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Influencing factors of atomic order in the binary sigma phase

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Abstract

The present work brings new insights into the influencing factors of atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal structure) of the binary sigma phase. We have calculated the volumes and atomic charges of the constituent elements of 32 stoichiometric end-member compounds (i.e. the complete set of ordered configurations) of the binary sigma phase by using first-principles calculations. The calculation results show that besides size factor and the number of valence electrons, the total number of

electron shells is found as the third factor that affects the atomic order of the sigma phase. Moreover, the calculation results indicate that between the two constituent elements, the one with a larger atomic size, smaller number of valence electrons or smaller total number of electron shells prefers occupying large coordination number (CN) sites (i.e. 4f, 8i₁, 8j) and the other prefers occupying small CN sites (i.e. 2a, 8i₂). Furthermore, we have dissociated the effect of individual influencing factor on atomic order of the sigma phase combining with the measured site occupancies from the literature.

Keywords: sigma phase, atomic order, atomic charge, size factor, number of valence electrons, total number of electron shells.

1. INTRODUCTION

The sigma phase is a non-stoichiometric intermetallic compound that crystallizes in a tetragonal structure (space group P4₂/mnm) with 30 atoms distributed on five inequivalent sites, namely 2a, 4f, 8i₁, 8i₂ and 8j¹⁻³. It is a hard, brittle phase mostly formed between transition elements. It deteriorates various properties of stainless and other high-alloy steels as well as Ni-based superalloys¹⁻².

The investigation of the sigma phase has attracted many interests since 1950s⁴. There are numerous investigations on the atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal structure) of the sigma phase, e.g. (Ref. 1-2, 5-17), by using XRD (X-ray diffraction), ND (neutron diffraction), mathematical methods or first-principles calculations. At first, Kasper and Waterstrat⁶ indicated that 2a and 8i₂ sites should be occupied by elements to the right of Mn in the periodic table; 4f site by elements to the left and 8i₁ and 8j sites by a mixture of both. Spooner and Wilson⁸ stated that the size of the constituent atoms was a

major factor in governing the filling of 2a, 4f, and 8i₂ sites but in addition some valence electron factor governed the filling of 8i₁ and 8j sites. Afterwards, a systematic review of the sigma phase was conducted by Hall and Algie¹ and then by Joubert². They indicated that atoms with large size or poor in *d*-electrons preferentially occupy sites with large coordination number (CN), namely 4f, 8i₁ and 8j; atoms with small size or rich in *d*-electrons preferentially occupy sites with small CN, namely 2a and 8i₂.

However, all the conclusions above cannot explain the measured site occupancies of the sigma phase perfectly. The main reason is that the size factor and the number of valence electrons are not enough to explain the atomic order. Taking Re-Mn system as an example, the numbers of valence electrons of Re (5d⁵6s²) and Mn (3d⁵4s²) are the same so the size factor should be the primary influencing factor on the atomic order. However, large differences can be observed in the site occupancies measured for sites with the same CN (8i₁ vs 8j, CN=14) and thus with similar size, as discussed in the following Section 3.2. In fact, the experimental site occupancies show that the atomic order among the large CN sites (i.e. 4f, 8i₁, 8j) or between the small CN sites (i.e. 2a, 8i₂) can be very large, more examples being Nb-Re (4f vs 8i₁ / 8j)², Re-Fe (8i₁ vs 8j)². The early conclusions¹⁻² about the atomic order cannot distinguish among the large CN sites or the small CN sites.

In addition, Sluiter et al. calculated the site occupancies of the sigma compounds in Cr-Fe¹⁴, Os-Cr¹⁷, Re-Ta¹⁵, Re-W¹⁵⁻¹⁶ and Ru-Cr¹⁷ systems by using a first-principle statistical thermodynamic approach. Their calculation results do not fit the experimental data very well, especially for Cr-Fe¹⁴ and Os-Cr¹⁷ systems because of their simplified assumptions. They confirmed the influencing factors on atomic order of Ru-Cr and Os-Cr systems from the perspective of the crystal structure¹⁷. They considered 1) the size factor (the size difference among the five inequivalent sites), 2)

electronic degeneracy arguments and 3) the pairwise interaction (A-A, A-B or B-B) within the sigma unit cell. It was indicated that their conclusion has no predictive value¹⁷. Actually, their argument about the pairwise interaction was based on the deduction that all five crystal sites were equivalent as Cr and Ru/Os do not have an overwhelming preference for any of the sites. However, this deduction is not totally correct, which will be discussed in Section 3.2.3.

Besides, Crivello et al.⁵ systematically discussed the site occupancy behavior of the sigma phase in binary Re-X (X= Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Os, Ru, Ta, Tc, Ti, V, W and Zr) systems using the compound energy formalism (CEF) combined with first-principles calculations. These studied systems include stable sigma compounds (Re-V, Re-Cr, Re-Mn, Re-Fe, Nb-Re, Mo-Re, Ta-Re and W-Re) and as well as some hypothetically unstable ones (Ti-Re, Zr-Re, Hf-Re, Re-Co, Re-Ni, Re-Tc, Re-Ru and Re-Os). The site occupancies of the above binary sigma compounds were calculated at 2000K (see Fig. 9 in Ref. (5)) and Crivello et al.⁵ proposed that the site occupancy behavior of the binary sigma phase is related to whether Re bears a larger size than the other constituent element or not. The site occupancy behavior between the same CN (i.e. CN12: 2a vs 8i₂; CN14: 8i₁ vs 8j) sites were not clearly clarified. If Re bears a larger size (e.g. for Re-V, Re-Cr, Re-Mn, Re-Fe, Re-Co, Re-Ni, Re-Tc, Re-Ru and Re-Os systems), the site occupancy preference for Re atom follows $4f > 8i_1 > 8j > 8i_2 > 2a$ and if Re bears a smaller size (e.g. for Nb-Re, Mo-Re, Ta-Re, W-Re, Ti-Re, Zr-Re and Hf-Re systems), the site occupancy preference for Re atom follows $8i_2/2a > 8i_1/8j > 4f$. However, for Re-Os, Re-Ru and Re-V systems where Re bears a larger size, the calculation results showed that the site occupancy preference for Re atom follows $8j > 8i_1$ (for Re-Os and Re-Ru systems) and $8i_2 > 8j$ (for Re-V system) which is inconsistent with the above conclusion. Besides, from the experimental perspective, for Re-V system the site

occupancy sequence follows $8i_2 > 2a > 8i_1 > 4f > 8j$ (see Section 3) which is almost the opposite sequence as the one proposed by Crivello et al.⁵

At present, plentiful site occupancy measurements have been conducted on the binary sigma compounds with high accuracy, but the influencing factors on the atomic order of the sigma compounds are still not clear. Apparently, size factor and the number of valence electrons are not enough for the explanation of the atomic order. Another obstacle to sort out the connections is that the experimental site occupancies are results of competition and cooperation of the influencing factors on atomic order and it is hard to dissociate the effect of individual influencing factor, as sometimes for a specific system, different factors have similar effects¹⁴ (e.g. for Cr-Fe system, larger size and also poorer in *d*-electrons of Cr comparing to Fe both cause Cr preferentially occupy sites with large CN).

In the present work, besides the size factor and the number of valence electrons, we also considered the total number of electron shells as an influencing factor affecting the atomic order of the sigma compounds. Finally, we dissociated the effect of individual influencing factor on atomic order. It is noteworthy that the present findings have predictive ability. To facilitate explanation, all the binary sigma compounds investigated were designated as A-B where the size of atom A is always larger than that of atom B. The sizes of the constituent elements (A and B) are determined by the molar volumes of their pure elements in the sigma phase structure from the CALPHAD assessments¹⁸. Besides, the site occupancy of atom A was given in the present work. Atom B complements atom A on different sites. We use $Y_S(A)$ to denote the site occupancy of atom A on site S. The site occupancy of atom B on site S is equal to $1 - Y_S(A)$. The sequence of atomic order of atom A was given in the present work. For example, the sequence of atomic order,

$4f > 8i_1 > 8j > 8i_2 > 2a$, denotes a descending site occupancy preference of atom A from the site 4f to 2a. The sequence of atomic order of atom B is the opposite.

2. METHODOLOGY AND CALCULATION DETAILS

2.1. First-principles calculations

The first-principles calculations were performed using the plane wave method with projector augmented wave (PAW) pseudo-potentials¹⁹, as implemented in the Vienna ab initio simulation package (VASP)²⁰. We used the exchange-correlation functional within the generalized gradient approximation (GGA) as parameterized by Perdew and Wang (i.e. GGA-PW91)²¹. The magnetic parameter for ferromagnetism was set and spin-polarized calculations were conducted. The structure was fully relaxed and after the relaxation, a final static calculation was performed by adopting tetrahedron method with Blöchl corrections. A large plane-wave cutoff energy of 400 eV was used. The k-point meshes (8*8*15) for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme²². The convergence criteria for electronic self-consistency and ionic relaxation were 10⁻⁵ eV/atom and 10⁻⁴ eV/atom, respectively. These settings ensure the energy converge to at least 1 meV/atom. To facilitate the calculations, ZenGen script-tool was used to automatically generate input files for VASP calculations²³.

