Zn. Using the Goldschmidt atomic radii for solute Zn and solvent Cu ($R_A = R_{\text{Zn}}$ = 1.39 Å and $R_B = R_{\text{Cu}}$ = 1.28 Å), Equation (1) yields $1.28x + y = 4.87$. A close-integer (x, y) solution is (3.8, 0). The corresponding integer formula is $[\text{Zn-Cu}_{12}](\text{Zn}_4)$, with Z = 17. The corresponding weight percent Cu-30.0Zn matches closely with cartridge brass C26000 (Cu-30Zn), affirming $[\text{Zn-Cu}_{12}](\text{Zn}_4)$ is the optimal chemical unit in the Cu-Zn system.

Cu-Al also belongs to the negative-enthalpy category and is treated similarly. Its general chemical formula is $[\text{Al-Cu}_{12}](\text{Al}_x\text{Cu}_y)$. Using the Goldschmidt atomic radius 1.43 Å for Al, $1.39x + y = 5.59$ is obtained from Equation (1). The solution closest to integers for (x, y) is (1.9, 3), resulting in $[\text{Al-Cu}_{12}](\text{Al}_2\text{Cu}_3)$ = Cu-7.8Al, which matches well with the most popularly used alloy C61000 (Cu-8Al) [10] in this alloy system.

The Cu-Ni system is representative for alloys with a weak positive enthalpy of mixing [12] and is formulated as $[\text{Cu-Cu}_{12}](\text{Ni}_x\text{Cu}_y)$. The Goldschmidt radius of Ni is 1.25 Å. According to Equation (2), the (x, y) relationship is $0.93x + y = 3$. The solutions basically follow $x + y = 3$,

i.e., $[\text{Cu-Cu}_{12}](\text{Ni, Cu})_3$. Since the measured 2nd-neighbor α_{200} = -0.058 in $\text{Cu}_{80}\text{Ni}_{20}$ alloy [13] is only slightly negative, the glue atoms should be accordingly slightly Ni-rich in comparison with the average alloy composition. The only suitable formula is $[\text{Cu-Cu}_{12}](\text{Ni}_2\text{Cu}_1)$ = Cu-11.7Ni, which falls close to the composition of the most widely used C70600 alloy (Cu-10Ni, containing 1.0 -1.8Fe, ≤ 1.0Zn, $9.0-11.0$Ni, ≤ 1.0Mn [10], formulated as $[(\text{Zn,Mn,Cu})\text{-Cu}_{12}](\text{Ni,Fe})_2\text{Cu}_1$, where Zn and Mn show negative enthalpies of mixing with Cu, while Fe and Ni show positive ones).

The Cu-Be (beryllium bronzes) and Cu-Sn (tin bronzes) alloys, both showing repulsive atomic interactions, are treated like Cu-Ni (the measured α-parameters are all positive [14] for Cu-Be). The Goldschmidt radii of Be and Sn are 1.13 and 1.55 Å, respectively, and the corresponding relationship between x and y are $0.69x + y = 3$ and $1.78x + y = 3$. The close-integer solutions for (x, y) are respectively (2.0, 1.6) and (1.0, 1.2) (in the latter case, any $x > 1$ produces a negative y), leading to $[\text{Cu-Cu}_{12}]$-(Be_2Cu_2) = Cu-1.9Be and $[\text{Cu-Cu}_{12}](\text{Sn}_1\text{Cu}_1)$ = Cu-11.8Sn, which notably match with the most widely used C17200 (Cu-2Be) and C90800 (Cu-12Sn) [10] in each alloy system.

EXTENSION TO FCC-BASED COMPOSITION-COMPLEX ALLOYS

In this section, all FCC alloys of complex chemistries are formulated to demonstrate the generality of chemical units. Typical examples in Al alloys, stainless steels, and Ni-based superalloys are examined in details, as the elemental classification is system-dependent and should be taken care of case-by-case.

