



Mixing enthalpy of liquid phase calculated by miedema's scheme and approximated with sub-regular solution model for assessing forming ability of amorphous and glassy alloys

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ABSTRACT

The forming ability of amorphous and glassy alloys has been assessed with mixing enthalpy (ΔH^{mix}) of a liquid phase based on Miedema's scheme. The ΔH^{mix} 's were calculated as a function of composition in an alloy for possible 2628 binary systems from 73 elements, and were approximated with interaction parameter Q in a sub-regular solution model with coefficients Q_i ($i = 0$ to 3) for a cubic function of composition. The results revealed that 2627 systems were fitted by Q 's within errors denoted by statistical adjusted R-square (R^2) ≥ 0.999 , which includes $R^2 = 1$ for 2409 systems. The values of Q_i for 1378 systems from 53 elements were selected and tabulated for assessing the forming ability of amorphous and glassy alloys. The analysis revealed that P and C in Fe–P and Fe–C binary alloys and simultaneous additions of Ni and Cu in La-, Zr- and Pd-based bulk metallic glasses exhibit a marked and peculiar composition dependence of ΔH^{mix} . In a framework of Miedema's scheme, the most accurate values of ΔH^{mix} for a liquid phase have been provided as a function of composition in an alloy system, which makes it possible to consider the forming ability of amorphous and glassy alloys deeply.

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1. Introduction

Recently, amorphous and glassy alloys in nonequilibrium solid states have received considerable scientific and engineering attention. This is due to the superior mechanical, magnetic and corrosion-resistant properties of amorphous and glassy alloys than those of crystalline alloys [1]. It is widely-accepted that these superior properties of the amorphous and glassy alloys originate from their liquid-like atomic arrangements without long-range periodicity intrinsic to crystalline alloys. Needless to say, thermodynamics defines amorphous and glassy alloys together with in a solid state, which differs from a liquid state. In contrast, crystallographic aspects classify the amorphous and glassy alloys into noncrystalline alloys, together with alloys in liquid and supercooled liquid states. This crystallographic similarity in atomic arrangements among these noncrystalline alloys led to the historic discovery of an amorphous alloy.

The first evidence showing that noncrystalline solids are formable in alloys came in 1960. In that year, Klement et al. [2] succeeded in obtaining fragments of an amorphous alloy in Au–Si

system from a melt. Their experiment is a historically-significant event in point that they firstly demonstrated the way of preventing a liquid from crystallizing in a solidification process for a metallic system. The key technology used in the demonstration was splat quenching, which makes a molten alloy with random atomic arrangements at a certain time freeze into a solid alloy through a supercooled liquid state. Nowadays, an incoming melt-spinning technique has widely been used for fabricating continuous non-crystalline alloy specimens in a ribbon shape with thickness of the order of a few to several tens of micrometers. Furthermore, recent advances in fabrication technique for metallic glass makes it possible to produce bulk metallic glasses (BMGs) with dimensions up to a couple of tens of millimeters by using conventional casting process [1] within a framework of solidification processes from a liquid. Here, a reason for forming noncrystalline alloys and BMGs instead of crystalline alloys in an equilibrium state is due to some of the properties intrinsic to an alloy. These inherent properties are represented by a concept or an index, such as forming ability of noncrystalline alloys, and glass-forming ability (GFA) for a special case for glassy materials. Thus, the noncrystalline alloys including BMGs are closely related to a liquid state accompanied by a keyword of “forming ability”. Hence, we anticipate that quantities intrinsic of a liquid phase can be used for describing the forming ability of the noncrystalline alloys.

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Mixing enthalpy (ΔH^{mix}) of a liquid phase can be a candidate as an index for evaluating GFA. In reality, ΔH^{mix} is a criterion for GFA evaluations [1] as well as the atomic size ratios among the constituent elements [1]. Specifically, ΔH^{mix} based on Miedema's scheme [3,4] is sometimes utilized for estimating GFA due to its great advantages. For instance, a wide applicability of Miedema's scheme makes it possible to calculate the values of ΔH^{mix} for 2628 binary systems from 73 elements, which almost cover the constituent elements for noncrystalline alloys and BMGs. On the other hand, Miedema's model possesses the following disadvantageous aspects. First, one cannot calculate ΔH^{mix} by Miedema's scheme algebraically only using composition of an alloy, which differs from a regular solution model [5] and sub-regular solution models [6,7] with interaction parameter (Ω). Second, only the limited numbers of values of ΔH^{mix} for solutions are provided in the original literature [3,4] and in our previous studies [8,9], such as the ΔH^{mix} at the equi-atomic concentration $A_{0.5}B_{0.5}$ in an A–B binary alloy [3,8,9] and ΔH^{mix} at a dilute limits of solute and solvent elements as well [3,4]. However, every real system more or less should have unsymmetrical ΔH^{mix} value as a function of composition with respect to the $A_{0.5}B_{0.5}$. Hence, one should consider a composition dependence of ΔH^{mix} for analyzing the GFA more precisely by overcoming these disadvantages intrinsic to Miedema's scheme. In analyzing GFA, it is worth describing ΔH^{mix} in formulae of sub-regular solution models [6,7] by fitting ΔH^{mix} with Ω .

The purposes of the present study are to calculate all the possible ΔH^{mix} 's in accordance with Miedema's scheme as a function of composition in an alloy system, and then to fit the ΔH^{mix} 's with a sub-regular solution model with Ω 's to evaluate the applicability of the sub-regular solution model for ΔH^{mix} 's. Furthermore, the authors aim to assess the forming ability of amorphous and glassy alloys including BMGs using Ω 's obtained by fitting the ΔH^{mix} 's.

2. Methods

First, the values of ΔH^{mix} for possible 2628 binary systems from 73 elements were calculated as a function of composition on the basis of Miedema's scheme. We acquired three necessary quantities (V , ϕ and n_{ws}) for each element from the original literature [3,4] where V , ϕ and n_{ws} are molar volume, work function and the density at the boundary of the Wigner-Seitz cell, respectively. The ΔH^{mix} 's were calculated through the procedures described below.

The calculations started with Eq. (1) given in original literature [3,4] where $\Delta H^{\text{chem}}(\text{ss})$ is a chemical enthalpy for an A–B solution with fractions of c_A and c_B ($0 \leq c_A, c_B \leq 1$),

$$\Delta H^{\text{chem}}(\text{ss}) = c_A c_B \left(c_B^S \Delta H^{\text{inter}}(\text{A in B}) + c_A^S \Delta H^{\text{inter}}(\text{B in A}) \right). \quad (1)$$

The ΔH^{mix} described in the present study is identical to $\Delta H^{\text{chem}}(\text{ss})$ in Eq. (1). Here, $\Delta H^{\text{inter}}(\text{A in B})$ in Eq. (1) indicates the enthalpy upon alloying, and 'inter' stands for 'interfacial', and c_A^S is a surface fraction, or surface concentration of A atom in a system. The $\Delta H^{\text{inter}}(\text{A in B})$ can be obtained by the following form in Eq. (2),

$$\Delta H^{\text{inter}}(\text{A in B}) = \frac{V_A^{2/3}}{\frac{1}{2} \left(\frac{1}{n_{\text{ws A}}^{1/3}} + \frac{1}{n_{\text{ws B}}^{1/3}} \right)} \left\{ -P(\phi_A - \phi_B)^2 + Q \left(n_{\text{ws A}}^{1/3} - n_{\text{ws B}}^{1/3} \right)^2 - R \right\}, \quad (2)$$

where P , Q and R are constants. Specifically, Q has a value of 9.4, whereas P has a value of either 14.2, 12.35 or 10.2, depending on the valence of elements [3]. The term R should be taken into account

only for the binary systems comprising a transition metal (TM) and a non transition metal (NTM). More precisely, every R/P value for an atomic pair consisting of TM–NTM was calculated as a production of the parameters assigned to each TM and NTM elements [3]. The R/P value for liquid alloys, R^*/P , was calculated by multiplying a factor of 0.73 to the productions for solid alloys (R/P). Hence, $R^*/P = 0.73 R/P$ where asterisk indicate the liquid [3].

In Miedema's scheme, c_A^S term in Eq. (1) is describable as Eq. (3),

$$c_A^S = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}. \quad (3)$$

In reality, the actual calculation of c_A^S is rather complicated than the formula given in Eq. (3), because V also changes upon alloying. The difference in V upon alloying was estimated in the present study by referring to Eqs. (4) and (5) [3],

$$\left(V_A^{2/3} \right)_{\text{alloy}} = \left[1 + a f_B^A (\phi_A - \phi_B) \right] \left(V_A^{2/3} \right)_{\text{pure A}}, \quad (4)$$

$$f_B^A = c_B^S (= 1 - c_A^S), \quad (\text{for the random alloy}). \quad (5)$$

In Eq. (4), a is determined to be 0.14 for the alkaline metals, 0.10 for divalent metals, 0.07 for noble and trivalent metals and 0.04 for other metals [3]. Here, it should be noted that Eqs. (3) to (5) have a recurrence relationship in terms of c_A^S because c_A^S appears both in Eqs. (3) and (5). In the present study we avoided the recurrence problem on c_A^S in the following procedure. First, c_A^S was calculated with Eq. (3) for a given alloy with c_A and c_B , using $V_A^{2/3}$ and $V_B^{2/3}$ of pure A and B elements $\{(V_A^{2/3})_{\text{pure}}$ and $(V_B^{2/3})_{\text{pure}}\}$, respectively. Second, f_B^A value was determined from c_B^S by assuming a random alloy shown in Eq. (5). Then, f_B^A and $(V_A^{2/3})_{\text{pure A}}$ values obtained by Eqs. (3) and (5) were substituted into Eq. (4) to calculate $(V_A^{2/3})_{\text{alloy}}$. Next, the value of c_A^S calculated in a formula of Eq. (6) instead of Eq. (3) by interpreting c_A^S in Eq. (3) for pure metal as c_A^S in Eq. (6) for an alloy,

$$c_A^S = \frac{c_A \left(V_A^{2/3} \right)_{\text{alloy}}}{c_A \left(V_A^{2/3} \right)_{\text{alloy}} + c_B \left(V_B^{2/3} \right)_{\text{alloy}}}. \quad (6)$$

Finally, the c_A^S value obtained by Eq. (6) was substituted into Eq. (1) to calculate $\Delta H^{\text{chem}}(\text{ss})$. The modifications of $V_A^{2/3}$ and $V_B^{2/3}$ terms based on Eq. (4) were originally performed in the present study to have the most accurate and reliable values of ΔH^{mix} for a random solid solution. Using Eqs. (1) to (6) together with the parameters given in literature [3], we calculated ΔH^{mix} as a function of composition in any system.

Then, we approximated the ΔH^{mix} with a formula of a sub-regular solution model with interaction parameter (Ω). The selection of a sub-regular solution model is due to the awkward procedures for evaluating c_A^S term in Eq. (6) in Miedema's scheme, and to treat ΔH^{mix} more comprehensively as a function of composition of alloy using fractions of elements as only parameters. We used commercial software (Origin, version 8.1) to fit ΔH^{mix} by Ω in a formula shown in Eq. (7),

$$\Delta H_{c_A, c_B}^{\text{mix}} = 4 \left(\sum_{k=0}^3 \Omega_k (c_A - c_B)^k \right) c_A c_B. \quad (7)$$

The coefficient "four" on the right-side of Eq. (7) was intentionally introduced to account for the values of Ω at the equi-atomic concentrations, $A_{0.5}B_{0.5}$, in an A–B alloy in our previous studies [8,9]. It should be noted that the value of Ω at $A_{0.5}B_{0.5}$ for $k = 0$ in Eq. (7) is equivalent to the previous result [7,8], indicating that the

methods to obtain ΔH^{mix} in our previous studies can be regarded as the zero-order approximation in a framework of sub-regular solution model.

The degree of composition dependence of ΔH^{mix} was evaluated by introducing a homebuilt parameter, $\mathcal{Q}_{\text{asym.}}$, defined by Eq. (8),

$$\mathcal{Q}_{\text{asym.}} = \frac{|\mathcal{Q}_1| + |\mathcal{Q}_3|}{|\mathcal{Q}_0|}. \quad (8)$$

Equation. (8) contains coefficients \mathcal{Q}_i from odd orders ($i = 1$ and 3) to the principal coefficient (\mathcal{Q}_0), providing the degree of asymmetry of ΔH^{mix} in terms of $A_{0.5}B_{0.5}$ composition. In addition, we also use statistical adjusted R-square (R^2) as well as $\mathcal{Q}_{\text{asym.}}$.