2.2. Bader Charge Analysis

Bader charge analysis was developed by Richard Bader. It is an intuitive way of dividing molecules into atoms with definition of an atom based purely on the electronic charge density²⁴. Zero flux surfaces on which the charge density is a minimum perpendicular to the surface were

used to divide atoms. Typically in molecular systems, the charge density reaches a minimum between atoms where is a natural place to separate atoms from each other ²⁴.

Because the Bader analysis assumes that charge density maxima are located at the center of an atom, in the present calculations, the total charge was obtained by summing the core charge and the valence charge from the VASP code and the Bader analysis was done on this total charge density file.

After the calculation, we can obtain the electronic charges and atomic volumes of 30 atoms for each compound. To get the atomic charge for each atom, we use the valence electrons (for which the valence states were set by VASP calculation) minus the calculated electronic charge. The negative value of atomic charge indicates atom tends to gain electrons and the positive one indicates atom tends to lose electrons.

3. RESULTS AND DISCUSSION

In the present work, besides the size factor and the number of valence electrons (e), the total number of electron shells (s) is also considered to clarify the regularity of the atomic order of the sigma phase. We classify the A-B binary sigma systems involving transition elements according to the electron configuration of the constituent elements as shown in Fig. 1. The A-Al ($A = \text{Nb}$ and Ta) systems, for which the main element Al is concerned, are classified into a separate category. The reason will be discussed in the following sections.

The systems with experimental site occupancies available are as follows:

1) ***SMe*** (atom A is with the smaller number of valence electrons than atom B)

V-Mn ($3d^34s^2, 3d^54s^2$), *V-Fe* ($3d^34s^2, 3d^64s^2$), *V-Co* ($3d^34s^2, 3d^74s^2$), *V-Ni* ($3d^34s^2, 3d^84s^2$), *Cr-Mn* ($3d^54s^1, 3d^54s^2$), *Cr-Fe* ($3d^54s^1, 3d^64s^2$), *Cr-Co* ($3d^54s^1, 3d^74s^2$) *W-Re* ($5d^46s^2, 5d^56s^2$);

2) LAs (atom A is with the larger total number of electron shells than atom B)

Re-Mn ($5d^56s^2, 3d^54s^2$);

3) LAs-LAe (atom A is with the larger total number of electron shells and the larger number of valence electrons than atom B)

Ru-Cr ($4d^75s^1, 3d^54s^1$), *Re-Cr* ($5d^56s^2, 3d^54s^1$), *Re-V* ($5d^56s^2, 3d^34s^2$), *Os-Cr* ($5d^66s^2, 3d^54s^1$);

4) LAs-SMe (atom A is with the larger total number of electron shells and the smaller number of valence electrons than atom B)

Mo-Mn ($4d^55s^1, 3d^54s^2$), *Mo-Fe* ($4d^55s^1, 3d^64s^2$), *Mo-Co* ($4d^55s^1, 3d^74s^2$), *Ta-Rh* ($5d^36s^2, 4d^85s^1$),

Ta-Pd ($5d^36s^2, 4d^{10}$), *W-Ru* ($5d^46s^2, 4d^75s^1$), *Re-Fe* ($5d^56s^2, 3d^64s^2$);

5) SMs-SMe (atom A is with the smaller total number of electron shells and the smaller number of valence electrons than atom B)

Nb-Re ($4d^45s^1, 5d^56s^2$), *Nb-Os* ($4d^45s^1, 5d^66s^2$), *Nb-Ir* ($4d^45s^1, 5d^76s^2$), *Nb-Pt* ($4d^45s^1, 5d^96s^1$), *Mo-*

Re ($4d^55s^1, 5d^56s^2$), *Mo-Os* ($4d^55s^1, 5d^66s^2$), *Mo-Ir* ($4d^55s^1, 5d^76s^2$);

6) A-Al (A= *Nb* and *Ta*)

Nb-Al ($4d^45s^1, 3s^23p^1$), *Ta-Al* ($5d^36s^2, 3s^23p^1$).

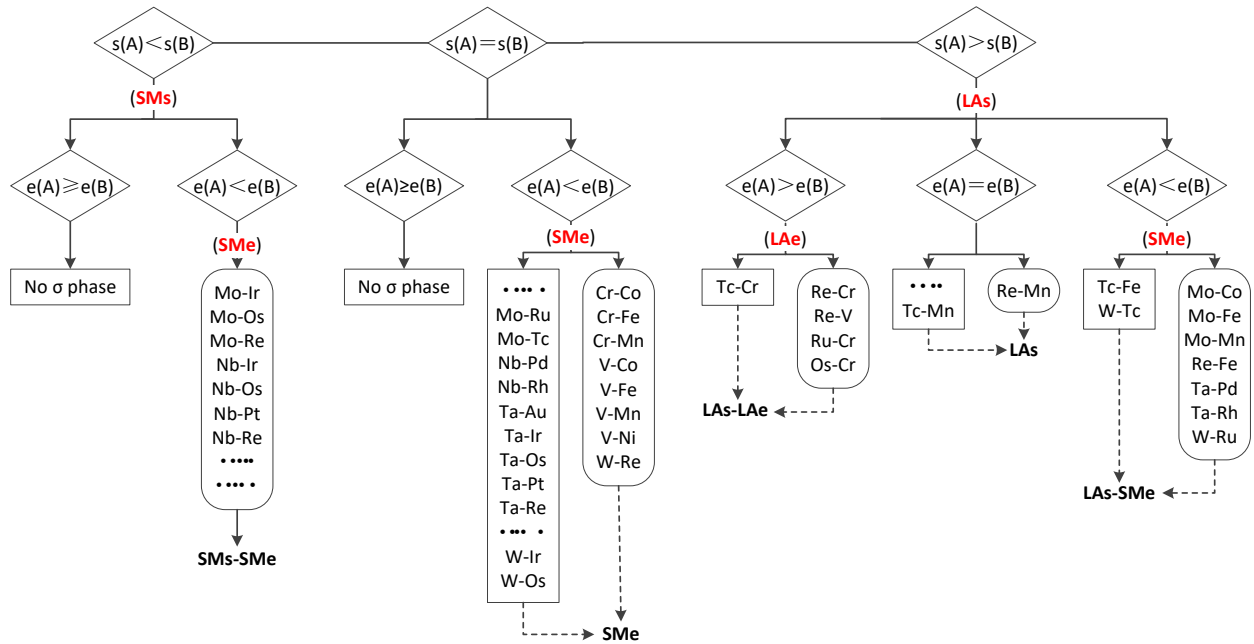


Fig. 1 A-B ($V(A) > V(B)$, where $V(A)$ and $V(B)$ are the molar volumes of element A and B in their hypothetical sigma phase structure from the CALPHAD assessments¹⁸ respectively) binary sigma systems divided into different categories according to the electron configuration of the constituent elements. The right angled rectangle indicates no sigma phase existing or no experimental site occupancies available for the included systems; the rounded rectangle indicates experimental data for site occupancies are available for the included systems. Note that the existence of the sigma phase in Cr-Ni, Ta-V, Ti-Mn, Zr-Ir and Zr-Re systems is not conformed. (LAs: Atom A is with the larger total number of electron shells than atom B; LAe: Atom A is with the larger number of valence electrons than atom B; SMs: Atom A is with the smaller total number of electron shells than atom B; SMe: Atom A is with the smaller number of valence electrons than atom B.)

3.1. Size and electronic factors affecting atomic order

3.1.1. Size factor

The size factor has twofold meanings. The first is the size difference among crystal sites. Both CN and nearest neighbor (NN) sites affect the size difference of sites, which will be discussed in the following 3.1.1(a). The second is the atomic size difference between the constituent elements, which was discussed in Section 1. If only the size factor affecting atomic order is considered, it is obvious that among the two constituent elements, the one with a large atomic size preferentially occupy sites with large size.

As respect to the atomic size sequence of the same element, normally, it follows the occupied site size sequence. However, it may not be always true owing to the influences of unlike NN atoms on atomic volume, which will be discussed in the following 3.1.1(b).

In the following discussion and shown in Fig. 2-5, the atomic charge indicates the tendency of electron loss or gain. When the value is negative, it means the atom tends to gain the corresponding number of electrons; when the value is positive, the atom tends to lose electrons.