Al-based alloys

Grade 5083 with nominal chemical composition Al-4.4Mg-0.7Mn-0.15Cr [10] is one of the most popular aluminum alloys. The corresponding atomic percent composition is $\text{Al}_{94.70}\text{Mg}_{4.88}\text{Mn}_{0.34}\text{Cr}_{0.08}$. Alloying elements Mg, Mn, and Cr all show attractive interactions with solvent Al and occupy the cluster center. They can be regarded as an average atom $\mathbf{M}$ = $\text{Mg}_{0.92}\text{Mn}_{0.06}\text{Cr}_{0.02}$. The introduction of average atoms is to simplify a multi-element system into pseudo-ternary one so that any alloy can be expressed in the cluster formulation composed of three distinct atomic sites, e.g., cluster center, cluster shell (nearest neighbors), and next-neighbor glue atoms. The classification scheme is however system-dependent, based mainly on the atomic interactions between solutes and solvent atoms. The general formula is expressed as [**M**-

$Al_{12}](M_xAl_y)$. Goldschmidt radii are R_{Mg} = 1.60 Å, R_{Mn} = 1.26 Å, R_{Cr} = 1.28 Å, and R_{Al} = 1.43 Å. Then the atomic radius of **M** is calculated as 1.57 Å. The relationship between x and y is obtained as $1.33x + y = 5.19$ according to Equation (1). The solution for (x, y) is (0, 5.2), resulting in an integer formula $[\mathbf{M}\text{-}Al_{12}](Al_5)$ = Al-4.6Mg-0.7Mn-0.2Cr, wt%.

Grade 7075 with the chemical composition Al-5.6Zn-2.5Mg-1.6Cu-0.23Cr in wt% [10], is similarly formulated as $[\mathbf{M}\text{-}Al_{12}](Al_4)$, by averaging Zn, Mg, Cu and Cr into **M** = $Mg_{0.47}Zn_{0.39}Cu_{0.12}Cr_{0.02}$ with an atomic radius of 1.47 Å.

Ni-based superalloy

TMS-196 is a well-known 5th-generation Ni-based single-crystal superalloy with chemical composition Ni-4.6Cr-5.6Co-2.4Mo-5W-5.6Al-5.6Ta-0.1Hf-6.4Re-5Ru in wt% according to the industrial standard [15]. The atomic percent composition is $Ni_{64.61}Cr_{5.61}Co_{6.03}Mo_{1.59}W_{1.72}$ $Al_{13.16}Ta_{1.96}Re_{2.18}Ru_{3.14}$ (the minor Hf for strengthening grain boundary is not considered). The alloying elements are classified into three kinds of average atoms, Ni-like **Ni** = $Ni_{0.85}Co_{0.08}Re_{0.03}Ru_{0.04}$, γ-forming Cr-like **Cr** = $Cr_{0.63}Mo_{0.18}W_{0.19}$, and γ′-forming Al-like **Al** = $Al_{0.87}Ta_{0.13}$, where γ and γ′ refer to FCC solid solution and AuCu₃-type precipitation phase, respectively. This classification is based on the enthalpies of mixing with solvent Ni. The Al-like elements **Al** showing large negative ΔH, occupy the cluster center and then the glue sites. The γ-forming **Cr** elements, with slightly negative ΔH, take the rest of the glue sites after **Al**. Finally, elements with near-zero ΔH substitute for Ni in the shell sites, i.e., the nearest neighbors are all **Ni**. The cluster formula fitted from the standard alloy composition, by setting the number of **Ni** to be equal to 12, is $[\mathbf{Al}\text{-}Ni_{12}](Al_{1.42}Cr_{1.43})$.

Goldschmidt radii are R_{Ni} = 1.25 Å, R_{Cr} = 1.28 Å, R_{Ta} = 1.47 Å , R_{Co} = 1.25 Å, R_{Re} = 1.38 Å, R_{Ru} = 1.34 Å, R_{Mo} = 1.40 Å, and R_W =1.41 Å. R_{Al} = 1.27 Å is estimated from the Al-Ni nearest-neighbor distance in γ′-AlNi₃, i.e., $a_{AlNi_3}/\sqrt{2}$ 2.52 Å (a_{AlNi_3} = 3.5720 Å [16]), assuming R_{Ni} = 1.25 Å is invariable. This radius is quite close to the covalent radius of Al, apparently due to the relatively strong atomic interaction between Al and Ni. The average atomic radii are 1.26 Å for **Ni** = $Ni_{0.85}Co_{0.08}Re_{0.03}Ru_{0.04}$, 1.30 Å for **Al** = $Al_{0.87}Ta_{0.13}$, and 1.33 Å for **Cr** = $Cr_{0.63}Mo_{0.18}W_{0.19}$. Since the lattice mismatch between γ and γ′ phases varies in different alloy systems only by about 10^{-3} in magnitude [17], the atomic radius of Al in the two phases should be reasonably treated as identical.