After obtaining all the \mathcal{Q}_i ($i = 0$ to 3) for all the 2628 binary systems from possible 73 elements by Miedema's scheme, we selected the 53 elements in the present study. In selecting 53 elements, we refer to BMGs [10–26] and the 351 ternary amorphous alloys [27], in which the latter partially contains glassy alloys. The constituent elements involved in BMGs were acquired from the authors' recent work [10] and its original references [11–26]. They are, $\text{Pd}_{0.4}\text{Cu}_{0.3}\text{Ni}_{0.1}\text{P}_{0.2}$ [11], $\text{Zr}_{0.412}\text{Ti}_{0.138}\text{Cu}_{0.125}\text{Ni}_{0.1}\text{Be}_{0.225}$ [12], $\text{Pd}_{0.35}\text{Pt}_{0.15}\text{Cu}_{0.3}\text{P}_{0.2}$ [13], $\text{Zr}_{0.55}\text{Al}_{0.10}\text{Ni}_{0.05}\text{Cu}_{0.30}$ [14], $\text{Mg}_{0.595}\text{Cu}_{0.229}\text{Ag}_{0.066}\text{Gd}_{0.11}$ [15], $\text{Mg}_{0.54}\text{Cu}_{0.265}\text{Ag}_{0.085}\text{Gd}_{0.11}$ [16], $\text{Zr}_{0.48}\text{Cu}_{0.36}\text{Ag}_{0.08}\text{Al}_{0.08}$ [17], $\text{Pd}_{0.4}\text{Ni}_{0.4}\text{P}_{0.2}$ [18], $\text{Y}_{0.36}\text{Sc}_{0.20}\text{Al}_{0.24}\text{Co}_{0.20}$ [19], $(\text{La}_{0.7}\text{Ce}_{0.3})_{0.65}\text{Co}_{0.25}\text{Al}_{0.10}$ [20], $\text{La}_{0.62}\{(\text{Cu}_{5/6}\text{Ag}_{1/6})_{0.14}\text{Ni}_{0.05}\text{Co}_{0.05}\}$ $\text{Al}_{0.14}$ [21], $\text{Zr}_{0.57}\text{Ti}_{0.05}\text{Cu}_{0.2}\text{Ni}_{0.08}\text{Al}_{0.1}$ [22], $\text{Pt}_{0.425}\text{Cu}_{0.27}\text{Ni}_{0.095}\text{P}_{0.21}$ [23], $(\text{Fe}_{0.8}\text{Co}_{0.2})_{0.48}\text{Cr}_{0.15}\text{Mo}_{0.14}\text{Ti}_{0.02}\text{Co}_{0.15}\text{B}_{0.06}$ [24], $\text{Pt}_{0.60}\text{Cu}_{0.16}\text{Ni}_{0.02}\text{P}_{0.22}$ [23], $\text{Mg}_{0.54}\text{Cu}_{0.28}\text{Ag}_{0.07}\text{Y}_{0.11}$ [16], $\text{Ca}_{0.65}\text{Mg}_{0.15}\text{Zn}_{0.2}$ [25], $\text{Zr}_{0.585}\text{Nb}_{0.028}\text{Cu}_{0.156}\text{Ni}_{0.128}\text{Al}_{0.103}$ [26]. On the other hand, the ternary amorphous alloys were referred to literature [27].

In calculating ΔH^{mix} for a multi-component alloy with n constituent elements, we summed up $\Delta H^{\text{mix}}_{\text{C}_i\text{C}_j}$ for each sub-binary system shown in Eq. (9) for the number of atomic pairs n_{C_2} ,

$$\Delta H^{\text{mix}}_{\text{alloy}} = \sum_{i \neq j}^{n_{\text{C}_2}} \Delta H^{\text{mix}}_{\text{C}_i\text{C}_j}. \quad (9)$$

A term on the right-side of Eq. (9) can be described as,

$$\Delta H^{\text{mix}}_{\text{C}_i\text{C}_j} = 4 \left(\sum_{k=0}^3 \mathcal{Q}_k (c_{i,\text{nor.}} - c_{j,\text{nor.}})^k \right) c_i c_j \quad (10)$$

by extending the sub-regular solution model [6] to higher order in terms of composition. We refer to literature [6,7] to extend the calculation procedures to multi-component alloys. In extending, the fraction of the constituents are normalized as $c_{i,\text{nor.}}$ and $c_{j,\text{nor.}}$ on the right-side in Eq. (10) in a sub-binary system, which are described in Eq. (11),

$$c_{i,\text{nor.}} = \left(\frac{c_i}{c_i + c_j} \right), c_{j,\text{nor.}} = \left(\frac{c_j}{c_i + c_j} \right). \quad (11)$$

The ΔH^{mix} at $A_{0.5}B_{0.5}$ calculated by the present study may differ from that by our previous studies [8,9] in point that we reconsidered the R term in Eq. (2) for systems with noble metal (NM: Cu, Ag and Au). In other words, in calculating R term, Cu, Ag and Au were considered as NTM in our previous studies [8,9], but were regarded as TM in the present study. The reason for the former consideration of NTM in our previous study is due to the assigned values of Cu, Ag and Au for calculating R/P , which are 0.3, 0.15 and 0.3 [3], respectively. These values for calculating R/P are considerably smaller than a value of unity for TMs, and smaller than 0.7 for Sc, Y and La and 0.4 for Ca, Sr and Ba [3], whereas the other NTMs than Cu, Ag and Au has a value ranging 0 to 2.3 [3]. Besides, we also

reconsidered additional enthalpy for metalloid (MLD: B, C, N, Si and Ge) elements. These MLD requires $\Delta H^{\text{trans.}}$ as the enthalpy for MLD element to transform to metallic element. According to the original literature [3], the values of $\Delta H^{\text{trans.}}/\text{kJ mol}^{-1}$ are 30 for B, 180 for C, 310 for N, 17 for P, 34 for Si and 25 for Ge where B, C, N and P are treated as elements to provide uncertainty in a value of ΔH^{mix} . In our previous studies [8,9], these uncertainty aspects were excluded by extracting the $\Delta H^{\text{trans.}}$ for all the MLD elements having $\Delta H^{\text{trans.}}$ by utilizing the linear composition dependence of $\Delta H^{\text{trans.}}$ for metal-MLD system. In strong contrast to these examples in our previous studies, in the present study we regarded the MLD element as a hypothetical metallic element throughout the study. Thus, the present results of ΔH^{mix} have been obtained as the most accurate and reliable calculations in terms of R and $\Delta H^{\text{trans.}}$ mentioned in this paragraph.

3. Results and discussion

In this Section we will show the principal results obtained in the present study and discuss the following items: (1) reproducibility of ΔH^{mix} with \mathcal{Q} , (2) analysis of BMGs for GFA, and (3) Effects of R term for noble metal (NM)-NTM systems in Miedema's scheme on ΔH^{mix} .

3.1. Reproducibility of ΔH^{mix} with \mathcal{Q}

First, we assessed the reproducibility of ΔH^{mix} with \mathcal{Q} for 2628 binary systems using statistical adjusted R-square (R^2). The results revealed that ΔH^{mix} 's of the 2409 systems (91.96%) exhibit $R^2 = 1$, whereas 2627 systems (99.96%) show $R^2 \geq 0.999$. Among all, only H–Cs system exhibits $R^2 = 0.99872 < 0.999$. These results denoted by R^2 values suggests that a cubic function of composition with coefficients \mathcal{Q}_i ($i = 0$ to 3) shown in Eq. (7) is adequate for approximating ΔH^{mix} calculated by Miedema's scheme.

Next, an especial analysis was performed for H–Cs system, which gave the worst reproducibility of ΔH^{mix} with \mathcal{Q} . Fig. 1 shows the ΔH^{mix} 's for H–Cs system plotted as a function of composition of Cs. The solid curve shows the calculated ΔH^{mix} by Miedema's scheme, whereas the broken curve denotes the ΔH^{mix} approximated by sub-regular solution model with \mathcal{Q}_k 's ($k = 0$ to 3) in Eq. (7). The dash-dotted curve exhibits the zero-order approximation with \mathcal{Q}_0 , which is a case of $k = 0$ in Eq. (7) and is coincident with the treatments in our previous references [7,8] for ΔH^{mix} at equi-atomic composition. The ΔH^{mix} 's for H–Cs system denoted by solid and

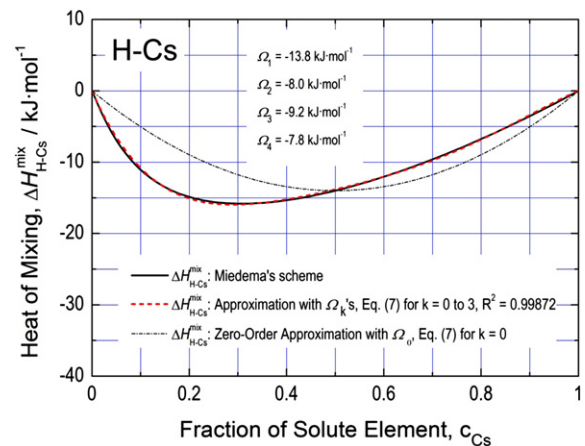


Fig. 1. Calculated ΔH^{mix} of H–Cs system by Miedema's scheme and its approximation with \mathcal{Q}_i ($i = 0$ to 3).

broken curves exhibit the minimum ΔH^{mix} around $c_{\text{Cs}} \sim 0.3$, indicating a rather strong composition dependence of ΔH^{mix} . However, despite the strong composition dependence of ΔH^{mix} , Fig. 1 shows that the curves of ΔH^{mix} for H–Cs system calculated by Miedema’s scheme denoted by solid curve and its approximation with \mathcal{Q}_i ($i = 1$ to 3) by broken curve agree consistently over all composition range, but the zero-order approximation with \mathcal{Q}_0 for a case of $k = 0$ in Eq. (7) drawn by a dash-dotted curve in a form of a parabola function for ΔH^{mix} considerably deviate at small fraction ranges of c_{Cs} . Thus, it is possible that the ΔH^{mix} was appropriately fitted by \mathcal{Q}_k ’s ($k = 0$ to 3) with a cubic function of composition even for H–Cs system with $R^2 = 0.99872 < 0.999$. On the basis of the results showing enough reproducibility of ΔH^{mix} ’s with \mathcal{Q}_i even for the H–Cs system, we selected 53 elements as the constituent elements involving amorphous and glassy alloys as well as BMGs. Table 1 summarizes the selected 53 elements, which were acquired from constituent elements from our previous literature [10] and its original references [11–26] on BMGs and 351 ternary amorphous and glassy alloys [27]. The values of \mathcal{Q}_i ($i = 1$ to 3) for 1378 binary systems from the 53 elements are summarized in Table 2. It should be noted that Table 2 provides \mathcal{Q}_i ’s in the order of the atomic number in the periodic table for atomic pair A–B where the element A always has the smaller atomic number than element B. This notation indicates that the sign of \mathcal{Q}_i ’s for $i = 1$ and 3 in Table 2 became opposite for B–A atomic pair, which also affects the sign in the case of $k = 1$ and 3 for the right-sides of $\Delta H^{\text{mix}}_{\text{C}_A\text{C}_B}$ in Eq. (7) and $\Delta H^{\text{mix}}_{\text{C}_i\text{C}_j}$ in Eq. (10), and Fig. 1 and so forth. A part of Table 2 will be utilized for further analysis below.

Then, we analyzed the reproducibility of ΔH^{mix} with \mathcal{Q} for 2628 binary systems using $\mathcal{Q}_{\text{asym}}$, defined by Eq. (8) as well as R^2 . Fig. 2 shows the $\mathcal{Q}_{\text{asym}} - R^2$ diagram, in which H-, C- and N-containing systems are marked with closed circle, square and diamond, respectively, to separate from the other binary systems marked with open circle. In Fig. 2, one can see that H–Cs system with $R^2 = 0.99872$ has the greatest value of $\mathcal{Q}_{\text{asym}} = 1.140$, which indicates the strongest composition dependence in terms of $\text{H}_{0.5}\text{Cs}_{0.5}$ composition. The dotted and broken curves in Fig. 2 given guide for eyes exhibit two tendencies underlying $\mathcal{Q}_{\text{asym}} - R^2$ diagram. The first tendency is that both curves approach a point ($R^2, \mathcal{Q}_{\text{asym}}$) = (1,0) with increasing R^2 . The second tendency is that the dotted and broken curves separate with decreasing R^2 , approaching the plots of N–Cs and H–Cs systems, respectively. It appears that the dotted and broken curves approach the value of $\mathcal{Q}_{\text{asym}}$ near 0.6 and 1.2, respectively, with decreasing R^2 to 0.9985. The second tendency provides the following general trends with small R^2 value: (1) Both \mathcal{Q}_1 and \mathcal{Q}_3 term are approximately equal to two-thirds of the \mathcal{Q}_0 terms, and (2) H-containing alloy systems, in particular, exhibit greater $|\mathcal{Q}_3/\mathcal{Q}_0|$ than $|\mathcal{Q}_1/\mathcal{Q}_0|$. In reality, these trends were derived by calculating indices of $|\mathcal{Q}_3/\mathcal{Q}_0|$ and $|\mathcal{Q}_1/\mathcal{Q}_0|$. The values of ($\mathcal{Q}_0, \mathcal{Q}_1, \mathcal{Q}_2, \mathcal{Q}_3$)/kJ·mol^{−1} were acquired from Table 2 for N–Cs and H–Cs as (−130.5, −70.1, −25.6, 6.26) and (−13.8, −8.0, −9.2, −7.8), respectively. Thus, $|\mathcal{Q}_3/\mathcal{Q}_0|$ was calculated to be 0.048 for N–Cs and 0.57 for H–Cs and $|\mathcal{Q}_1/\mathcal{Q}_0|$ is 0.54 for N–Cs and 0.58 for H–Cs. These $|\mathcal{Q}_3/\mathcal{Q}_0|$ and $|\mathcal{Q}_1/\mathcal{Q}_0|$ values for N–Cs and H–Cs explain the second tendency mentioned above and the greater

composition dependence of ΔH^{mix} for H–Cs system than N–Cs. Besides to H–Cs and N–Cs systems, Fig. 2 shows that H-, C- and N-containing binary systems covers principally the plots for $R^2 < 1$, together with alkaline- and alkaline-earth-containing systems, such as Li-, Ce- and Rb-containing systems. Among H, C, N, and alkaline- and alkaline-earth elements, it should be noted that C is an essential element for forming Fe-based BMGs [1]. Thus, the results of the reproducibility of ΔH^{mix} ’s with \mathcal{Q}_i indicate that one should pay attention to assess the forming ability of C-containing alloy systems in the BMGs as well as amorphous and glassy alloys.