(a) Size difference among the five inequivalent sites

To clarify the size difference among the five inequivalent sites of the sigma phase, we calculated the atomic volume and the corresponding atomic charge of the two constituent elements in the complete set ($2^5=32$) of ordered configurations (i.e. the stoichiometric end-member compounds in the following discussions) of the sigma phase for different binary systems. Fig. 2 presents the atomic volume varies with the atomic charge of the constituent elements in the 32 stoichiometric end-member compounds for 12 typical sigma phase systems. For systems in SMe, SMs-SMe categories and some systems (i.e. Ta-Pd and Ta-Rh systems) in LAs-SMe category, a nearly linear relationship with a constant slope can be observed between atomic volume and atomic charge for atoms on a specific site; for systems in LAs, LAs-LAe, A-Al (A= Nb and Ta) categories and a

system (i.e. Mo-Mn system) in LAs-SMe category, no evident linear relationship can be observed as the atomic volume difference for a specific site when occupied by either A or B can be very large, even when the atomic charge is constant. The large difference is due to the influence of NN atoms which will be discussed in Section 3.1.1. (b).

Fig.3 shows the atomic volume versus atomic charge of the pure elements in the hypothetical sigma structure. In this respect, we can observe that the size difference among the five inequivalent sites without the effect of unlike NN atoms. If we consider a linear relation (with an almost constant slope) between atomic volume and atomic charge as observed in Fig. 2, and extrapolate to a specific atomic charge (e.g. the vertical line in Fig.3), we can obtain the corresponding atomic volumes for all five sites. Then we can propose from Fig.3 that the site size sequence is as follows:

$4f_{(CN15)} > 8i_{1(CN14)} > 8j_{(CN14)} > 8i_{2(CN12)} > 2a_{(CN12)}$. This result agrees with the weighted average of the interatomic distances reported for Cr-Fe sigma by Hall and Algie [1], i.e. $2.701 \text{ \AA} (4f) > 2.652 \text{ \AA} (8i_1) > 2.638 \text{ \AA} (8j) > 2.526 \text{ \AA} (8i_2) > 2.508 \text{ \AA} (2a)$.

The above results follow the analysis by considering crystal structure. Firstly, sites with large CN (i.e. CN=14 or 15) are expected to bear a large size, as with more surrounding atoms the space of a site is larger. Thus the size difference among different CN sites are expected to be $4f_{(CN15)} > 8i_{1(CN14)}/8j_{(CN14)} > 8i_{2(CN12)}/2a_{(CN12)}$. Secondly, regarding the sites with the same CN, namely CN14 (i.e. $8i_1$ and $8j$) and CN12 (i.e. $8i_2$ and $2a$), we should consider the effect of the NN sites. The size of the site is expected to be larger when the surrounding small CN sites (i.e. CN=12) are fewer, which implies that the surrounding large CN sites are more. Table 1 shows the number of the NN sites for the five inequivalent sites of the sigma phase. The $8i_1$ site is surrounded by 4 CN12 sites and the $8j$ site is surrounded by 5 CN12 sites, so the size of the $8i_1$ site is expected to be larger than the $8j$ site. The $8i_2$ site is surrounded by 2 CN12 sites and the $2a$ site is surrounded by 4 CN12

sites, so the size of the $8i_2$ site is expected to be larger than the 2a site. The above analysis is well consistent with the calculation results based on Fig. 2 and Fig. 3, i.e. the site size sequence follows

$$4f_{(CN15)} > 8i_{1(CN14)} > 8j_{(CN14)} > 8i_{2(CN12)} > 2a_{(CN12)}.$$

(b) Effect of unlike NN atoms and their configuration on atomic volume

For some binary sigma compounds, the atomic volumes sometimes may not follow the size sequence of the correspondingly occupied site. To figure this out, the influencing factors on atomic volume are specially discussed. For a specific atom in the sigma phase structure, two factors determine its atomic volume. The first one is its occupying crystal site (i.e. one among 2a, 4f, $8i_1$, $8i_2$, 8j). The second concerns its NN atoms and their configuration or distribution around this atom. The effect of the next NN atoms is assumed small that can be neglected. The NN atoms mainly affect its atomic charge and thus affect its atomic volume; the configuration of the NN atoms mainly affects the space to accommodate this specific atom (in this case the atomic charge changes in a small range) and thus affects its atomic volume.

It can be seen from Fig. 2 that for SMe and SMs-SMe categories, the atomic size and site size follow the same sequence, i.e. $4f_{(CN15)} > 8i_{1(CN14)} > 8j_{(CN14)} > 8i_{2(CN12)} > 2a_{(CN12)}$. Moreover, for the same or a small variation of the atomic charge, the atomic volume of the same element for a specific site is constant or changes but to a small extent. While, on the one hand, for LAs and A-Al (A=Nb and Ta) categories, for the same or a small variation of the atomic charge, the atomic volume difference of the same element for a specific site can be very large. It indicates that the configuration of the NN atoms have a large effect on atomic size for LAs and A-Al categories. On the other hand, the NN atoms can affect the atomic size relationship between different sites. Taking Re-Mn system (LAs) as an example, when Re occupy $8i_2$ and 8j sites, and Mn occupy $8i_1$ site, 4f

and 2a sites occupied by Re or Mn respectively, the atomic sizes of Re on $8i_2$ and $8j$ sites become close (normally the atomic size sequence of the same element follows the occupied site size sequence, i.e. $8j_{(CN14)} > 8i_{2(CN12)}$) as seen in, e.g. Fig. 4 (a). When Mn occupy $8i_1$ and $8j$ sites, and in the meanwhile the number of the NN Re surrounding $8j$ site is large enough, the atomic sizes of Mn on $8i_1$ and $8j$ follows $8j > 8i_1$ (normally the atomic size sequence of the same element follows the occupied site size sequence, i.e. $8i_{1(CN14)} > 8j_{(CN14)}$) as seen in, e.g. Fig. 4 (b).

Some interesting phenomena found in Fig. 2 can also be explained by considering the effects of NN atoms, which further validate our arguments. Fig. 5 (a-f) shows the calculated atomic volume varies with the atomic charge of W and Re in 6 stoichiometric sigma end-member compounds for the W-Re system. By replacing site by site W atom by Re atom, one obtains 6 compounds in succession going from pure W sigma to pure Re sigma. By following the path $W \rightarrow 2a \rightarrow 4f \rightarrow 8i_1 \rightarrow 8i_2 \rightarrow 8j \rightarrow Re$, the atomic charge changes in a way that i) the pure sigma compounds show a smaller range of atomic charge around zero in comparison with binary ones; ii) when the content of Re increases, in general the atomic charge of both W and Re increases. For W-Re system, Re atoms tend to gain electrons and W atoms tend to lose electrons. The above conclusions are universal and valid for all the binary sigma systems. As a corollary with the atomic charge increasing, for the corresponding compound, the content of atoms which tend to gain electrons increases. Notably, it can be seen from Fig. 2 that for SMe and SMs-SMe categories, atom B tend to gain electrons; for LAs-LAe and LAs categories, atom A tend to gain electrons. With all the above observations, we can explain the following phenomenon: for SMe and SMs-SMe category, when the atomic charge increases, the size difference among the different CN sites (CN12, CN14 and CN15) decreases. That is because when the atomic charge increases, the content of atom B increases, and thus irrespective of the atom, the number of NN atom B (smaller than atom A) increases. However, this

observation is not obvious for LAs-LAe and LAs categories, as the configuration of the NN atoms affect atomic volume remarkably.

3.1.2. Electronic factors: valence electron and electron shell

Fig. 2 indicates that when the atomic charge decreases, the atomic volume increases. Moreover, it also indicates that between the two constituent elements, the one with smaller total number of electron shells or smaller number of valence electrons tends to lose electrons; the one with larger total number of electron shells or larger number of valence electrons tends to gain electrons. On the other hand, Fig.3 indicates that generally, atoms on 2a and 8i₂ sites tend to gain electrons and atoms on 4f, 8i₁ and 8j sites tend to lose electrons. It is worth mentioning that the atoms on 8j site bear a relatively larger atomic charge range as compared to the atoms on the other sites. In some cases, atoms on 8j site can either gain or lose electrons. Thus in general, between the two constituent elements, the one with smaller total number of electron shells or smaller number of valence electrons prefers occupying large CN sites (4f, 8i₁, 8j) and the one with larger total number of electron shells or larger number of valence electrons prefers occupying small CN sites (2a, 8i₂).