The general formula is $[\mathbf{Al}\text{-}Ni_{12}](Al_xCr_y)$, where the cluster is **Al**-centered and nearest-neighbored by 12 **Ni**.

The cluster radius (i.e., the nearest-neighbor distance) r_1 = $1.25\lambda_{Fr}$ is then the sum of atomic radii of **Al** and **Ni**, 1.30 + 1.26 = 2.56 Å. Then λ_{Fr} = 2.56/1.25 = 2.05 Å. The atomic volume of the chemical unit is $(4/3)(\pi/0.74)$ $(12R_{Ni}^3 + (1 + x)R_{Al}^3 + yR_{Cr}^3)$, which is equal to the spherical volume enclosed by $1.74\lambda_{Fr}$, $(4\pi/3)(1.74\lambda_{Fr})^3$ = $(4\pi/3)(1.74 \times 2.05)^3$. From this relationship, we obtain $0.93x + y = 3.14$. The close-integer solution is $x + y = 3$. By referring to the fitted formula $[\mathbf{Al}\text{-}Ni_{12}](Al_{1.42}Cr_{1.43})$, the ideal solution is $[\mathbf{Al}\text{-}Ni_{12}](Al_{1.5}Cr_{1.5})$ = Ni-4.8Cr-5.6Co-2.6Mo-5.2W-5.8Al-5.8Ta-6.6Re-4.8Ru, wt%.

TMS-82 represents the 2nd-generation single-crystal superalloys with chemical compositionNi-4.9Cr-7.8Co-1.9Mo-8.7W-5.3Al-6.0Ta-0.1Hf-0.5Ti-2.4Re in wt% [18]. It is also formulated as $[\mathbf{Al}\text{-}Ni_{12}](Al_{1.5}Cr_{1.5})$ in a similar way, with average atoms **Ni** = $Ni_{0.88}Co_{0.11}Re_{0.01}$, **Cr** = $Cr_{0.59}Mo_{0.12}W_{0.29}$, and **Al** = $Al_{0.82}Ti_{0.04}Ta_{0.14}$. Corresponding atomic radii are 1.25, 1,32 and 1.31 Å respectively with the Goldschmidt radius of Ti, R_{Ti} = 1.46 Å.

Stainless steels

Maraging stainless steels are characterized by a Martensite matrix plus γ′ precipitation and are produced by aging of quenched martensite from parent FCC austenite state. Then this kind of alloys can be formulated using their austenite state. The content of carbon is usually below 0.03 wt% and can be neglected in the chemical formula. The main alloying elements are Cr (at least 10 wt% to guarantee good corrosion resistance) and Ni (at least 6 wt% of Ni, to stabilize austenite and for easy formation of Martensite upon quenching). Co-free Custom 465 is analyzed here as it is among the most popularly used alloys.

Its chemical composition is Fe-11.10Ni-11.75Cr-0.98Mo-1.50Ti in wt%, or $Fe_{74.54}Ni_{10.54}Cr_{12.60}Mo_{0.57}Ti_{1.75}$ in at%. Because of the attractive interaction with solvent Fe, Ni and Ti belong to the γ′-formers [19] and occupy preferentially the cluster center and then the glue sites; Cr and Mo belong to the same group in the periodic table and take the glue-atom position. By fixing the number of solvent Fe atoms at 12, the chemical formula composition is thus proposed: $[\mathbf{Ni}\text{-}Fe_{12}]Ni_{0.98}Cr_{2.12}$, where **Cr** stands nor $Cr_{0.96}Mo_{0.04}$ and **Ni** for $Ni_{0.86}Ti_{0.14}$.