3.2. Analysis of BMGs for GFA

We performed especial analysis of BMGs for their GFA. We referred to La-, Zr-, Fe-, Mg-, Pd-, Pt-, Cu-, Ni- and Ca-based alloy systems as BMGs from our previous study [9,28], in which we reported that these systems represent the seven classes of BMGs (C-1 to C-7). In addition to the BMGs mentioned above, we also included Y-based BMG [19] in the present study. The classification of BMGs is based on the considerations of combinations of constituent elements from s-, d-, f- and p-blocks in the periodic table that forms sub-groups of s, d_{ef}, d_{lp} and p [28]. Here, “s” stands for s-block element, “d_{ef}” consists of d-block element for early transition metal and lanthanide (Ln) in f-block, “d_{lp}” comprises d-block element for late-transition metal and B-group metallic element in p-block in the periodic table, and “p” is composed of p-block metalloid. In our previous study [28], we reported that seven classes of BMGs can be formed from a couple of combinations of these sub-groups, s, d_{ef}, d_{lp} and p,

- C-1 (s-d_{ef}-d_{lp}): La-, Zr- and Y-based BMGs, such as, Al–La–Ni,
- C-2 (d_{ef}-d_{lp}-p): Fe-based BMGs, such as, Zr–Fe–B,
- C-3 (s-d_{lp}-p): Fe-based multi-component BMGs, such as, (Al, Ga)-Fe-(P,C,B,Si)
- C-4 (s-d_{ef}-d_{lp}): Mg-based BMGs, such as, Mg–Y–Cu
- C-5 (d_{lp}-p): Pd- and Pt-based BMGs, such as, (Pd,Ni)-P,
- C-6 (d_{ef}-d_{lp}): Cu- and Ni-based BMGs, such as, (Zr,Ti)-Cu, and
- C-7 (s-d_{lp}): Ca-based BMGs, such as, (Ca,Mg)-Zn.

Besides, BMGs in C-1, C-4, C-6 and C-7 are categorized in metal–metal type, whereas those in C-2, C-3 and C-5 in metal–metalloid types. Fig. 3 shows ΔH^{mix} ’s for the alloy systems in seven classes. Fig. 3 demonstrates that the compositions that give minimum ΔH^{mix} ($c_{X,\text{min}}$) lie at 0.45–0.55 for most of the alloy systems, indicating that composition dependence of ΔH^{mix} is not as large for practical BMGs as H–Cs system shown in Fig. 1. However, it should be noted that P and C elements in Fe-based BMGs exhibit peculiar behavior, as shown in Fig. 3 (d). Specifically, the ΔH^{mix} at $\text{Fe}_{0.5}\text{P}_{0.5}$ and $\text{Fe}_{0.5}\text{C}_{0.5}$ has different values about −40 kJ mol^{−1} and −50 kJ mol^{−1}, respectively. However, the values of ΔH^{mix} at Fe-rich side for Fe–P and Fe–C tend to give smaller difference than that at $\text{Fe}_{0.5}\text{X}_{0.5}$ ($\text{X} = \text{P}$ and C) with decreasing fraction of X from 0.5. At lower composition of X, ΔH^{mix} for Fe–P agree with that for Fe–C around $\text{Fe}_{0.8}\text{X}_{0.2}$. The coincidence of ΔH^{mix} ’s at $X = 0.2$ indicates that P and C affect the formation of amorphous and glassy phase almost the same degree.

Table 1
The atomic number (No.) and symbol (Symb.) of 53 elements selected in the present study as the ones involving amorphous and glassy alloys including BMGs. These 53 elements were selected from ternary amorphous alloys as well as glassy alloys [27] and original literature for BMGs [11–26] with critical diameters more than half inches (~1.27 cm). The atomic pairs from the 53 elements amount to 1378, and their \mathcal{Q}_i ’s are shown in Table 2.

No.	1	4	5	6	12	13	14	15	20	21	22	23	24	25	26	27	28	29	30	31	32	38	39	40	41	42	44
Symb.	H	Be	B	C	Mg	Al	Si	P	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	Sr	Y	Zr	Nb	Mo	Ru
No.	45	46	47	49	50	56	57	58	59	60	62	64	65	66	67	68	69	70	72	73	74	77	78	79	82	90	–
Symb.	Rh	Pd	Ag	In	Sn	Ba	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Hf	Ta	W	Ir	Pt	Au	Pb	Th	–

Table 2

The values of Q_i ($i = 1$ to 3) in units of kJ mol^{-1} for 1378 systems from 53 elements. Note that $Q_0 = \Delta H^{\text{mix}}$ at $A_{0.5}B_{0.5}$ in an A–B alloy.