The above argument about the valence electron factor is consistent with the previous investigations^{1-2,26} that atoms poor in *d*-electrons preferentially occupy sites with large CN (4f, 8i₁, 8j) and atoms rich in *d*-electrons preferentially occupy sites with small CN (2a, 8i₂). However, they^{1-2,26} did not consider the effect of the total number of electron shells on atomic order, which makes it unable to well explain the experimental site occupancies. Besides, Berne²⁶ indicates that CN12 sites show predominance for atoms with filled or nearly filled or else empty *d* shells. The reason is that the CN12 sites have approximate icosahedral symmetry causing high degeneracy of

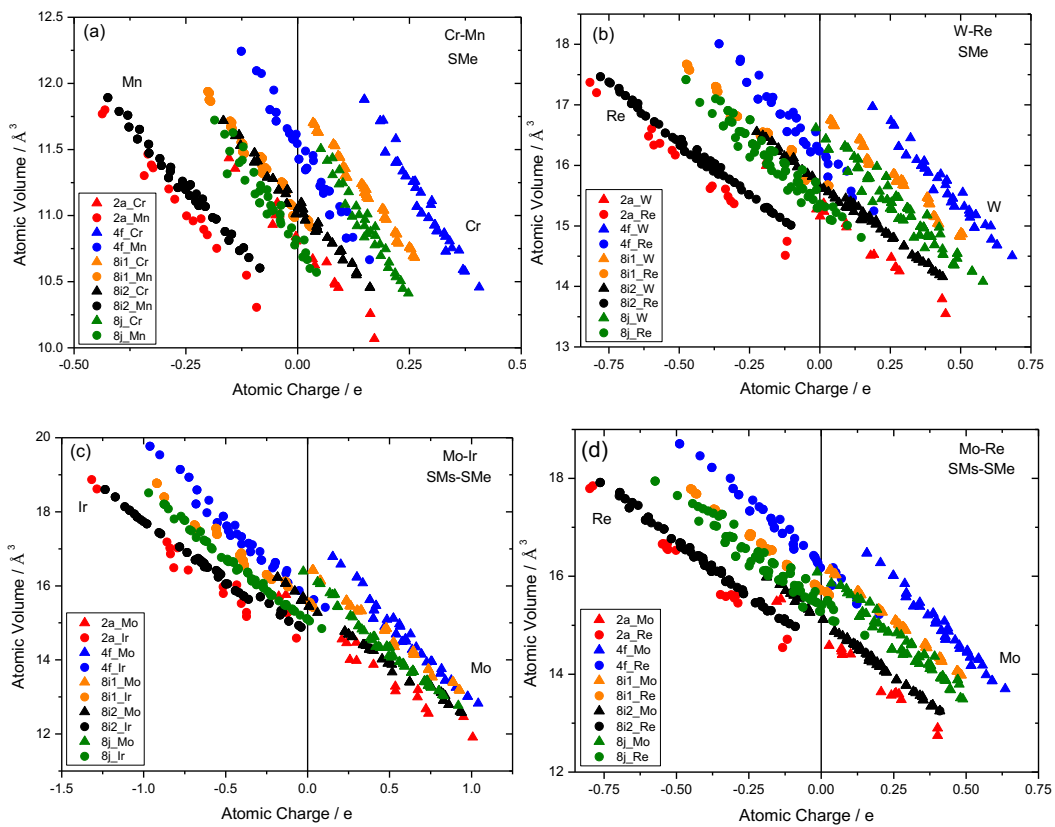
electronic d-like levels ^{17,26}. Atoms with half-filled d shells would have high density of states when occupying the CN12 site and thus consequently occupy high CN sites, which allows a better separation of bonding and antibonding d bands ⁵.

For A-Al (A= Nb and Ta) category shown in Fig. 2 (k) (l), the characteristics of atomic charge seem a little different, i.e. the tendency of electron loss or gain for the two constituent elements is similar. Hence for this category, the atomic order is mainly determined by the size factor, i.e. large atoms (atom A) occupy large CN (4f, 8i₁, 8j) sites and small atoms (atom B) occupy small CN (2a and 8i₂) sites. This is consistent with the measured occupancies presented in Section 3.2.3.

The A-Al (A= Nb and Ta) systems could wrongly be classified into the LAs-LAe category as atoms Nb and Ta bear both a larger number of valence electrons and larger total number of electron shells than atom Al. However, the behavior of A-Al category as mentioned above is similar to that of LAs-SMe category. The compromise of LAs and SMe factors causes the tendency of electrons loss or gain for the two constituent elements similar. Actually, as can be seen in Fig. 2 (f) (k) (l), the behavior of A-Al (A= Nb and Ta) systems is similar as that of Mo-Mn system (which belongs to LAs-SMe category). This is consistent with the discovery by Joubert ², who indicates that Al behaves as if it had 9 or 10 valence electrons in the sigma phase structure. Apparently, the behavior of A-Al category in Fig. 2 (k) (l) results from a compromise between the effects of LAs and SMe factors. Besides, Fig. 2 (k) (l) shows that Ta atoms prefer to gain electrons as compared to Nb, because Ta bears a larger total number of electron shells than Nb. Thus LAs factor plays more important role for Ta-Al system.

Table 1. Number of nearest neighbor (NN) atoms for the five inequivalent sites of the sigma phase

NN						
Site	2a	4f	8i1	8i2	8j	Total
2a	-	4	-	4	4	12
4f	2	1	2	4	6	15
8i1	-	1	5	4	4	14
8i2	1	2	4	1	4	12
8j	1	3	4	4	2	14