Goldschmidt radii are R_{Fe} = 1.27 Å, R_{Cr} = 1.28 Å, R_{Ni} = 1.25 Å, R_{Mo} = 1.40 Å, and R_{Ti} = 1.46 Å. The average atomic radii are 1.28 Å for Ni-like atoms **Ni** = $Ni_{0.86}Ti_{0.14}$ and 1.28 Å for **Cr** = $Cr_{0.96}Mo_{0.04}$. The general chemical formula is $[\mathbf{Ni}\text{-}Fe_{12}](Ni_xCr_y)$. The cluster radius (i.e., the nearest-neighbor distance) r_1 = $1.25\lambda_{Fr}$ is the sum of atomic radii of **Ni** and Fe, 1.28 + 1.27 = 2.55 Å. Then λ_{Fr} =

Table 1 Chemical units of Cu-based binary alloys, Al-based multicomponent alloys, Ni-based superalloys, and stainless steels

Alloy composition (wt%)	General formula	Average atom	Radii of average atoms (Å)	Relationship of x and y	Calculated chemical units	Calculated compositions (wt%)	Alloy specifications
Cu-30Zn	$[\text{Zn-Cu}_{12}](\text{Zn}_x\text{Cu}_y)$	—	—	$1.28x + y = 4.87$	$[\text{Zn-Cu}_{12}](\text{Zn}_4)$	Cu-30.0Zn	C26000
Cu-8Al	$[\text{Al-Cu}_{12}](\text{Al}_x\text{Cu}_y)$	—	—	$1.39x + y = 5.59$	$[\text{Al-Cu}_{12}](\text{Al}_2\text{Cu}_3)$	Cu-7.8Al	C61000
Cu-10Ni	$[\text{Cu-Cu}_{12}](\text{Ni}_x\text{Cu}_y)$	—	—	$0.93x + y = 3$	$[\text{Cu-Cu}_{12}](\text{Ni}_2\text{Cu}_1)$	Cu-11.7Ni	C70600
Cu-12Sn	$[\text{Cu-Cu}_{12}](\text{Sn}_x\text{Cu}_y)$	—	—	$1.78x + y = 3$	$[\text{Cu-Cu}_{12}](\text{Sn}_1\text{Cu}_1)$	Cu-11.85Sn	C90800
Cu-2Be	$[\text{Cu-Cu}_{12}](\text{Be}_x\text{Cu}_y)$	—	—	$0.69x + y = 3$	$[\text{Cu-Cu}_{12}](\text{Be}_2\text{Cu}_2)$	Cu-1.9Be	C17200
Al-4.4Mg-0.7Mn-0.15Cr	$[\text{M-Al}_{12}](\text{M}_x\text{Al}_y)$	$\text{M}= \text{Mg}_{0.92}\text{Mn}_{0.06}\text{Cr}_{0.02}$	$R_\text{M} = 1.57$	$1.33x + y = 5.19$	$[\text{M-Al}_{12}](\text{Al}_5)$	Al-4.6Mg-0.7Mn-0.2Cr	5083
Al-5.6Zn-2.5Mg-1.6Cu-0.23Cr	$[\text{M-Al}_{12}](\text{M}_x\text{Al}_y)$	$\text{M}= \text{Mg}_{0.47}\text{Zn}_{0.39}\text{Cu}_{0.12}\text{Cr}_{0.02}$	$R_\text{M} = 1.47$	$1.10x + y = 3.66$	$[\text{M-Al}_{12}](\text{Al}_4)$	Al-5.3Zn-2.4Mg-1.6Cu-0.22Cr	7075
Ni-4.6Cr-5.6Co-2.4Mo-5W-5.6Al-5.6Ta-0.1Hf-6.4Re-5Ru	$[\text{Al-Ni}_{12}](\text{Al}_x\text{Cr}_y)$	$\text{Al}= \text{Al}_{0.87}\text{Ta}_{0.13}$ $\text{Ni}= \text{Ni}_{0.85}\text{Co}_{0.08}\text{Re}_{0.03}\text{Ru}_{0.04}$ $\text{Cr}= \text{Cr}_{0.63}\text{Mo}_{0.18}\text{W}_{0.19}$	$R_\text{Al} = 1.30$ $R_\text{Ni} = 1.26$ $R_\text{Cr} = 1.33$	$0.93x + y = 3.14$	$[\text{Al-Ni}_{12}](\text{Al}_{1.5}\text{Cr}_{1.5})$	Ni-4.8Cr-5.6Co-2.6Mo-5.2W-5.8Al-5.8Ta-6.6Re-4.8Ru	5th superalloy TMS-196
Ni-4.9Cr-7.8Co-1.9Mo-8.7W-5.3Al-6.0Ta-0.1Hf-0.5Ti-2.4Re	$[\text{Al-Ni}_{12}](\text{Al}_x\text{Cr}_y)$	$\text{Al}= \text{Al}_{0.82}\text{Ti}_{0.04}\text{Ta}_{0.14}$ $\text{Ni}= \text{Ni}_{0.88}\text{Co}_{0.11}\text{Re}_{0.01}$ $\text{Cr}= \text{Cr}_{0.59}\text{Mo}_{0.12}\text{W}_{0.29}$	$R_\text{Al} = 1.31$ $R_\text{Ni} = 1.25$ $R_\text{Cr} = 1.32$	$0.98x + y = 3.35$	$[\text{Al-Ni}_{12}](\text{Al}_{1.5}\text{Cr}_{1.5})$	Ni-4.6Cr-7.8Co-1.8Mo-8.2W-5.6Al-6.4Ta-0.5Ti-2.4Re	2nd superalloy TMS-82
Fe-11.10Ni-11.75Cr-0.98Mo-1.50Ti	$[\text{Ni-Fe}_{12}](\text{Ni}_x\text{Cr}_y)$	$\text{Ni}= \text{Ni}_{0.86}\text{Ti}_{0.14}$ $\text{Cr}= \text{Cr}_{0.96}\text{Mo}_{0.04}$	$R_\text{Ni} = 1.28$ $R_\text{Cr} = 1.28$	$0.99x + y = 3.02$	$[\text{Ni-Fe}_{12}](\text{Ni}_1\text{Cr}_2)$	Fe-11.32Ni-11.19Cr-0.86Mo-1.50Ti	Maraging stainless steel Custom-465
Fe-19.4Ni-24.6Cr-1.7Mn-0.2V-0.6Si	$[\text{Cr-Fe}_{12}](\text{Cr}_x\text{Fe}_y)$	$\text{Fe}= \text{Fe}_{0.71}\text{Ni}_{0.25}\text{Mn}_{0.02}\text{Si}_{0.02}$ $\text{Cr}= \text{Cr}_{0.99}\text{V}_{0.01}$	$R_\text{Fe} = 1.27$ $R_\text{Cr} = 1.28$	$1.03x + y = 3.24$	$[\text{Cr-Fe}_{12}](\text{Cr}_3)$	Fe-19.7Ni-23.4Cr-1.8Mn-0.2V-0.6Si	Austenitic stainless steel 310s