Pair	H–Be	H–B	H–C	H–Mg	H–Al	H–Si	H–P	H–Ca	H–Sc	H–Ti	H–V	H–Cr	H–Mn	H–Fe	H–Co	H–Ni	H–Cu	H–Zn	H–Ga	H–Ge	H–Sr	H–Y	H–Zr	H–Nb	H–Mo	H–Ru	H–Rh	H–Pd	H–Ag	H–In	H–Sn	H–Ba
Q_0	2.0	4.7	–2.9	–17.7	–7.8	–2.2	0.8	–41.2	–56.7	–52.4	–38.0	–27.7	–33.7	–23.2	–23.0	–22.8	–13.6	–7.6	–7.6	–2.3	–40.4	–56.3	–65.0	–44.8	–27.3	–19.8	–23.5	–27.1	–9.6	–5.8	–4.1	–40.6
Q_1	0.6	1.6	–0.9	–7.7	–3.4	–1.0	0.4	–20.3	–25.3	–22.2	–15.3	–11.1	–13.0	–9.7	–9.6	–9.7	–5.0	–3.0	–3.5	–1.1	–21.1	–28.0	–29.8	–20.0	–12.7	–9.9	–11.8	–14.2	–4.4	–2.9	–2.2	–21.7
Q_2	0.2	0.6	–0.1	–5.0	–2.0	–0.6	0.2	–17.1	–18.5	–14.6	–8.7	–5.7	–6.8	–4.9	–4.6	–4.6	–2.5	–1.6	–2.4	–0.7	–20.2	–23.8	–22.8	–13.4	–7.7	–5.5	–6.6	–8.3	–2.7	–2.3	–1.9	–21.9
Q_3	0.1	0.2	0.0	–2.8	–1.1	–0.3	0.1	–11.8	–11.7	–8.6	–4.5	–2.7	–3.3	–2.3	–2.1	–2.0	–1.1	–0.8	–1.4	–0.4	–15.3	–16.8	–15.1	–7.9	–4.3	–2.8	–3.4	–4.4	–1.5	–1.5	–1.3	–17.2
Pair	H–La	H–Ce	H–Pr	H–Nd	H–Sm	H–Gd	H–Tb	H–Dy	H–Ho	H–Er	H–Tm	H–Yb	H–Hf	H–Ta	H–W	H–Ir	H–Pt	H–Au	H–Pb	H–Th	Be–B	Be–C	Be–Mg	Be–Al	Be–Si	Be–P	Be–Ca	Be–Sc	Be–Ti	Be–V	Be–Cr	Be–Mn
Q_0	–55.9	–56.1	–56.2	–56.2	–56.4	–56.3	–56.5	–56.4	–55.9	–56.6	–56.5	–56.4	–60.1	–44.9	–23.4	–20.6	–24.3	–8.4	–0.5	–57.4	0.0	–14.9	–3.1	0.2	2.2	–3.7	–13.6	–35.2	–30.0	–16.3	–7.2	–10.4
Q_1	–28.9	–28.7	–28.4	–28.3	–28.1	–28.0	–27.9	–27.7	–27.3	–27.5	–27.2	–27.1	–27.7	–20.1	–11.3	–10.8	–13.3	–4.4	–0.3	–29.4	0.0	0.8	–0.6	0.0	0.4	–0.8	–4.1	–7.6	–4.9	–2.0	–0.7	–1.0
Q_2	–26.1	–25.3	–24.6	–24.4	–23.9	–23.8	–23.3	–22.9	–22.5	–22.4	–22.0	–21.8	–20.8	–13.4	–7.0	–6.1	–7.9	–2.8	–0.3	–26.8	0.0	0.2	–0.1	0.0	0.1	–0.1	–1.5	–2.4	–1.5	–0.5	–0.1	–0.2
Q_3	–19.3	–18.5	–17.7	–17.5	–17.0	–16.8	–16.3	–15.9	–15.5	–15.4	–15.0	–14.8	–13.5	–8.0	–3.9	–3.2	–4.3	–1.6	–0.2	–20.1	0.0	–0.1	0.0	0.0	0.0	0.0	–0.4	–0.7	–0.4	–0.1	0.0	0.0
Pair	Be–Fe	Be–Co	Be–Ni	Be–Cu	Be–Zn	Be–Ga	Be–Ge	Be–Sr	Be–Y	Be–Zr	Be–Nb	Be–Mo	Be–Ru	Be–Rh	Be–Pd	Be–Ag	Be–In	Be–Sn	Be–Ba	Be–La	Be–Ce	Be–Pr	Be–Nd	Be–Sm	Be–Gd	Be–Tb	Be–Dy	Be–Ho	Be–Er	Be–Tm	Be–Yb	Be–Hf
Q_0	–3.7	–3.9	–4.2	–1.1	3.4	4.7	8.6	–9.6	–30.8	–42.0	–24.3	–6.7	–3.1	–6.0	–8.0	6.2	15.3	14.4	–8.9	–28.1	–29.1	–30.0	–29.9	–30.8	–30.8	–31.6	–31.5	–30.7	–32.3	–32.2	–32.2	–36.8
Q_1	–0.4	–0.4	–0.5	–0.1	0.4	1.0	1.7	–3.5	–9.1	–9.6	–4.6	–1.2	–0.6	–1.2	–1.8	1.1	4.3	4.6	–3.5	–9.2	–9.2	–9.2	–9.1	–9.1	–9.1	–8.9	–8.6	–8.9	–8.7	–8.6	–8.3	–8.3
Q_2	–0.1	0.0	0.0	0.0	0.0	0.3	0.4	–1.6	–3.7	–3.7	–1.4	–0.3	–0.1	–0.2	–0.3	0.3	1.6	1.9	–1.7	–4.2	–4.1	–3.9	–3.9	–3.8	–3.7	–3.7	–3.5	–3.4	–3.4	–3.3	–3.2	–3.1
Q_3	0.0	0.0	0.0	0.0	0.0	0.1	0.1	–0.6	–1.4	–1.3	–0.4	–0.1	0.0	0.0	–0.1	0.1	0.5	0.8	–0.7	–1.8	–1.7	–1.6	–1.5	–1.5	–1.4	–1.4	–1.3	–1.2	–1.2	–1.2	–1.1	–1.1
Pair	Be–Ta	Be–W	Be–Ir	Be–Pt	Be–Au	Be–Pb	Be–Th	B–C	B–Mg	B–Al	B–Si	B–P	B–Ca	B–Sc	B–Ti	B–V	B–Cr	B–Mn	B–Fe	B–Co	B–Ni	B–Cu	B–Zn	B–Ga	B–Ge	B–Sr	B–Y	B–Zr	B–Nb	B–Mo	B–Ru	B–Rh
Q_0	–24.1	–3.2	–5.5	–9.8	–0.1	25.0	–35.8	–10.2	–3.7	0.1	3.3	0.5	–21.1	–53.9	–57.2	–42.0	–31.4	–32.4	–26.5	–24.2	–23.6	–6.4	4.1	5.6	11.5	–16.7	–48.9	–70.1	–53.9	–34.1	–24.5	–25.2
Q_1	–4.6	–0.7	–1.2	–2.4	0.0	8.7	–11.4	0.7	–0.8	0.0	0.6	0.1	–7.0	–12.8	–10.4	–5.5	–3.3	–3.3	–3.0	–2.6	–2.5	–0.5	0.5	1.2	2.3	–6.6	–15.5	–17.6	–10.9	–6.5	–4.6	–4.8
Q_2	–1.4	–0.2	–0.2	–0.5	0.0	4.0	–5.5	0.0	–0.1	0.0	0.1	0.0	–2.3	–3.6	–2.9	–1.2	–0.6	–0.6	–0.5	–0.3	–0.3	0.0	0.0	0.3	0.6	–2.9	–6.1	–6.3	–3.1	–1.5	–0.9	–0.9
Q_3	–0.4	0.0	0.0	0.0	0.0	1.7	–2.5	0.0	0.0	0.0	0.0	0.0	–0.4	–0.9	–0.8	–0.2	–0.1	–0.1	–0.1	0.0	0.0	0.0	0.0	0.1	0.1	–0.9	–2.1	–2.2	–0.8	–0.4	–0.2	–0.2
Pair	B–Pd	B–Ag	B–In	B–Sn	B–Ba	B–La	B–Ce	B–Pr	B–Nd	B–Sm	B–Gd	B–Tb	B–Dy	B–Ho	B–Er	B–Tm	B–Yb	B–Hf	B–Ta	B–W	B–Ir	B–Pt	B–Au	B–Pb	B–Th	C–Mg	C–Al	C–Si	C–P	C–Ca	C–Sc	C–Ti
Q_0	–24.1	5.4	17.8	17.4	–15.9	–45.9	–47.0	–48.0	–47.9	–49.0	–48.9	–49.9	–49.8	–48.9	–50.7	–50.6	–50.5	–64.9	–53.3	–30.7	–25.7	–27.8	–2.4	29.5	–55.7	–52.9	–34.9	–21.3	–4.5	–84.0	–114.6	–106.8
Q_1	–5.2	1.0	5.2	5.7	–6.7	–16.1	–16.0	–15.8	–15.7	–15.7	–15.5	–15.5	–15.2	–14.8	–15.1	–14.8	–14.6	–16.0	–10.8	–6.2	–5.4	–6.6	–0.6	10.6	–19.1	–15.8	–9.1	–5.5	–1.3	–36.4	–38.8	–30.6
Q_2	–1.1	0.2	1.8	2.4	–3.2	–7.1	–6.7	–6.4	–6.3	–6.1	–6.1	–5.9	–5.7	–5.4	–5.5	–5.2	–5.1	–5.5	–3.1	–1.5	–1.1	–1.4	–0.1	4.9	–9.0	–2.9	–2.2	–1.6	–0.4	–13.8	–12.9	–10.3
Q_3	–0.2	0.0	0.6	0.9	–1.2	–2.8	–2.6	–2.4	–2.3	–2.2	–2.1	–2.0	–1.9	–1.8	–1.8	–1.6	–1.6	–1.9	–0.8	–0.4	–0.2	–0.3	0.0	2.1	–4.0	0.8	–0.3	–0.4	–0.1	–2.1	–3.0	–3.2
Pair	C–V	C–Cr	C–Mn	C–Fe	C–Co	C–Ni	C–Cu	C–Zn	C–Ga	C–Ge	C–Sr	C–Y	C–Zr	C–Nb	C–Mo	C–Ru	C–Rh	C–Pd	C–Ag	C–In	C–Sn	C–Ba	C–La	C–Ce	C–Pr	C–Nd	C–Sm	C–Gd	C–Tb	C–Dy	C–Ho	C–Er
Q_0	–81.2	–60.9	–65.5	–49.1	–41.9	–38.5	–38.4	–31.4	–32.4	–16.8	–82.3	–112.7	–128.0	–99.8	–65.8	–35.1	–35.0	–31.9	–31.7	–25.9	–22.5	–82.5	–111.2	–111.8	–112.3	–112.1	–112.8	–112.7	–113.4	–113.1	–111.9	–113.6
Q_1	–18.7	–12.2	–13.0	–10.1	–8.1	–7.4	–6.3	–6.3	–9.9	–4.9	–40.4	–46.6	–45.3	–30.1	–18.5	–9.4	–9.5	–9.4	–8.7	–9.8	–9.4	–42.4	–49.4	–48.5	–47.7	–47.3	–46.8	–46.6	–46.0	–45.4	–44.6	–44.8
Q_2	–5.0	–2.8	–2.9	–2.3	–1.7	–1.6	–0.6	–0.3	–3.0	–1.7	–20.0	–21.2	–19.6	–10.6	–6.0	–2.8	–2.8	–3.1	–2.3	–4.0	–4.8	–23.1	–25.1	–23.8	–22.5	–22.2	–21.4	–21.2	–20.4	–19.7	–19.2	–18.9
Q_3	–1.3	–0.6	–0.6	–0.5	–0.4	–0.3	0.1	0.5	–0.7	–0.5	–6.5	–8.0	–7.8	–3.5	–1.8	–0.8	–0.8	–1.0	–0.5	–1.4	–2.3	–8.8	–10.8	–9.8	–9.0	–8.7	–8.1	–8.0	–7.4	–7.1	–6.8	–6.5
Pair	C–Tm	C–Yb	C–Hf	C–Ta	C–W	C–Ir	C–Pt	C–Au	C–Pb	C–Th	Mg–Al	Mg–Si	Mg–P	Mg–Ca	Mg–Sc	Mg–Ti	Mg–V	Mg–Cr	Mg–Mn	Mg–Fe	Mg–Co	Mg–Ni	Mg–Cu	Mg–Zn	Mg–Ga	Mg–Ge	Mg–Sr	Mg–Y	Mg–Zr	Mg–Nb	Mg–Mo	Mg–Ru
Q_0	–113.3	–113.1	–119.9	–99.0	–59.1	–31.7	–30.2	–19.6	–12.2	–118.9	–1.9	–9.1	–39.3	–5.6	–3.4	15.8	23.1	23.6	10.0	17.5	2.8	3.6	–4.4	–3.5	–4.3	–14.3	–3.9	–6.0	5.7	31.7	35.8	0.0
Q_1	–44.1	–43.8	–41.8	–29.8	–17.2	–9.0	–9.3	–6.1	–5.5	–52.3	0.1	0.7	0.7	–0.7	0.0	–1.1	–2.7	–3.3	–1.5	–2.2	–0.4	0.5	0.6	0.3	0.0	0.6	–0.7	–0.6	0.0	–1.4	–1.8	0.0
Q_2	–18.3	–18.0	–17.6	–10.6	–5.7	–2.8	–3.2	–2.0	–3.0	–29.5	0.0	0.1	1.6	–0.1	0.0	0.0	0.1	0.1	0.1	–0.1	0.0	0.0	–0.1	0.0	0.0	0.2	–0.2	–0.1	0.0	–0.2	–0.6	0.0
Q_3	–6.1	–5.9	–6.9	–3.5	–1.8	–0.9	–1.0	–0.6	–1.5	–15.0	0.0	0.1	–0.5	0.0	0.0	0.0	0.1	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	–0.1	0.0	0.0	0.0	0.0	0.2	0.0
Pair	Mg–Rh	Mg–Pd	Mg–Ag	Mg–In	Mg–Sn	Mg–Ba	Mg–La	Mg–Ce	Mg–Pr	Mg–Nd	Mg–Sm	Mg–Gd	Mg–Tb	Mg–Dy	Mg–Ho	Mg–Er	Mg–Tm	Mg–Yb	Mg–Hf	Mg–Ta	Mg–W	Mg–Ir	Mg–Pt	Mg–Au	Mg–Pb	Mg–Th	Al–Si	Al–P	Al–Ca	Al–Sc	Al–Ti	Al–V
Q_0	–16.9	–39.9	–10.4	–3.8	–8.6	–3.5	–6.9	–6.6	–6.4	–6.3	–6.0	–6.0	–5.7	–5.6	–5.5	–5.3	–5.2	–5.2	9.7	29.6	38.1	–12.7	–34.7	–31.5	–8.1	–2.8	–2.3	–21.0	–20.1	–37.7	–29.5	–16.3
Q_1	0.7	0.6	0.3	–0.3	–0.9	–0.8	–0.9	–0.8	–0.7	–0.7	–0.6	–0.6	–0.5	–0.5	–0.4	–0.4	–0.3	–0.3	0.0	–1.3	–1.3	0.2	–0.3	–1.2	–1.1	–0.3	0.1	–0.5	–3.7	–2.6	0.1	0.9
Q_2	0.6	1.6	0.1	0.0	0.0	–0.2	–0.1	–0.1	–0.1	–0.1	–0.1	–0.1	–0.1	–0.1	0.0	0.0	0.0	0.0	0.0	–0.2	–0.9	0.5	1.6	0.8	0.0	0.0	0.3	–0.5	–0.2	–0.1	0.0	0.0
Q_3	–0.2	–0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	–0.2	–0.5	–0.1	0.0	0.0	0.0	0.2	–0.2	0.0	0.0	0.0
Pair	Al–Cr	Al–Mn	Al–Fe	Al–Co	Al–Ni	Al–Cu	Al–Zn	Al–Ga	Al–Ge	Al–Sr	Al–Y	Al–Zr	Al–Nb	Al–Mo	Al–Ru	Al–Rh	Al–Pd	Al–Ag	Al–In	Al–Sn	Al–Ba	Al–La	Al–Ce	Al–Pr	Al–Nd	Al–Sm	Al–Gd	Al–Tb	Al–Dy	Al–Ho	Al–Er	Al–Tm
$Q_$																																

Table 2 (continued)