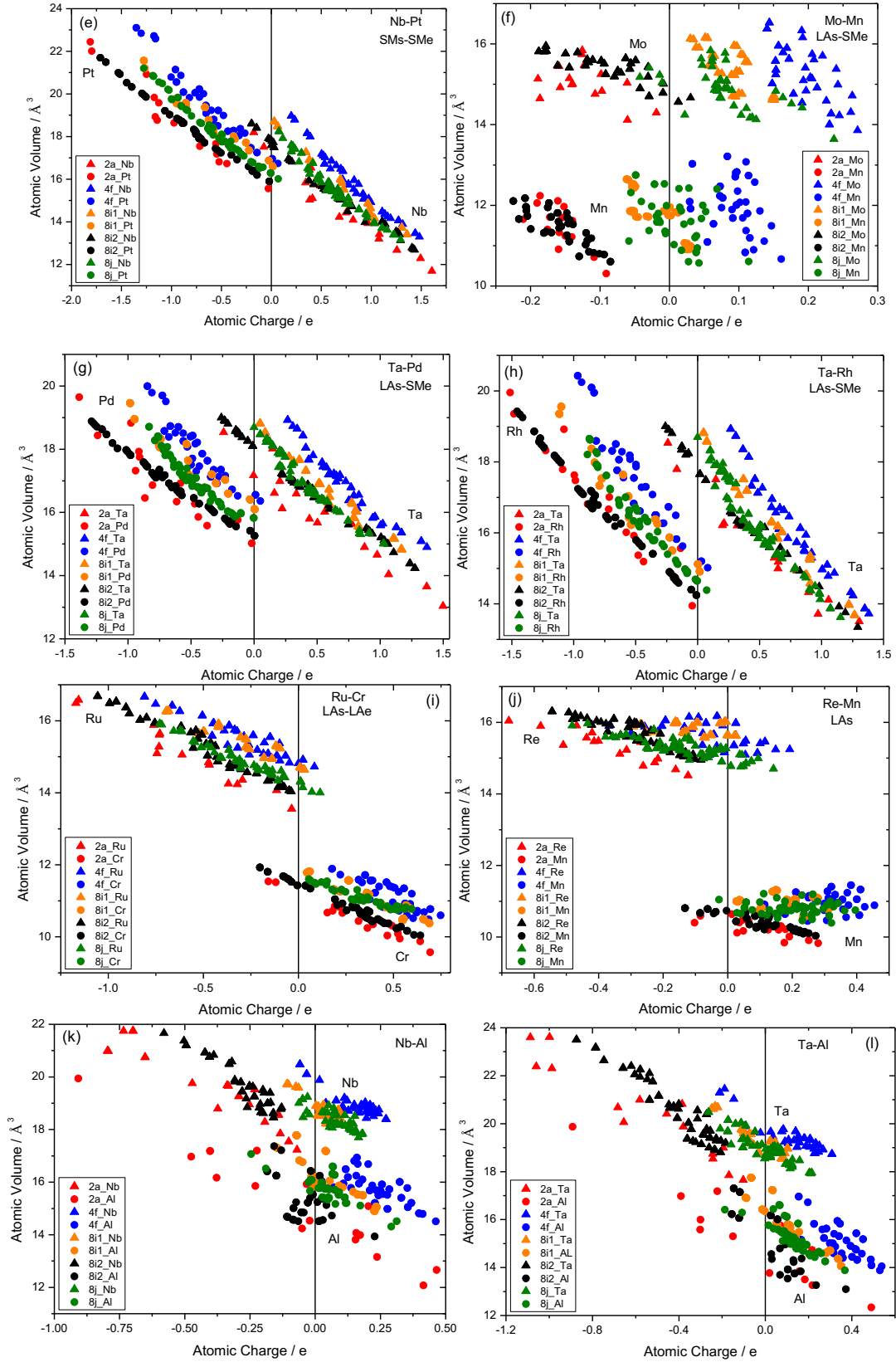
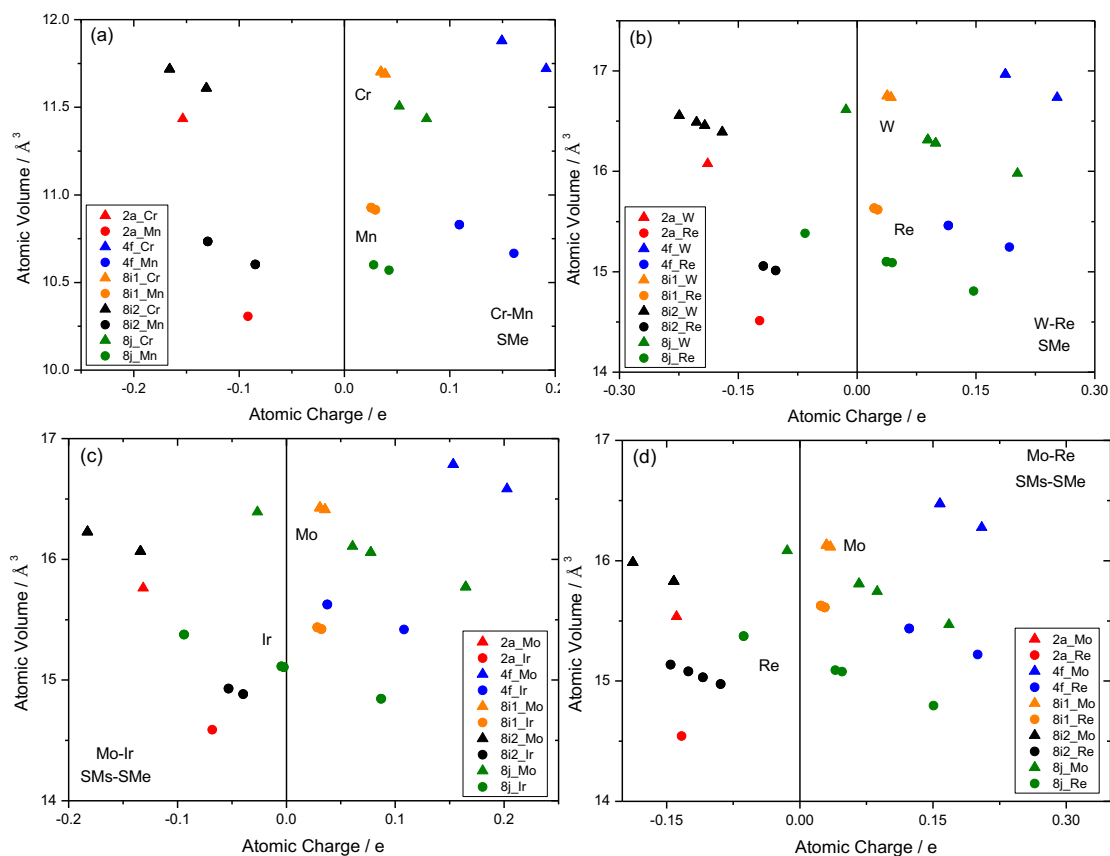
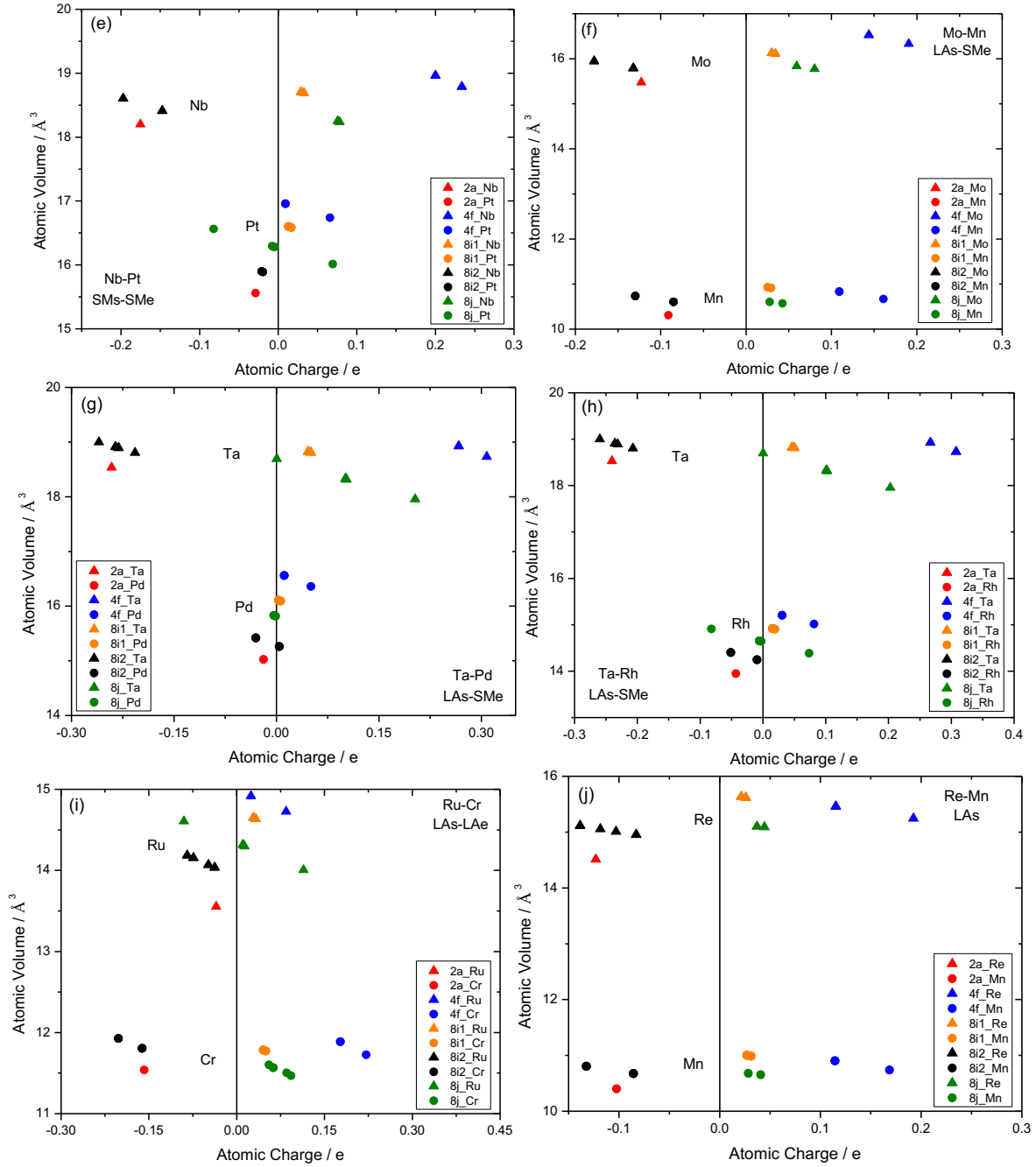


Fig. 2. Atomic volume with respect to atomic charge of the constituent elements in 32 ($2^5=32$) stoichiometric sigma end-member compounds (e.g. $\text{Mo}_2\text{Mo}_4\text{Mo}_8\text{Mo}_8\text{Mo}_8$, $\text{Re}_2\text{Mo}_4\text{Mo}_8\text{Mo}_8\text{Mo}_8$ etc.) for binary systems calculated using VASP and Bader Charge Analysis. (Every figure contains the results of 32 stoichiometric sigma end-member compounds for a specific system and every compound contains 30 atoms. Thus, every figure contains 30×32 points but some of them are overlapped).





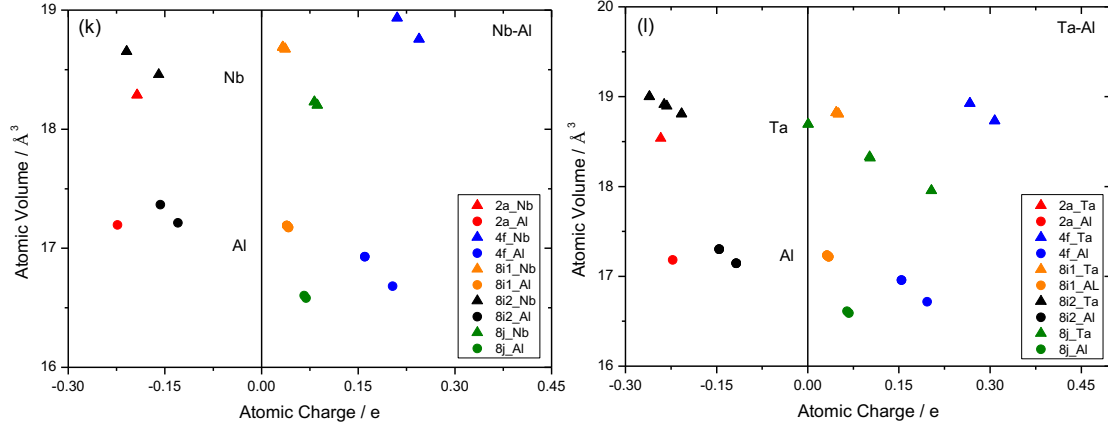


Fig. 3. Atomic volume with respect to atomic charge of the pure elements in the hypothetical sigma phase structure calculated using VASP and Bader Charge Analysis. Every figure contains the results for two elements and thus, every figure contains 30×2 points but some of them are overlapped.