2.55/1.25 = 2.04 Å. The atomic volume of the chemical unit is $(4/3)(\pi/0.74)(12R_{Fe}^3 + (1+x)R_{Ni}^3 + yR_{Cr}^3)$, which is equal to the spherical volume enclosed by $r = 1.74\lambda_{Fr}$, $(4\pi/3)(1.74\lambda_{Fr})^3 = (4\pi/3)(1.74 \times 2.04)^3$. From this relationship, we obtain $0.99x + y = 3.02$. The corresponding integer formula is $[\mathbf{Ni}\text{-}\mathbf{Fe}_{12}](\mathbf{Ni}_1\mathbf{Cr}_2)$ = Fe-11.32Ni-11.19Cr-0.86Mo-1.50Ti, wt%.

310s is a typical austenitic stainless steel enriched with Cr and Ni, Fe-19.4Ni-24.6Cr-1.7Mn-0.2V-0.6Si [20]. It is formulated as $[\mathbf{Cr}\text{-}\mathbf{Fe}_{12}](\mathbf{Cr}_3)$, by averaging Fe, Ni, Mn and Si into $\mathbf{Fe} = Fe_{0.71}Ni_{0.25}Mn_{0.02}Si_{0.02}$, and Cr and V into $\mathbf{Cr} = Cr_{0.99}V_{0.01}$. Corresponding atomic radii are 1.27 Å for $\mathbf{Fe}$ and 1.28 Å for $\mathbf{Cr}$ with Goldschmidt radii $R_{Mn} = 1.26$ Å, $R_V = 1.35$ Å, and $R_{Si} = 1.32$ Å.