Q_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	1.1	0.0	0.5	2.0	1.3	1.5	-0.2	0.0	0.1	0.0	-0.2	-0.2	-0.5	-0.6	-0.7	-0.5	0.0	0.3	0.9	0.0	0.0	0.0	0.0
Q_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.3	1.1	-0.9	-2.2	-1.4	-0.4	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.1	0.1	0.1	0.0	-0.2	0.1	0.0	0.0	0.0	0.0
Pair	Sc-Ru	Sc-Rh	Sc-Pd	Sc-Ag	Sc-In	Sc-Sn	Sc-Ba	Sc-La	Sc-Ce	Sc-Pr	Sc-Nd	Sc-Sm	Sc-Gd	Sc-Tb	Sc-Dy	Sc-Ho	Sc-Er	Sc-Tm	Sc-Yb	Sc-Hf	Sc-Ta	Sc-W	Sc-Ir	Sc-Pt	Sc-Au	Sc-Pb	Sc-Th	Ti-V	Ti-Cr	Ti-Mn	Ti-Fe	Ti-Co
Q_0	-43.3	-60.4	-85.5	-28.3	-30.2	-45.1	27.3	2.1	1.6	1.3	1.3	0.9	0.9	0.6	0.6	0.7	0.4	0.4	0.4	5.1	15.8	9.2	-61.4	-88.0	-73.7	-39.8	0.0	-1.7	-7.5	-8.2	-16.8	-28.3
Q_1	3.7	5.0	4.8	1.4	-1.8	-3.5	6.2	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	-0.1	-1.0	-0.6	4.0	3.3	-0.1	-4.5	0.0	0.1	0.7	0.8	1.5	2.8
Q_2	0.5	0.7	1.5	0.0	0.0	0.2	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	1.1	2.1	0.7	-0.1	0.0	0.0	-0.1	-0.1	-0.3	
Q_3	-0.3	-0.5	-0.7	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.5	-0.8	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair	Ti-Ni	Ti-Cu	Ti-Zn	Ti-Ga	Ti-Ge	Ti-Sr	Ti-Y	Ti-Zr	Ti-Nb	Ti-Mo	Ti-Ru	Ti-Rh	Ti-Pd	Ti-Ag	Ti-In	Ti-Sn	Ti-Ba	Ti-La	Ti-Ce	Ti-Pr	Ti-Nd	Ti-Sm	Ti-Gd	Ti-Tb	Ti-Dy	Ti-Ho	Ti-Er	Ti-Tm	Ti-Yb	Ti-Hf	Ti-Ta	Ti-W
Q_0	-34.5	-8.9	-14.8	-23.1	-39.5	52.5	15.1	-0.2	2.0	-3.6	-43.2	-51.9	-64.5	-1.5	-5.5	-21.3	56.1	19.5	18.0	16.5	16.5	15.1	15.1	13.8	13.7	14.0	12.5	12.4	12.4	0.2	1.4	-5.7
Q_1	3.5	0.9	0.4	-1.2	-0.3	15.0	2.7	0.0	0.0	0.0	0.9	0.9	-0.5	0.0	-0.7	-3.3	17.8	4.2	3.6	3.1	3.1	2.7	2.7	2.3	2.2	2.2	1.9	1.8	1.8	0.0	0.0	0.0
Q_2	-0.4	-0.1	-0.1	-0.1	0.0	3.8	0.4	0.0	0.0	0.0	0.0	0.1	0.2	0.0	-0.1	-0.5	5.2	0.9	0.7	0.6	0.5	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.0	0.0	0.0	
Q_3	0.0	0.0	0.0	0.0	0.0	0.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	1.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair	Ti-Ir	Ti-Pt	Ti-Au	Ti-Pb	Ti-Th	V-Cr	V-Mn	V-Fe	V-Co	V-Ni	V-Cu	V-Zn	V-Ga	V-Ge	V-Sr	V-Y	V-Zr	V-Nb	V-Mo	V-Ru	V-Rh	V-Pd	V-Ag	V-In	V-Sn	V-Ba	V-La	V-Ce	V-Pr	V-Nd	V-Sm	V-Gd
Q_0	-57.1	-74.4	-47.4	-7.7	8.4	-2.0	-0.7	-7.1	-14.0	-18.0	5.0	-1.6	-8.0	-18.8	52.6	16.6	-3.7	-1.0	0.0	-24.7	-29.4	-35.3	16.9	11.9	-0.9	55.8	21.8	20.0	18.3	18.2	16.6	16.6
Q_1	0.2	-1.8	-2.9	-1.5	1.6	0.1	0.0	0.2	0.6	0.7	-0.2	0.0	-0.9	-1.3	17.4	3.8	-0.5	-0.1	0.0	-1.0	-1.3	-2.4	1.2	2.3	-0.2	20.1	5.8	5.1	4.4	4.3	3.8	3.8
Q_2	0.1	0.2	-0.4	-0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.1	5.2	0.8	-0.1	0.0	0.0	0.0	0.0	-0.1	0.1	0.4	0.0	6.8	1.5	1.3	1.0	1.0	0.8	0.8
Q_3	0.0	0.0	0.0	-0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	1.7	0.4	0.3	0.2	0.2	0.2	0.2
Pair	V-Tb	V-Dy	V-Ho	V-Er	V-Tm	V-Yb	V-Hf	V-Ta	V-W	V-Ir	V-Pt	V-Au	V-Pb	V-Th	Cr-Mn	Cr-Fe	Cr-Co	Cr-Ni	Cr-Cu	Cr-Zn	Cr-Ga	Cr-Ge	Cr-Sr	Cr-Y	Cr-Zr	Cr-Nb	Cr-Mo	Cr-Ru	Cr-Rh	Cr-Pd	Cr-Ag	Cr-In
Q_0	15.0	14.9	15.4	13.4	13.4	13.3	-2.2	-1.0	-3.8	-34.4	-45.6	-19.2	15.1	8.5	2.1	-1.5	-4.6	-6.7	12.5	4.7	-0.6	-6.3	46.0	11.0	-0.2	-7.2	0.4	-11.5	-13.4	-14.6	27.0	20.2
Q_1	3.3	3.2	3.2	2.7	2.7	2.6	-0.3	-0.1	-0.1	-2.0	-3.8	-2.2	3.8	2.1	0.0	0.0	0.0	0.1	-0.2	0.2	-0.1	-0.6	16.2	2.8	-2.0	-0.8	0.0	-0.8	-1.0	-1.5	2.7	4.3
Q_2	0.7	0.6	0.6	0.5	0.5	0.5	0.0	0.0	0.0	0.0	-0.1	-0.3	1.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	5.0	0.7	-0.4	-0.1	0.0	0.0	-0.1	0.2	0.9	
Q_3	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.1	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Pair	Cr-Sn	Cr-Ba	Cr-La	Cr-Ce	Cr-Pr	Cr-Nd	Cr-Sm	Cr-Gd	Cr-Tb	Cr-Dy	Cr-Ho	Cr-Er	Cr-Tm	Cr-Yb	Cr-Hf	Cr-Ta	Cr-W	Cr-Ir	Cr-Pt	Cr-Au	Cr-Pb	Cr-Th	Mn-Fe	Mn-Co	Mn-Ni	Mn-Cu	Mn-Zn	Mn-Ga	Mn-Ge	Mn-Sr	Mn-Y	Mn-Zr
Q_0	10.0	48.7	16.6	14.7	12.8	12.8	11.0	11.0	9.3	9.3	9.9	7.6	7.6	7.5	-9.3	-6.7	1.0	-17.8	-24.5	-0.2	27.6	2.1	0.2	-5.2	-8.2	3.8	-6.4	-12.9	-19.0	26.0	-1.4	-15.3
Q_1	2.5	18.5	4.8	4.1	3.4	3.4	2.8	2.8	2.3	2.2	2.3	1.8	1.7	1.7	-1.5	-0.7	0.1	-1.6	-2.8	0.0	7.7	0.6	0.0	0.0	0.0	0.0	-0.3	-1.8	-1.9	9.3	-0.4	-2.6
Q_2	0.6	6.6	1.4	1.1	0.9	0.9	0.7	0.7	0.5	0.5	0.5	0.4	0.4	0.3	-0.3	-0.1	0.0	-0.1	-0.3	0.0	2.3	0.2	0.0	0.0	0.0	0.0	0.0	-0.2	-0.2	3.1	-0.1	-0.5
Q_3	0.2	1.6	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	-0.1
Pair	Mn-Nb	Mn-Mo	Mn-Ru	Mn-Rh	Mn-Pd	Mn-Ag	Mn-In	Mn-Sn	Mn-Ba	Mn-La	Mn-Ce	Mn-Pr	Mn-Nd	Mn-Sm	Mn-Gd	Mn-Tb	Mn-Dy	Mn-Ho	Mn-Er	Mn-Tm	Mn-Yb	Mn-Hf	Mn-Ta	Mn-W	Mn-Ir	Mn-Pt	Mn-Au	Mn-Pb	Mn-Th	Fe-Co	Fe-Ni	Fe-Cu
Q_0	-15.3	4.9	-10.7	-16.2	-22.6	12.7	-2.6	-6.9	28.0	2.5	1.1	-0.2	-0.2	-1.4	-1.4	-2.6	-4.6	-2.0	-3.8	-3.8	-3.6	-11.9	-3.8	6.3	-18.2	-28.3	-11.3	-6.8	-7.6	-0.6	-1.6	12.9
Q_1	-2.6	0.4	-0.8	-1.3	-2.3	1.3	0.6	-1.7	10.8	0.7	0.3	0.0	0.0	-0.4	-0.4	-0.7	-0.6	-0.5	-0.9	-0.9	-0.9	-2.0	-0.4	0.6	-1.7	-3.4	-1.6	1.9	-2.1	0.0	0.0	-0.3
Q_2	-0.5	0.0	0.0	-0.1	-0.2	0.1	0.1	-0.5	4.0	0.2	0.1	0.0	0.0	-0.1	-0.1	-0.2	-0.2	-0.1	-0.2	-0.2	-0.2	-0.4	-0.1	0.1	-0.1	-0.3	-0.3	0.6	-0.6	0.0	0.0	0.0
Q_3	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	1.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.2	-0.2	0.0	0.0	0.0
Pair	Fe-Zn	Fe-Ga	Fe-Ge	Fe-Sr	Fe-Y	Fe-Zr	Fe-Nb	Fe-Mo	Fe-Ru	Fe-Rh	Fe-Pd	Fe-Ag	Fe-In	Fe-Sn	Fe-Ba	Fe-La	Fe-Ce	Fe-Pr	Fe-Nd	Fe-Sm	Fe-Gd	Fe-Tb	Fe-Dy	Fe-Ho	Fe-Er	Fe-Tm	Fe-Yb	Fe-Hf	Fe-Ta	Fe-W	Fe-Ir	Fe-Pt
Q_0	3.6	-1.7	-3.4	33.4	-1.1	-24.6	-15.7	-2.0	-4.6	-5.4	-4.3	28.1	18.9	10.6	35.6	4.4	2.5	0.7	0.7	-1.1	-1.1	-2.9	-2.9	-2.0	-4.6	-4.5	-4.5	-20.5	-15.0	0.0	-8.8	-13.0
Q_1	0.1	-0.2	-0.3	11.4	-0.3	-4.1	-1.6	-0.2	-0.3	-0.4	-0.4	2.6	3.9	2.5	13.2	1.3	0.7	0.2	0.2	-0.3	-0.3	-0.7	-0.7	-0.5	-1.0	-1.0	-1.0	-3.3	-1.6	0.0	-0.8	-1.5
Q_2	0.0	0.0	0.0	3.2	-0.1	-0.8	-0.2	0.0	0.0	0.0	0.0	0.1	0.8	0.7	4.3	0.4	0.2	0.0	0.0	-0.1	-0.1	-0.1	-0.1	-0.1	-0.2	-0.2	-0.2	-0.6	-0.2	0.0	-0.1	-0.1
Q_3	0.0	0.0	0.0	0.3	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.7	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pair	Fe-Au	Fe-Pb	Fe-Th	Co-Ni	Co-Cu	Co-Zn	Co-Ga	Co-Ge	Co-Sr	Co-Y	Co-Zr	Co-Nb	Co-Mo	Co-Ru	Co-Rh	Co-Pd	Co-Ag	Co-In	Co-Sn	Co-Ba	Co-La	Co-Ce	Co-Pr	Co-Nd	Co-Sm	Co-Gd	Co-Tb	Co-Dy	Co-Ho	Co-Er	Co-Tm	Co-Yb
Q_0	8.0	29.0	-10.5	-0.2	6.4	-5.1	-11.0	-9.1	9.2	-21.2	-40.3	-24.5	-4.9	-0.7	-2.1	-1.5	19.0	6.6	0.2	10.8	-16.6	-18.2	-19.7	-19.7	-21.2	-21.2	-22.7	-22.6	-21.6	-24.0	-23.9	-23.9
Q_1	1.1	7.9	-2.8	0.0	-0.1	-0.2	-1.5	-1.0	3.2	-5.4	-7.2	-2.9	-0.5	-0.1	-0.2	-0.2	1.9	1.4	0.0	4.1	-4.8	-5.1	-5.3	-5.2	-5.5	-5.4	-5.6	-5.5	-5.2	-5.6	-5.4	-5.4
Q_2	0.1	2.4	-0.9	0.0	0.0	0.1	-0.1	-0.1	0.9	-1.3	-1.5	-0.4	0.0	0.0	0.0	0.0	0.1	0.3	0.0	1.4	-1.4	-1.4	-1.3	-1.3	-1.3	-1.3	-1.2	-1.2	-1.1	-1.1	-1.1	-1.0
Q_3	0.0	0.7	-0.3	0.0	0.0	0.0	0.0	0.0	0.1	-0.2	-0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	-0.3	-0.3	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1
Pair	Co-Hf	Co-Ta	Co-W	Co-Ir	Co-Pt	Co-Au	Co-Pb	Co-Th	Ni-Cu	Ni-Zn	Ni-Ga	Ni-Ge	Ni-Sr	Ni-Y	Ni-Zr	Ni-Nb	Ni-Mo	Ni-Ru	Ni-Rh	Ni-Pd	Ni-Ag	Ni-In	Ni-Sn	Ni-Ba	Ni-La	Ni-Ce	Ni-Pr	Ni-Nd	Ni-Sm	Ni-Gd	Ni-Tb	Ni-Dy
Q_0	-34.7	-23.9	-1.4	-3.5	-7.2	7.2	17.2	-29.6	3.6	-8.8	-15.0	-11.3	-1.0	-30.6	-48.4	-29.9	-7.3	0.5	-0.9	-0.1	15.5	1.7	-3.9	0.2	-26.2	-27.7	-29.2	-29.1	-30.6	-30.6	-32.0	-31.8
Q_1	-5.9	-2.8	-0.1	-0.3	-0.9	1.0	4.9	-8.3	-0.1	-0.3	-2.0	-1.2	-0.4	-7.8	-8.6	-3.5	-0.7	0.0	-0.1	0.0	1.5	0.4	-1.0	0.1	-7.6	-7.7	-7.8	-7.7	-7.8	-7.8	-7.9	-7.7
Q_2	-1.2	-0.4	0.0	0.0	-0.1	0.1	1.																									