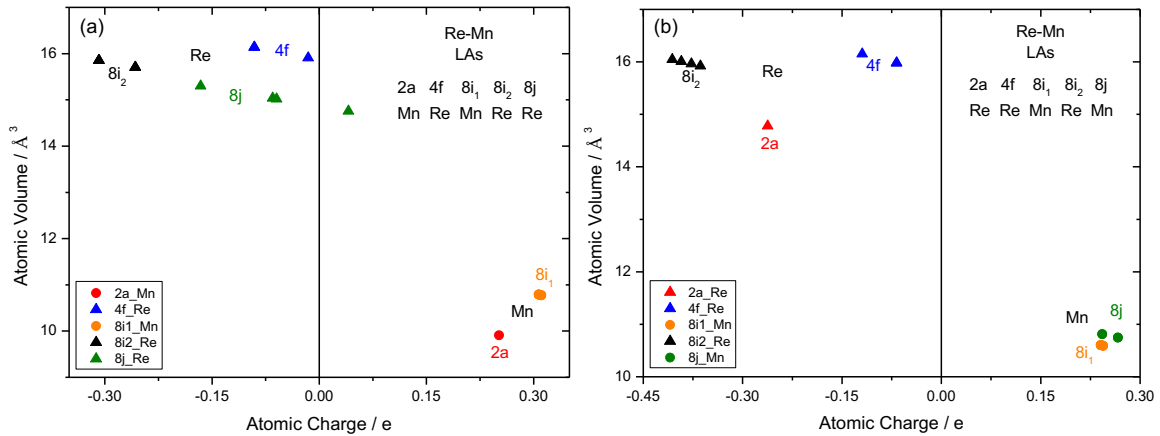


Fig. 4. Atomic volume with respect to atomic charge of the constituent elements in two stoichiometric sigma end-member compounds for Re-Mn system calculated using VASP and Bader Charge Analysis. a) $\text{Mn}_2\text{Re}_4\text{Mn}_8\text{Re}_8\text{Mn}_8$; b) $\text{Re}_2\text{Re}_4\text{Mn}_8\text{Re}_8\text{Mn}_8$. Every figure contains 30 points but some of them are overlapped.

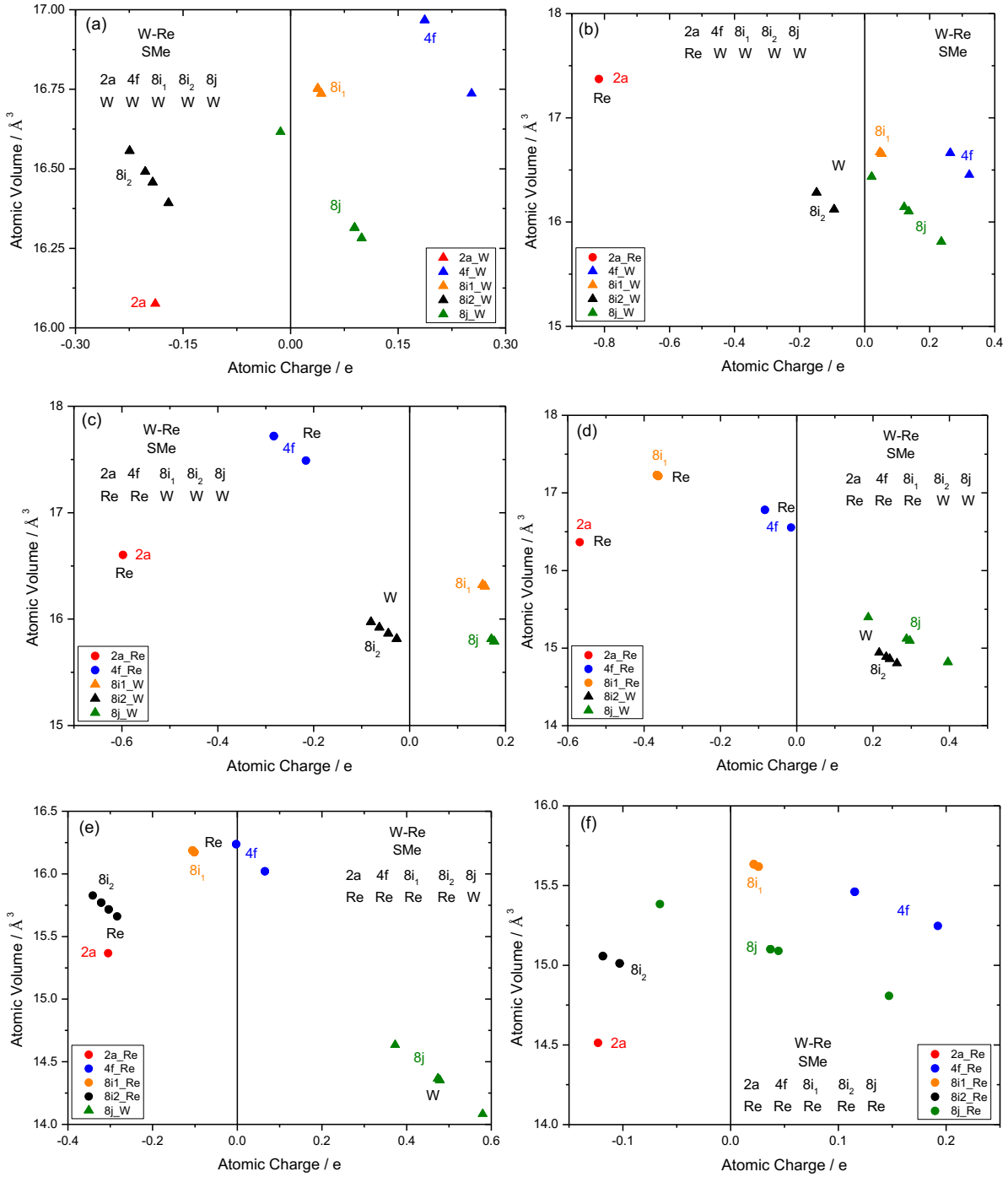


Fig. 5. Atomic volume with respect to atomic charge of the constituent elements in stoichiometric sigma end-member compounds for W-Re system calculated using VASP and Bader Charge Analysis. Every figure contains 30 points but some of them are overlapped.

3.2. Effects of electronic factors on atomic order

Section 3.1.2 indicates that between the two constituent elements, the one with the smaller total number of electron shells or the smaller number of valence electrons prefer occupying large CN sites (i.e. 4f, 8i₁, 8j) and the one with the larger total number of electron shells or the larger number of valence electrons prefer occupying small CN sites (i.e. 2a, 8i₂). To reveal the atomic order among the large CN sites (i.e. 4f, 8i₁, 8j) and between the small CN sites (i.e. 2a, 8i₂) of the sigma phase, we present in Fig. 6 the measured site occupancies from the literature category by category and considering the accuracy, generally, recent data were collected. Fig. 7 shows the size differences of the constituent elements of the binary sigma phase with respect to their differences in the number of valence electrons and the total number of electron shells. For a specific system, when the size difference is smaller and in the meantime, the differences in both the number of valence electrons and the total number of electron shells are larger as compared to other systems, the electronic factors affect the atomic order more remarkably.

It should be noted that the experimental site occupancies are results of competition and cooperation of these factors. In this section, we aim in dissociating the effects of individual influencing factor on atomic order based on first-principles calculation results in Section 3.1 and experimental data from the literature in order to further analyze and explain the atomic order.

3.2.1. Effect of the number of valence electrons on atomic order

Fig. 6 (a) shows that in most cases for the SMe category, the site occupancy follows $Y_{2a}(A) > Y_{8i_2}(A)$ and $Y_{4f}(A) > Y_{8j}(A) > Y_{8i_1}(A)$. We showed above that the size sequence of the crystal site

is $4f > 8i_1 > 8j > 8i_2 > 2a$. It is thus clear that it is the electronic factor (SMe) that affects the sequence of atomic order to be $2a > 8i_2$ and $8j > 8i_1$.

Besides, for all the measurements in Fig. 6 (a), only among the measurements of Cr-Co, Cr-Mn and V-Ni systems, there are experimental data indicating that 4f site is not the most favorable site for atom A, which exhibit $Y_{8i_1}(A) > Y_{4f}(A)$ and $Y_{8j}(A) > Y_{4f}(A)$ for Cr-Co system, $Y_{8j}(A) > Y_{4f}(A)$ for Cr-Mn and V-Ni systems, respectively. It must be owing to the effect of the electronic factor (SMe), since in terms of the size factor, 4f site should be the most favorable site for atom A. It can also be seen from Fig. 7 (a) that the electronic factor can be more remarkable for these systems than the other ones in SMe category, as for Cr-Mn system, the two constituent atoms bear the smallest size difference, for V-Ni system, the two constituent atoms bear the largest difference of valence electrons, and Cr-Co system is in between.

Therefore, we can expect that SMe factor affects the atomic order in a sequence of $8j(A) > 8i_1(A) > 4f(A) > 2a(A) > 8i_2(A)$. Vice versa, LAe factor affects the atomic order in a sequence of $8i_2(A) > 2a(A) > 4f(A) > 8i_1(A) > 8j(A)$.