Despite the above success to identify the molecule-like chemical units in typical industrially important alloys, as summarized in Table 1, a few critical issues remain unsolved and should be carefully addressed in order to optimize the use of the present composition interpretation and design approach. First, the formula calculation relies on the assumption that atoms are spherical and have invariant radii (Goldschmidt radii are generally used). In fact, atomic radii usually vary and may change in alloys with different crystalline structures. Additionally, most industrial alloys contain multiple alloying elements and their amounts in the basic chemical units are not always integers. This means that the composition unit should be larger. For example, the formula for superalloy TMS-196 $[\mathbf{Al}\text{-}\mathbf{Ni}_{12}](\mathbf{Al}_{1.5}\mathbf{Cr}_{1.5})$ can be understood as an equal proportion mixing of two units, $[\mathbf{Al}\text{-}\mathbf{Ni}_{12}](\mathbf{Cr}_3)$ + $[\mathbf{Al}\text{-}\mathbf{Ni}_{12}](\mathbf{Al}_3)$, which correspond respectively to γ solid-solution matrix and γ′ precipitate. Furthermore, the relationship between the chemical unit formulism and the alloy properties is not known yet. It is important to unveil the structural stabilities to predict the microstructural evolution upon thermomechanical treatments, which in turn affect the properties of the alloys. It is extremely complex and beyond the scope of this paper. *Ab initio* calculation based on the presented SRO model should be the next step.

CONCLUSIONS AND PROSPECTS
In this paper, we present a cluster-plus-glue-atom model for solid solutions. The model is based on Friedel oscillation imposed with a condition that electronic charge is neutralized within a limited local zone, which covers a nearest-neighbor cluster plus a few glue atoms in the next outer shell, formulated as [cluster](glue atoms). Within this local zone, the structural unit, just like a chemical molecule, has its unique structure and chemistry, thus we

name it chemical unit. We subsequently identify the chemical units in FCC, HCP, and BCC lattices and deduce equations to calculate the chemical formulas, in particular, for FCC solid solutions. Chemical formulas of Cu-based binary alloys, including of Cu-Zn, Cu-Al, Cu-Ni, Cu-Be, and Cu-Sn, were derived and found to match remarkably well with popularly used alloys. For instance, the ideal chemical unit $[\mathbf{Zn}\text{-}\mathbf{Cu}_{12}]\mathbf{Zn}_4$ matches with cartridge α-brass Cu-30Zn, which is the most widely used among all Cu-Zn alloys. We further extend the model to chemically complex alloys, such as Al-based commercial alloys 5083 and 7075, Ni-based superalloys TMS-196 and TMS-82, and maraging stainless steel Custom-465 and austenitic stainless steel 310s. The success in formulating popular industrial alloys of FCC types demonstrates the generality of the current model. The present work provides convincing evidence for the existence of molecule-like chemical units in solid-solution alloys. These units are anticipated to be useful to guide alloy development, as already verified in high-entropy alloys [21] and Cu-based [22] high-temperature alloys featuring cuboidal precipitation.

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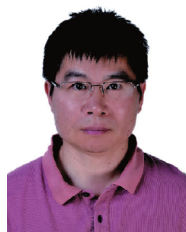
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金属合金中的类分子化学结构单元

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摘要 本文引入Friedel振荡理论, 揭示固溶体合金中存在类似分子式的结构单元, 指出在特定的成分下, 合金中的原子在近程序上倾向于聚集为理想的有序结构, 这个结构包括最近邻壳层原子(记作团簇)和次近邻壳层原子(记作连接原子), 用团簇式: [团簇](连接原子)来表示. 这种近程序结构被称为化学结构单元, 类似于固溶体中的"分子". 本文给出了FCC结构固溶体合金中化学结构单元的计算公式, 通过计算得到Cu基二元体系的理想化学结构单元, 包括Cu-Zn、Cu-Al、Cu-Ni、Cu-Be和Cu-Sn, 均为工业中最常用的合金成分. 此外, 工业上常用的多元合金, 如Al合金5083和7075、高温合金TMS-196和TMS-82、马氏体时效不锈钢Cutom-465和奥氏体不锈钢310s, 其成分均满足模型的预测, 表明本模型可以为FCC结构复杂固溶体合金的成分设计提供理论指导.