Pair	Ge-Pr	Ge-Nd	Ge-Sm	Ge-Gd	Ge-Th	Ge-Dy	Ge-Ho	Ge-Er	Ge-Tm	Ge-Yb	Ge-Hf	Ge-Ta	Ge-W	Ge-ir	Ge-Pt	Ge-Au	Ge-Pb	Ge-Th	Sr-Y	Sr-Zr	Sr-Nb	Sr-Mo	Sr-Ru	Sr-Rh	Sr-Pd	Sr-Ag	Sr-In	Sr-Sn	Sr-Ba	Sr-La	Sr-Ce	Sr-Pr	
Z0	-598	-597	-596	-595	-593	-591	-583	-588	-586	-584	-525	-250	4.9	-11.5	-24.9	-9.4	4.7	-59.4	17.1	47.2	75.1	67.3	4.4	-21.6	-59.4	-26.8	-36.8	-45.8	0.0	13.5	14.7	15.3	
Z1	-104	-101	-96	-95	-8.9	-8.6	-8.2	-8.0	-7.6	-7.4	-3.4	-0.3	0.0	0.0	-0.4	0.0	0.2	-2.2	0.1	1.8	4.1	3.3	0.1	-0.6	-0.7	-1.2	-0.2	0.5	0.0	0.0	0.0	0.1	
Z2	-1.4	-1.3	-1.1	-1.1	-0.9	-0.8	-0.7	-0.6	-0.5	-0.5	-0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.4	0.0	-0.2	0.5	0.1	-0.6	-0.7	-1.2	-0.2	0.5	0.0	0.0	0.0	0.0	
Z3	-0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.4	0.0	-0.2	0.5	0.1	-0.6	-0.7	-1.2	-0.2	0.5	0.0	0.0	0.0	0.0	
Pair Sr-Nd	Sr-Sm	Sr-Sm	Sr-Gd	Sr-Th	Sr-Dy	Sr-Ho	Sr-Er	Sr-Tm	Sr-Yb	Sr-Hf	Sr-Ta	Sr-W	Sr-ir	Sr-Pt	Sr-Au	Sr-Pb	Sr-Th	Y-Zr	Y-Nb	Y-Mo	Y-Ru	Y-Pd	Y-Ag	Y-Sn	Y-Ba	Y-La	Y-Ce	Y-Pr	Y-Nd	Y-Sm			
Z0	15.9	17.1	17.1	18.4	18.3	17.8	19.6	19.4	19.4	49.4	71.5	68.7	-15.1	-48.9	-57.4	-55.6	27.0	9.4	29.4	23.9	-33.2	-53.5	-82.9	-29.3	-36.0	-50.7	19.5	0.2	0.1	0.0	0.0	0.0	
Z1	-1.6	-1.9	-1.9	-2.2	-2.3	-2.3	-2.6	-2.7	-2.8	-11.0	-18.9	-17.8	3.8	11.1	10.2	5.0	-3.2	-1.0	-4.6	4.1	5.8	9.2	12.2	4.1	1.0	0.7	2.8	0.0	0.0	0.0	0.0	0.0	
Z2	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	1.9	3.9	2.5	-0.2	0.2	-0.2	1.1	0.0	0.1	0.6	0.5	-0.6	-0.8	-0.5	-0.6	0.4	0.3	0.0	0.0	0.0	0.0	0.0	0.0	
Z3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.2	0.9	-0.5	-2.1	-1.3	-0.7	0.1	0.0	0.1	0.0	-0.2	-0.3	-0.6	0.1	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Y-Gd	Y-Th	Y-Dy	Y-Ho	Y-Er	Y-Tm	Y-Yb	Y-Hf	Y-Ta	Y-W	Y-ir	Y-Pr	Y-Au	Y-Pb	Y-Th	Zr-Nb	Zr-Mo	Zr-Ru	Zr-Rh	Zr-Pd	Zr-Ag	Zr-In	Zr-Sn	Zr-Ba	Zr-La	Zr-Ce	Zr-Pr	Zr-Nd	Zr-Sm	Zr-Cd	Zr-Th	Zr-Dy		
Z0	8.5	7.4	7.4	7.4	-0.2	2.7	-9.1	-76.1	-99.5	-73.9	-32.6	4.2	-5.7	-40.6	-45.5	-52.5	16.4	15.5	-0.9	79.5	35.9	33.6	31.5	31.4	29.5	29.4	27.5	27.4	27.8	25.5	25.4	25.3	
Z1	0.7	0.6	0.5	0.5	0.0	-0.2	0.0	-1.2	-4.2	-3.7	8.2	10.6	6.4	-1.0	0.0	-0.2	0.0	-0.2	5.8	6.9	6.5	1.1	-1.6	-3.4	12.9	1.8	1.5	1.2	1.0	1.0	0.8	0.7	
Z2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.6	0.4	-0.4	-0.3	0.4	0.0	0.0	-0.1	-0.6	-0.7	-0.4	-0.2	-0.2	-0.2	2.8	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	
Z3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.4	-0.8	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Zr-Ho	Zr-Er	Zr-Tm	Zr-Yb	Zr-Hf	Zr-Ta	Zr-W	Zr-ir	Zr-Pt	Zr-Nb	Zr-Mo	Zr-Ru	Zr-Rh	Zr-Pd	Zr-Ag	Zr-In	Zr-Sn	Nb-Ba	Nb-Ag	Nb-In	Nb-Sn	Nb-Pb	Nb-Ce	Nb-Pr	Nb-Nd	Nb-Sm	Nb-Cd	Nb-Th	Nb-Dy	Nb-Ho	Nb-Er	Nb-Tm	Nb-Yb	
Z0	8.5	7.4	7.4	7.4	-0.2	2.7	-9.1	-76.1	-99.5	-73.9	-32.6	4.2	-5.7	-40.6	-45.5	-52.5	16.4	15.5	-0.9	79.5	35.9	33.6	31.5	31.4	29.5	29.4	27.5	27.4	27.8	25.5	25.4	25.3	
Z1	0.7	0.6	0.5	0.5	0.0	-0.2	0.0	-1.2	-4.2	-3.7	8.2	10.6	6.4	-1.0	0.0	-0.2	0.0	-0.2	5.8	6.9	6.5	1.1	-1.6	-3.4	12.9	1.8	1.5	1.2	1.0	1.0	0.8	0.7	
Z2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.6	0.4	-0.4	-0.3	0.4	0.0	0.0	-0.1	-0.6	-0.7	-0.4	-0.2	-0.2	-0.2	2.8	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	
Z3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	-0.4	-0.8	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Nb-Hf	Nb-Ta	Nb-Yb	Nb-Pr	Nb-Ag	Nb-Ru	Nb-Pd	Nb-Sn	Nb-Pb	Nb-Mo	Nb-Rh	Nb-Pt	Nb-Au	Nb-ir	Nb-Sm	Nb-Cd	Nb-Th	Nb-Ba	Nb-Ag	Nb-In	Nb-Sn	Nb-Pb	Nb-Ce	Nb-Pr	Nb-Nd	Nb-Sm	Nb-Cd	Nb-Th	Nb-Dy	Nb-Ho	Nb-Er	Nb-Tm	Nb-Yb	
Z0	3.9	0.0	-8.3	-52.9	-66.5	-32.1	17.3	19.7	14.4	-15.0	-14.6	37.2	32.4	20.3	71.0	31.1	28.6	26.2	26.2	23.9	21.7	21.6	22.3	19.5	19.4	19.3	-4.0	-4.9	-0.2	-21.4	-27.7		
Z1	0.2	0.0	0.1	1.0	-0.4	-1.3	3.0	3.3	0.2	-0.2	-0.2	0.5	4.2	3.3	21.6	6.5	5.6	4.8	4.7	4.1	3.5	3.4	3.4	2.9	2.7	2.7	-0.3	-0.1	0.0	-0.1	-0.8	-0.8	
Z2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	-0.1	0.4	0.6	4.9	1.2	0.9	0.7	0.7	0.5	0.5	0.4	0.3	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Z3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Mo-Au	Mo-Pb	Mo-Th	Mo-Sm	Mo-Gd	Mo-Rh	Mo-Pd	Mo-Ag	Mo-In	Mo-Sn	Mo-Ba	Mo-La	Mo-Ce	Mo-Pr	Mo-Nd	Mo-Sm	Mo-Gd	Mo-Th	Mo-Sm	Mo-Gd	Mo-Th	Mo-Sm	Mo-Gd	Mo-Th	Mo-Sm	Mo-Gd	Mo-Th	Mo-Sm	Mo-Gd	Mo-Th	Mo-Sm	Mo-Gd	Mo-Th	Mo-Pr
Z0	3.4	41.6	12.8	1.2	6.2	23.4	9.9	4.0	6.1	-27.6	-29.5	-31.5	-31.4	-33.3	-33.2	-35.1	-35.0	-33.7	-36.7	-36.6	-36.5	-51.5	-39.4	-9.8	-0.6	-1.1	15.0	25.3	-44.3	1.9	9.5	-7.8	
Z1	0.2	8.2	2.4	0.0	0.2	0.4	1.3	0.7	1.9	-5.9	-6.0	-6.0	-5.8	-5.9	-5.8	-5.9	-5.6	-5.3	-5.6	-5.4	-5.2	-4.8	-1.5	-0.3	0.0	0.0	0.9	5.3	-9.1	0.0	0.1	-1.0	
Z2	0.0	1.7	0.5	0.0	0.0	-0.2	0.1	0.1	0.0	0.1	0.0	0.0	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	-0.2	-0.5	0.0	0.0	0.0	0.0	0.0	0.3	-0.2	0.0	0.0	0.0	
Z3	0.0	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Rh-Sn	Rh-Ba	Rh-La	Rh-Ce	Rh-Pr	Rh-Nd	Rh-Sm	Rh-Gd	Rh-Th	Rh-Yb	Rh-Hf	Rh-Ta	Rh-W	Rh-ir	Rh-Sm	Rh-Pd	Rh-Ag	Rh-La	Rh-Pr	Rh-Nd	Rh-Sm	Rh-Pd	Rh-Ag	Rh-La	Rh-Pr	Rh-Nd	Rh-Sm	Rh-Pd	Rh-Ag	Rh-La	Rh-Pr	Rh-Nd	Rh-Sm	
Z0	-83.7	-83.3	-81.9	-84.1	-83.7	-83.5	-80.2	-52.2	-6.5	6.0	2.0	0.1	-18.3	-89.9	-1.5	-2.9	-27.2	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	-29.3	
Z1	-11.6	-11.1	-10.6	-10.4	-9.8	-9.6	-5.2	-0.5	0.0	-0.1	0.0	0.0	-3.4	-16.1	-0.2	0.0	-0.0	-0.1	-0.9	-0.8	-0.7	-0.6	-0.5	-0.5	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	
Z2	-0.2	0.0	0.2	0.3	0.4	0.4	-0.3	0.1	0.0	0.0	0.0	0.0	-0.7	-3.3	0.0	-0.1	-1.8	-1.1	-0.9	-0.8	-0.7	-0.6	-0.5	-0.5	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	
Z3	0.6	0.7	0.7	0.7	0.7	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	
Pair Ag-ir	Ag-Pb	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th	Ag-Sm	Ag-Th	Ag-Ba	Ag-Th
Z0	15.5	-0.8	-5.5	2.6	-28.4	-0.3	-38.2	-38.4	-37.7	-36.9	-36.8	-36.1	-36.0	-35.3	-35.1	-34.6	-34.3	-34.1	-34.0	-17.6	13.4	37.9	-0.3	-21.3	-10.6	-0.7	-31.2	-47.4	-52.9	-52.2	-51.5	-51.4	-51.4
Z1	0.1	0.0	0.3	0.5	-4.5	0.0	-6.2	-2.6	-2.1	-1.6	-1.5	-1.1	-1.0	-0.7	-0.5	-0.4	-0.2	0.0	0.1	1.2	-1.6	-4.4	0.0	1.9	0.6	0.0	-1.4	-7.5	-2.9	-2.1	-1.5	-1.3	-1.3
Z2	-0.2	0.0	0.0	0.1	-1.0	0.0	-0.6	-0.2	-0.1	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	0.2	0.3	0.0	0.1	0.0	0.0	-0.2	0.1	0.2	0.3	0.4	0.4	
Z3	0.0	0.0	0.0	0.0	-0.2	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Sn-Sm	Sn-Gd	Sn-Th	Sn-Dy	Sn-Yb	Sn-Pr	Sn-Sm	Sn-ir	Sn-Sm	Sn-Hf	Sn-Th	Sn-W	Sn-ir	Sn-Pt	Sn-Sm	Sn-Pb	Sn-Th	Sn-Ba	Sn-Ce	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba	Sn-Gd	Sn-Ba
Z0	-50.8	-50.7	-50.1	-49.8	-49.1	-49.1	-48.9	-48.7	-35.3	-2.7	26.5	-5.1	-24.6	-10.3	1.6	-47.5	15.7	16.9	18.2	18.2	19.5	20.9	20.7	20.2	22.1	22.0	21.9	53.3	75.8	72.4	-13.9	-13.9	
Z1	-0.8	-0.7	-0.2	0.0	0.2	0.5	0.8	0.9	3.0	0.4	-4.0	0.8	3.3	1.0	0.1	-1.5	-1.6	-2.0	-2.3	-2.4	-2.7	-2.8	-3.1	-3.2	-3.2	-3.6	-3.7	-3.8	-13.6	-22.4	-21.1	-4.0	-4.0
Z2	0.0	0.2	0.4	0.4	0.4	0.4	0.4	0.4	-0.2	-0.1	0.7	-0.1	-0.5	-0.2	0.0	0.0	0.1	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Z3	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Pair Ba-Pb	Ba-Au	Ba-Pb	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	Ba-Ce	Ba-Th	B									