3.2.2. Effect of the total number of electron shells on atomic order

For LAs category presented in Fig. 6 (b), only measured site occupancies for Re-Mn system is available. The figure shows $Y_{8i_2}(A) > Y_{2a}(A)$ and $Y_{8i_1}(A) > Y_{8j}(A)$. Moreover, the difference in A occupancies in $8i_2$ and $2a$ sites, and in $8i_1$ and $8j$ sites for LAs category, is too large to explain with only size factor. It is expected that LAs factor affects the atomic order in a sequence of $8i_2(A) > 2a(A)$ and $8i_1(A) > 8j(A)$.

On the other hand, for LAs-LAe category, Fig. 7 (b) indicates that the electrons factors affect the atomic order most remarkably for the Re-V system. Fig. 6 (d) shows for Re-V system, the site occupancies follows $Y_{8i_2}(A) > Y_{2a}(A) > Y_{8i_1}(A) > Y_{4f}(A) > Y_{8j}(A)$ and the difference in A occupancies on $8i_1$ and $8j$ sites is dramatically large. Thus we can expect the electronic factors (both LAs and LAe) affect the atomic order in a sequence of $8i_2 > 2a > 8i_1 > 4f/8j$ for LAs-LAe category. As discussed above, for LAe and LAs-LAe categories the electronic factors affect the atomic order in a sequence of $8i_2 > 2a > 4f > 8i_1 > 8j$ and $8i_2 > 2a > 8i_1 > 4f/8j$, respectively. In this regard, LAs factor must affect the atomic order in a sequence of $8i_1 > 4f$. Thus LAs factor affects the atomic order in a sequence of $8i_2 > 2a > 8i_1 > 4f/8j$. Vice versa, SMs factor affects the atomic order in a sequence of $4f/8j > 8i_1 > 2a > 8i_2$.

As mentioned in Section 1, Spooner and Wilson ⁸ indicated that the site occupancies of 2a, 4f, and $8i_2$ sites were mainly determined by size factor and the site occupancies of $8i_1$ and $8j$ sites were in addition determined by valence electrons. The reason for Spooner and Wilson ⁸ reaching the above conclusion is that for some systems, the effects of the size and electronic factors are similar, such as SMe and SMs-SMe categories for which both size and electronic factors cause the atomic order in a sequence of $4f/8i_1/8j > 8i_2/2a$. Actually, there are many exceptions considering this argument. One is that for Cr-Mn, Cr-Co and V-Ni systems in SMe category, 4f site is not the most favorable site for atom A while the size factor indicates otherwise. Another one is that for Re-V system in LAs-LAe category, $8i_2$ and 2a sites have become the most favorable sites for atom A, because of the larger effects of the electronic factors (LAs and LAe) than the size factor.

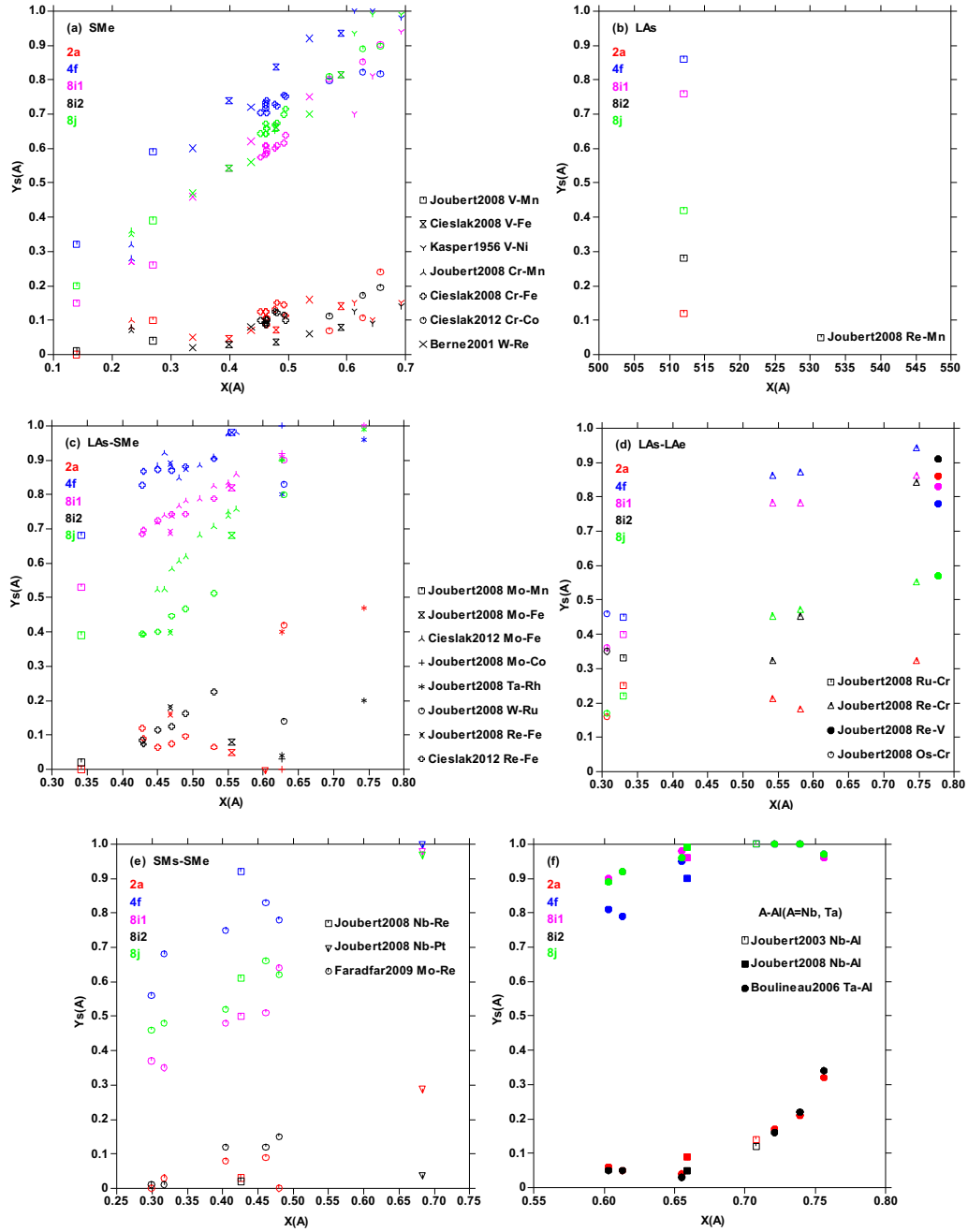


Fig. 6. Site occupancy, $Y_s(A)$, varies with mole fraction of A, $X(A)$. Measured data are from Ref. (2-3, 6-13, 27-32).

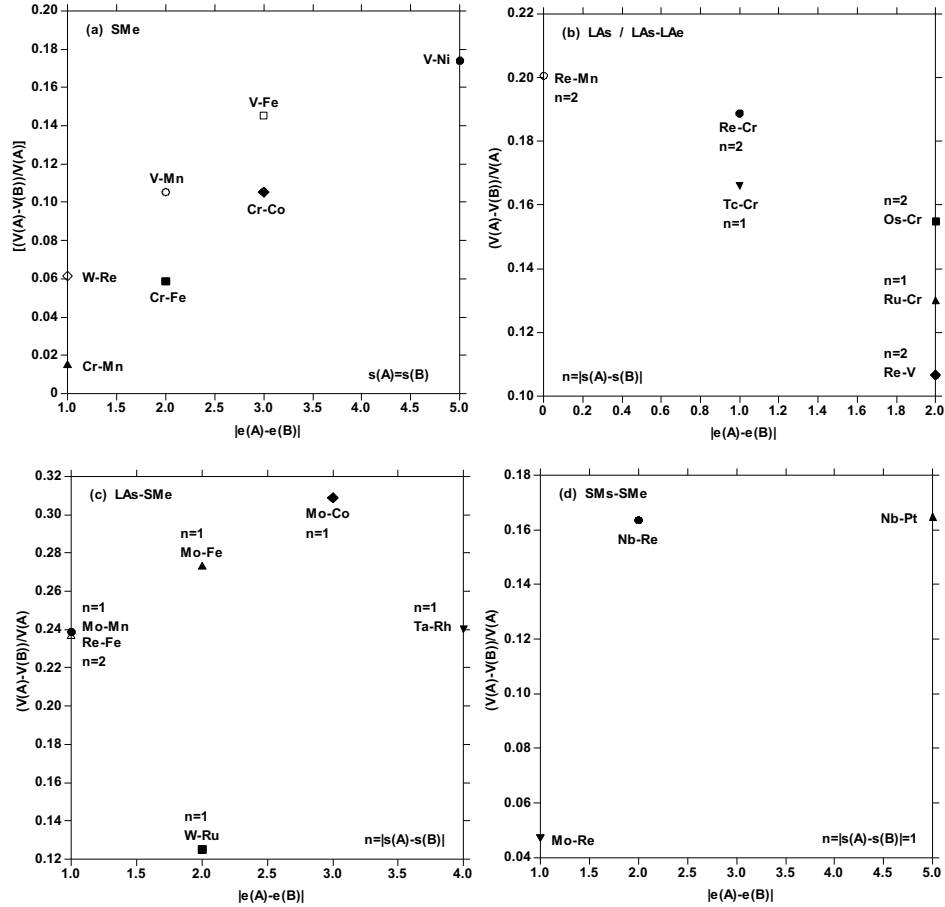


Fig. 7. Molar volume difference with respect to differences between the number of valence electrons of the constituent elements (A and B) of the binary sigma compounds. The assessed molar volume for Mn can be found in Appendix A. The other assessed molar volume data are from the previous CALPHAD assessments¹⁸. The differences between the total number of electron shells of the elements are indicated. $s(A)$ and $s(B)$: the number of valence electrons of atom A and B respectively; $e(A)$ and $e(B)$: the number of valence electrons of atom A and B respectively; $V(A)$ and $V(B)$: the molar volume of atom A and B respectively.