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[illegible]

Next, the effect of composition dependence of ΔH^{mix} on GFA for multi-component BMGs [11–26] was analyzed by calculating the ΔH^{mix} values by Eqs. (9–11), by comparing to the cases of $k = 0$ to 3 and $k = 0$, the latter of which corresponds to our previous studies [8,9]. The results are summarized in Table 3. Table 3 shows that the ΔH^{mix} varies a couple of kJ mol^{-1} by considering high order term of $k = 1$ –3. The large difference in ΔH^{mix} , $\Delta(\Delta H^{\text{mix}})$, between the two cases of $k = 0$ and $k = 0$ –3 are seen for $\text{La}_{0.62}(\text{Cu}_{5/6}\text{Ag}_{1/6})_{0.14}\text{Ni}_{0.05}\text{Co}_{0.05}\text{Al}_{0.14}$ BMG [21], (3.7 kJ mol^{-1}) and $\text{Zr}_{0.412}\text{Ti}_{0.138}\text{Cu}_{0.125}\text{Ni}_{0.1}\text{Be}_{0.225}$ [12] and $\text{Zr}_{0.57}\text{Ti}_{0.05}\text{Cu}_{0.2}\text{Ni}_{0.08}\text{Al}_{0.1}$ [22] BMGs (2.3 kJ mol^{-1}), followed by $(\text{Fe}_{0.8}\text{Co}_{0.2})_{0.48}\text{Cr}_{0.15}\text{Mo}_{0.14}\text{Ti}_{0.02}\text{C}_{0.15}\text{B}_{0.06}$ BMG [24] (2.2 kJ mol^{-1}). The former three BMGs possess a common feature of simultaneous inclusions of Ni and Cu, which cause 7% or greater differences in ΔH^{mix} . On the other hand, $\text{Pd}_{0.35}\text{Pt}_{0.15}\text{Cu}_{0.3}\text{P}_{0.2}$ [13] and $\text{Pd}_{0.4}\text{Ni}_{0.4}\text{P}_{0.2}$ [18] BMGs exhibit $\Delta(\Delta H^{\text{mix}}) = 0.4 \text{ kJ mol}^{-1}$, which account for less than 2%. The $\text{Pd}_{0.4}\text{Cu}_{0.3}\text{Ni}_{0.1}\text{P}_{0.2}$ BMG [11] exhibits a small $\Delta(\Delta H^{\text{mix}})$ of 1.2 kJ mol^{-1} but it accounts for 11.9% for the $\Delta H^{\text{mix}} = -10.1 \text{ kJ mol}^{-1}$. These results indicate that simultaneous additions of Ni and Cu greatly affects the composition dependence of ΔH^{mix} . A reason for this might be the positive value of ΔH^{mix} for Ni–Cu atomic pair. Specifically, the values of $(Q_0, Q_1, Q_2, Q_3)/\text{kJ mol}^{-1}$ shown in Table 2 for Ni–Cu are (3.6, -0.1 , 0.0 , 0.0) and the changes in ΔH^{mix} as a function of composition are shown in Fig. 3 (g) and (h). These values of Q_1 and ΔH^{mix} indicate that Ni–Cu atomic pair exhibits considerably weak composition dependence of ΔH^{mix} , but the presence of the Ni–Cu atomic pair in an alloy affect for the system, in which the other atomic pairs have negative ΔH^{mix} s. Besides, Table 4 shows that the simultaneous additions Ni and Cu in $\text{Pd}_{0.4}\text{Cu}_{0.3}\text{Ni}_{0.1}\text{P}_{0.2}$ [11] greatly affects the $\Delta(\Delta H^{\text{mix}})$, but less effects are seen individual addition of Cu or Ni in $\text{Pd}_{0.35}\text{Pt}_{0.15}\text{Cu}_{0.3}\text{P}_{0.2}$ [13] and $\text{Pd}_{0.4}\text{Ni}_{0.4}\text{P}_{0.2}$ [18]. Thus, it is possible that Pd-based BMGs containing either Ni or Cu do not have strong composition dependence of ΔH^{mix} . Hence, we tentatively conclude that simultaneous additions of Ni and Cu with positive ΔH^{mix} affect the composition dependence of ΔH^{mix} for BMGs.

We analyzed the effect of R term in Miedema's scheme on ΔH^{mix} for the atomic pairs consisting of NM-NTM. Here, NM is composed

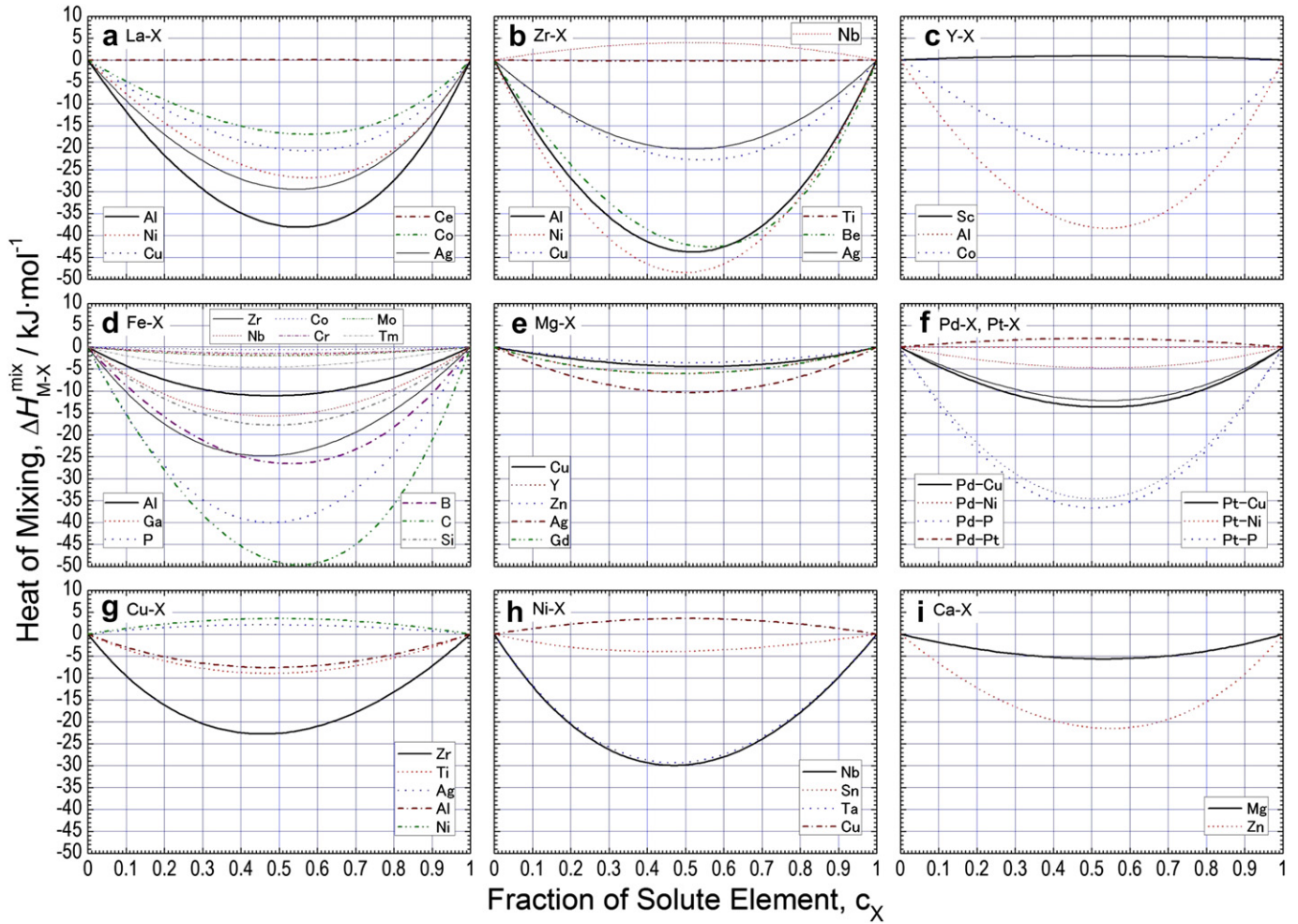


Fig. 3. Calculated ΔH^{mix} values of representative BMG systems.

of Cu, Ag or Au, whereas NTM is from either metalloids (B, C, N, Si, P, Ge or As), alkaline-, alkaline-earth metals or metallic elements in group B in the periodic elements. In a framework of the analysis, we also focused on the ΔH^{mix} of NM-NTM including Si or Ge as MLD.

The reason for discussing R term in this Section is due to the description in Section 2 that we adopted different calculation procedure of R term for NM between our previous studies [8,9] and the present study. The values of \mathcal{Q}_i ($i = 1$ to 3) for above NM-NTM

Table 3

Representative bulk metallic glasses (BMGs) and their ΔH^{mix} values calculated by Eqs. (9) for (a) $k = 0$ to 3 and (b) $k = 0$, and (c) the difference in these values in absolute units and (d) percentages.

BMG	Ref.	$\Delta H^{\text{mix}}/\text{kJ mol}^{-1}$		$ \Delta(\Delta H^{\text{mix}}) /\text{kJ mol}^{-1}$ (c) = (a)–(b)	Difference (d) = (c)/ (a)
		^a (a)	^b (b)		
Pd _{0.4} Cu _{0.3} Ni _{0.1} P _{0.2}	[11]	–10.1	–9.1	1.2	11.9%
Zr _{0.412} Ti _{0.138} Cu _{0.125} Ni _{0.1} Be _{0.225}	[12]	–32.9	–34.8	2.3	7.0%
Pd _{0.35} Pt _{0.15} Cu _{0.3} P _{0.2}	[13]	–28.4	–28.2	0.4	1.4%
Zr _{0.55} Al _{0.10} Ni _{0.05} Cu _{0.30}	[14]	–29.2	–31.0	1.8	6.2%
Mg _{0.595} Cu _{0.229} Ag _{0.066} Gd _{0.11}	[15]	–8.7	–8.5	0.6	6.9%
Mg _{0.54} Cu _{0.265} Ag _{0.085} Gd _{0.11}	[16]	–9.5	–9.3	0.6	6.3%
Zr _{0.48} Cu _{0.36} Ag _{0.08} Al _{0.08}	[17]	–25.5	–26.2	0.8	3.1%
Pd _{0.4} Ni _{0.4} P _{0.2}	[18]	–23.1	–22.8	0.4	1.7%
Y _{0.36} Sc _{0.20} Al _{0.24} Co _{0.20}	[19]	–33.8	–34.6	0.9	2.7%
(La _{0.7} Ce _{0.3}) _{0.65} Co _{0.25} Al _{0.10}	[20]	–21.5	–22.8	1.7	7.9%
La _{0.62} {(Cu _{5/6} Ag _{1/6}) _{0.14} Ni _{0.05} Co _{0.05} }Al _{0.14}	[21]	–23.6	–27.3	3.7	15.7%
Zr _{0.57} Ti _{0.05} Cu _{0.2} Ni _{0.08} Al _{0.1}	[22]	–29.5	–31.7	2.3	7.8%
Pt _{0.425} Cu _{0.27} Ni _{0.095} P _{0.21}	[23]	–26.7	–27.0	0.5	1.9%
(Fe _{0.8} Co _{0.2}) _{0.48} Cr _{0.15} Mo _{0.14} Tm _{0.02} C _{0.15} B _{0.06}	[24]	–32.9	–33.3	2.2	6.7%
Pt _{0.60} Cu _{0.16} Ni _{0.02} P _{0.22}	[23]	–26.7	–27.4	0.7	2.6%
Mg _{0.54} Cu _{0.28} Ag _{0.07} Y _{0.11}	[16]	–9.3	–9.1	0.6	6.5%
Ca _{0.65} Mg _{0.15} Zn _{0.2}	[25]	–12.5	–13.7	1.2	9.6%
Zr _{0.585} Nb _{0.028} Cu _{0.156} Ni _{0.128} Al _{0.103}	[26]	–14.6	–15.0	0.9	6.2%

^a Eq. (9) for $k = 0-3$.

^b Eq. (9) for $k = 0$.

Table 4
The relationships between the ΔH^{mix} values for Cu-, Ag- and Au-containing systems in our previous studies [8,9] and the present study (a) ΔH^{mix} value at $A_{0.5}X_{0.5}$ alloy composition obtained in our previous studies [8,9]. (b) \mathcal{Q}_0 value obtained in the present study. Note that $\mathcal{Q}_0 = \Delta H^{\text{mix}}$ at $A_{0.5}X_{0.5}$ in an A–B alloy. (c) Difference in ΔH^{mix} value at $A_{0.5}X_{0.5}$ in our previous studies and \mathcal{Q}_0 value in the present study: (a)–(b).

(a)	1	3	4	5	6	7	11	12	13	14	15	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	37	38	39	40	41	42	43	44	45	46	47
	H	Li	Be	B	C	N	Na	Mg	Al	Si	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
29 Cu	–6	–5	0	0	–33	–84	16	–3	–1	–19	–17.5	25	–13	–24	–9	5	12	4	13	6	4	–	1	1	–11.5	–3	27	–9	–22	–23	3	19	8	7	–2	–14	2
47 Ag	–10	–16	6	5	–32	–94	0	–10	–4	–20	–18.5	7	–28	–28	–2	17	27	13	28	19	15	2	–4	–5	–17.5	–8	7	–27	–29	–20	16	37	24	23	10	–7	–
79 Au	–8	–37	0	–2	–20	–58	–14	–32	–22	–30	–13.5	–9	–60	–74	–47	–19	0	–11	8	7	7	–9	–16	–19	–21.5	–11	–10	–59	–74	–74	–32	3	14	15	7	0	–6
	48	49	50	51	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	90	92	94	–
	Cd	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	Pu	–
29 Cu	6	10	7	7	28	–9	–21	–21	–22	–22	–23	–22	–10	–22	–23	–22	–22	–23	–23	–12	–24	–17	2	22	18	10	0	–12	–9	8	15	15	15	–24	–7	–9	–
47 Ag	–2	–2	–3	–4	8	–28	–30	–30	–30	–29	–30	–30	–27	–29	–29	–29	–29	–29	–29	–28	–30	–13	15	43	38	28	16	–1	–6	–1	3	3	2	–29	0	–6	–
79 Au	–11	–11	–10	–4	–9	–60	–73	–73	–73	–73	–75	–74	–58	–74	–74	–74	–72	–74	–74	–59	–75	–63	–32	12	20	18	13	4	Au	–4	–2	2	2	–78	–43	–45	–
(b)	1	3	4	5	6	7	11	12	13	14	15	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	37	38	39	40	41	42	43	44	45	46	47
	H	Li	Be	B	C	N	Na	Mg	Al	Si	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
29 Cu	–13.6	–4.8	–1.1	–6.4	–38.4	–86.8	15.2	–4.4	–7.6	–9.2	–26.3	24.2	–12.2	–23.9	–8.9	5.0	12.5	3.8	12.9	6.4	3.6	–	–3.7	–5.5	–6.7	–11.9	25.6	–8.7	–21.8	–22.6	2.6	18.5	8.2	7.0	–2.5	–13.6	2.2
47 Ag	–9.6	–15.7	6.2	5.4	–31.7	–88.2	0.4	–10.4	–4.4	–3.3	–18.3	6.2	–27.9	–28.3	–1.5	16.9	27.0	12.7	28.1	19.0	15.5	2.2	–3.8	–5.0	–5.3	–8.4	6.9	–26.8	–29.3	–20.3	16.4	37.2	24.4	23.4	9.5	–7.3	–
79 Au	–8.4	–37.0	–0.1	–2.4	–19.6	–55.5	–14.2	–31.5	–21.6	–13.0	–13.3	–9.0	–59.0	–73.7	–47.4	–19.2	–0.2	–11.3	8.0	7.2	7.1	–8.8	–16.3	–19.2	–9.4	–10.7	–9.0	–57.4	–72.9	–73.9	–32.1	3.4	13.7	15.0	7.1	0.1	–5.5
	48	49	50	51	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	90	92	94	–
	Cd	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	Pu	–
29 Cu	0.6	2.4	–1.0	–1.8	26.6	–8.2	–20.2	–20.8	–21.3	–21.3	–22.5	–21.8	–21.8	–21.8	–22.3	–22.2	–21.6	–22.6	–22.5	–22.5	–23.6	–16.9	1.9	22.5	18.2	10.3	0.2	–12.1	–8.8	2.4	8.1	7.3	6.1	–23.9	–6.8	–9.4	–
47 Ag	–2.2	–1.5	–2.9	–3.6	7.5	–27.2	–29.3	–29.3	–29.3	–29.3	–30.0	–29.3	–29.3	–29.3	–29.3	–29.1	–28.4	–29.1	–29.0	–28.9	–29.5	–12.6	15.1	43.1	38.1	28.2	15.5	–0.8	–5.5	–0.8	2.8	2.6	1.9	–28.4	0.2	–6.0	–
79 Au	–10.7	–10.6	–10.3	–3.9	–8.9	–58.2	–71.7	–72.2	–72.7	–72.5	–74.4	–73.1	–73.0	–72.9	–73.5	–73.1	–71.7	–73.5	–73.2	–73.0	–74.8	–63.3	–32.3	11.5	19.8	17.9	12.6	4.4	–	–4.1	–1.7	2.2	1.8	–77.3	–43.1	–44.6	–
(c)	1	3	4	5	6	7	11	12	13	14	15	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	37	38	39	40	41	42	43	44	45	46	47
	H	Li	Be	B	C	N	Na	Mg	Al	Si	P	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
29 Cu	7.6	–0.2	1.1	6.4	5.4	2.8	0.8	1.4	6.6	–9.8	8.8	0.8	–0.8	–0.1	–0.1	0	–0.5	0.2	0.1	–0.4	0.4	–	4.7	6.5	–4.8	8.9	1.4	–0.3	–0.2	–0.4	0.4	0.5	–0.2	0	0.5	–0.4	–0.2
47 Ag	–0.4	–0.3	–0.2	–0.4	–0.3	–5.8	–0.4	0.4	0.4	–16.7	–0.2	0.8	–0.1	0.3	–0.5	0.1	0	0.3	–0.1	0	–0.5	–0.2	–0.2	0	–12.2	0.4	0.1	–0.2	0.3	0.3	–0.4	–0.2	–0.4	–0.4	0.5	0.3	0
79 Au	0.4	0	0.1	0.4	–0.4	–2.5	0.2	–0.5	–0.4	–17	–0.2	0	–1	–0.3	0.4	0.2	0.2	0.3	0	–0.2	–0.1	–0.2	0.3	0.2	–12.1	–0.3	–1	–1.6	–1.1	–0.1	0.1	–0.4	0.3	0	–0.1	–0.1	–0.5
	48	49	50	51	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	90	92	94	–
	Cd	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	Pu	–
29 Cu	5.4	7.6	8	8.8	1.4	–0.8	–0.8	–0.2	–0.7	–0.7	–0.5	–0.2	11.8	–0.2	–0.7	0.2	–0.4	–0.4	–0.5	10.5	–0.4	–0.1	0.1	–0.5	–0.2	–0.3	–0.2	0.1	–0.2	5.6	6.9	7.7	8.9	–0.1	–0.2	0.4	–
47 Ag	0.2	–0.5	–0.1	–0.4	0.5	–0.8	–0.7	–0.7	0.3	0	–0.7	2.3	0.3	0.3	0.3	0.1	–0.6	0.1	0	0.9	–0.5	–0.4	–0.1	–0.1	–0.1	–0.2	0.5	–0.2	–0.5	–0.2	0.2	0.4	0.1	–0.6	–0.2	0	–
79 Au	–0.3	–0.4	0.3	–0.1	–0.1	–1.8	–1.3	–0.8	–0.3	–0.5	–0.6	–0.9	15	–1.1	–0.5	–0.9	–0.3	–0.5	–0.8	14	–0.2	0.3	0.3	0.5	0.2	0.1	0.4	–0.4	–	0.1	–0.3	–0.2	0.2	–0.7	0.1	0.4	–

atomic pairs are summarized in Table 4, together with the ΔH^{mix} at $A_{0.5}B_{0.5}$ alloy composition obtained in our previous studies [8,9]. The Table 4 (a) and (b) show the data in our previous study [8,9] and the current study, respectively, whereas Table 4 (c) summarizes the difference in ΔH^{mix} s between (a) and (b). Table 4 (c) shows that differences of ΔH^{mix} s between the previous and current studies are smaller than 1 kJ mol^{-1} for NM-TM pairs, whereas those are in the order of several kJ mol^{-1} for the other pairs including NTM. Here, it should be noted that Table 4(c) shows relatively large difference in ΔH^{mix} for Si- and Ge-containing alloys. However, these large differences are due to $\Delta H^{\text{trans.}}$ [3] for the Si (34 kJ mol^{-1}) and Ge (25 kJ mol^{-1}), and are resulted from different definitions for dealing with $\Delta H^{\text{trans.}}$ between our previous studies [8,9] and the current study. Hence, the large difference in ΔH^{mix} s for Si- and Ge-containing alloy in Cu, Ag and Au systems is not considerable results that should be taken into account.

Instead, much more important difference in ΔH^{mix} s is seen in Table 4 for Cu–Al atomic pair. Table 4 shows that Cu–Al atomic pair exhibits ΔH^{mix} s/ kJ mol^{-1} of -1 for (a), -7.6 for (b), and resultant 6.6 for (c). This difference in ΔH^{mix} s is of great importance when considering that Cu and Al are frequently included in amorphous and glassy alloys as well as BMGs as constituent elements. Of the NM consisting of Cu, Ag and Au, it was found that the R term tends to affect greatly for Cu-metalloid atomic pairs than Ag- and Au-metalloid atomic pairs. One reason for Cu element to exhibit the greater effect on R should be the parameters for evaluating R/P : Cu, Au (0.3) > Ag (0.15) [3] as described in Section 2, since these parameters directly affect the R term. However, only R/P values for Cu and Ag do not account for the similarity in behavior because of the same values of 0.3 is assigned for Cu and Au. A possible another reason may be the difference in ϕ 's between NM-NTM where ϕ for Cu, Ag and Au is 4.45 , 4.35 and 5.15 V [3,4], respectively. Besides, other parameters in Miedema's scheme, such as, n_{WS} and V also can be candidates for explaining the greater effect on R for Cu. The NMs of Cu, Ag and Au in Miedema's scheme have (n_{WS} and $V/10^{-6} \text{ m}^3 \text{ mol}^{-1}$) = (3.18 and 7.12) for Cu, (2.52 and 10.25) for Ag and (3.87 and 10.20) for Au. Considerations for parameters R^*/P , ϕ , n_{WS} and V among Cu, Ag and Au suggests that Ag and Au have a similar tendency for V . Accordingly, it is considered that similar tendencies in V for Ag and Au, accompanied by R^*/P greatly affect R term, leading to the difference in ΔH^{mix} between Cu and other elements of Pt and Au. Thus, it is concluded that modification of R term in the present study principally affects ΔH^{mix} values for the Cu-containing alloys system; in particular, for Cu-NTM atomic pairs.

4. Conclusions

We have performed the most accurate and reliable calculations of mixing enthalpy (ΔH^{mix}) as a function of composition in an alloy system in a framework of Miedema's scheme. We have shown that ΔH^{mix} of a liquid phase based on Miedema's scheme for all the possible 2628 binary systems can be approximated by a sub-regular solution model with interaction parameter (Q) of the third order

dependence on composition of an alloy. The composition dependence of ΔH^{mix} is not strong for conventional alloy systems even for metal-metalloid systems, except for some of the H-, C- and N-containing alloys. The analysis for bulk metallic glasses (BMGs) revealed that simultaneous inclusions of Ni and Cu in La-, Zr- and Pd-based BMGs cause marked differences in ΔH^{mix} , compared to the zero-order approximation of Q . Another peculiar composition dependence of ΔH^{mix} is found for P and C in Fe–P and Fe–C binary alloys, in which the values of ΔH^{mix} at a fraction of solute element of P or C ~ 0.2 are the same, whereas Fe–C alloy has the large and negative value of ΔH^{mix} than Fe–P alloy at higher fraction up to 0.5 . In a framework of Miedema's scheme, the present study differs from both the original literature and the authors' previous works in point that the original and previous works deal with ΔH^{mix} only at the equi-atomic composition or the dilute limits of solute and solvent elements. This difference makes it possible for the present study to show these marked and peculiar behaviors of ΔH^{mix} . In the present study we have provided a table for Q 's for 1378 systems from 53 elements that are involved in BMGs as well as amorphous and glassy alloys. We think that this table for Q 's provides a great benefit of further understanding the forming ability of the amorphous and glassy alloys.

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