3.2.3. Experimental site occupancies

(a) SMe category (Fig. 6 (a))

The influencing factors on atomic order for this category are the size and SMe factors which lead to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$ and $8j > 8i_1 > 4f > 2a > 8i_2$, respectively. In this category, the site occupancy data on sites with the same CN (CN12: $8i_2$ vs $2a$, CN14: $8i_1$ vs $8j$) is close. Most data show $Y_{2a}(A) > Y_{8i_2}(A)$ and $Y_{8j}(A) > Y_{8i_1}(A)$. This is because SMe factor affects the atomic order more remarkably than the size factor.

For Cr-Mn, Cr-Co and V-Ni systems, as mentioned in Section 3.2.1, the effect of SMe factor on atomic order is particularly notable which leads to $Y_{8j}(A)/Y_{8i_1}(A) > Y_{4f}(A)$ or $Y_{8j}(A) > Y_{4f}(A)$. For the other systems, the size factor determines the site occupancy on $4f$ site. It is worth mentioning that data for Cr-Co system from Cieślak ²⁷ and data for W-Re system from Berne ¹⁶ show that site occupancies is inverted among sites with the same CN ($2a$ vs $8i_2$; $8i_1$ vs $8j$). This is due to a competition between electronic and size factors.

For V-Ni system, Joubert ² also measured the site occupancies by using the XRD method, but the data are not accurate due to the weak XRD contrast between the two constituent elements, which were not considered in the present work. On the contrary, the early data measured by Kasper ⁶ are more accurate, since they conducted neutron diffraction (ND) experiments yielding a better resolution for site occupancy measurements.

(b) LAs category (Fig. 6 (b))

The influencing factors on the atomic order for this category are the size and LAs factors which lead to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$ and $8i_2 > 2a > 8i_1 > 4f/8j$, respectively.

For the LAs category, experimental data are available for Re-Mn system only. Both size and electronic factors affect the atomic order in a sequence of $8i_2 > 2a$ and $8i_1 > 8j$. The size factor determines the site occupancy of $4f$ site.

(c) LAs-SMe category (Fig. 6 (c))

The influencing factors on the site occupancy for this category are the size, LAs and SMe factors which lead to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$, $8i_2 > 2a > 8i_1 > 4f/8j$ and $8j > 8i_1 > 4f > 2a > 8i_2$, respectively. The atomic order results from a competition among the three factors above. Atom A prefers occupying large CN sites (i.e. $4f$, $8i_1$, $8j$) rather than small CN sites (i.e. $2a$, $8i_2$), because of the both size and SMe factors.

For Mo-Fe, Mo-Mn and Re-Fe systems, Fig. 6 (c) presents $Y_{8i_1}(A) > Y_{8j}(A)$ and $Y_{8i_2}(A) > Y_{2a}(A)$, because the effect of SMe factor on atomic order is less significant than the combined effects of LAs and size factors. Besides, the difference of site occupancies between $8i_1$ and $8j$ sites for Re-Fe system is the largest among the three systems. It is because of the effect of LAs factor, as for Re-Fe system the size difference between the two constituent elements is the smallest and n ($n=s(A)-s(B)=2$) is the largest among the three systems as shown in Fig.7(c).

From Mo-Co to Ta-Rh system, SMe factor increasingly affects the atomic order as indicated in Fig. 7 (c). For Mo-Co system, Fig. 6 (c) shows $Y_{4f}(A) > Y_{8i_1}(A) \approx Y_{8j}(A)$ and $Y_{8i_2}(A) > Y_{2a}(A)$. It is because that SMe factor affects the atomic order almost equivalent as the combined effects of LAs and size factors. For Ta-Rh system, SMe factor affects the atomic order more dramatically, which presents $Y_{8i_1}(A) \approx Y_{8j}(A) > Y_{4f}(A)$ and $Y_{2a}(A) > Y_{8i_2}(A)$. Notably, both SMe and LAs factors tend to decrease occupancy of atom A on $4f$ site. Joubert ² also conducted the measurements for Ta-Pd compound, but the measured compositions describe a tie-line in disagreement with the published phase diagram. Hence the data were not considered.

For W-Ru system, the data from Joubert ² show that $Y_{2a}(A) > Y_{8i_2}(A)$ (due to SMe factor), $Y_{8i_1}(A) > Y_{8j}(A)$ (due to LAs and size factors) and $Y_{8i_1}(A) > Y_{4f}(A)$ (due to SMe and LAs factors).

In addition, it can be seen from Fig. 7 (c) that the value of n ($n=s(A)-s(B)$) and $e(A)-e(B)$ for W-Ru system is the same as that for Mo-Fe system, but the site occupancy orderings for these two systems are different as presented in Fig. 6 (c). The reason is that the size difference between W and Ru atoms is far smaller than that for Mo-Fe system (see Fig. 7(c)), thus less remarkable effect of size factor on the atomic order of W-Ru system than that of Mo-Fe system.

(d) LAs-LAe category (Fig. 6 (d))

The influencing factors on the atomic order for this category are the size, LAs and LAe factors leading to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$, $8i_2 > 2a > 8i_1 > 4f/8j$ and $8i_2 > 2a > 4f > 8i_1 > 8j$, respectively. The atomic order results from a competition among the three factors above.

The site occupancy behavior of Os-Cr, Re-V and Ru-Cr systems is almost completely disordered². This is because of the equivalent effects of the size and electron factors. A less disordered state for Re-Cr system as compared to Os-Cr, Re-V and Ru-Cr systems is because of a larger effect of the size factor.

For Re-V system, the size difference between the two constituent elements is the smallest and the value of n ($n=s(A)-s(B)$) and $e(A)-e(B)$ is the largest (see Fig. 7 (c)), which indicates that the effects of electron factors are stronger for Re-V system as compared to other systems. The experimental site occupancy of Re-V system shows $Y_{8i_2}(A) > Y_{2a}(A) > Y_{8i_1}(A) > Y_{4f}(A) > Y_{8j}(A)$, which is an evidence that the electronic factors affect more dramatically the atomic order than the size factor.

It is worth noting that as mentioned in Section 1, Sluiter and Patrel¹⁷ clarified that for Ru-Cr and Os-Cr systems, all five crystal sites were equivalent as no overwhelming ordering preference of constituent elements. However, the five crystal sites are different in CN and NN sites. With the

findings discussed in Section 3.2, we can conclude that the reason for no overwhelming ordering preference is because of a competition among the effects of electronic and size factors rather than an equivalence of five crystal sites.

(e) SMs-SMe category (Fig. 6 (e))

The influencing factors on the atomic order for this category are the size, SMs and SMe factors which lead to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$, $4f/8j > 8i_1 > 2a > 8i_2$ and $8j > 8i_1 > 4f > 2a > 8i_2$, respectively.

For Mo-Re system, in general, Faradfar's³⁰ measurements show $Y_{8i_2}(A) > Y_{2a}(A)$. This is caused by the size factor. Even though the size difference between Mo and Re atoms is the smallest among all systems in SMs-SMe category, it is the small value of n ($n=s(A)-s(B)$) and $e(A)-e(B)$ that causes the size factor more prominent (see Fig.7 (d)).

(f) A-Al (A= Nb and Ta) category (Fig. 6 (f))

As mentioned in Section 3.1.3, A-Al category behaves like LAs-SMe category with regard to the electron loss or gain. Thus the influencing factors on atomic order for this category are the size, LAs and SMe factors which lead to a sequence of $4f > 8i_1 > 8j > 8i_2 > 2a$, $8i_2 > 2a > 8i_1 > 4f/8j$ and $8j > 8i_1 > 4f > 2a > 8i_2$, respectively.

Fig. 6 (f) shows that in general, atom A and Al occupy large CN (i.e. $4f$, $8i_1$, $8j$) sites and small CN ($2a$ and $8i_2$) sites, respectively. In addition, the site occupancy is inverted between sites with the same CN ($2a$ and $8i_2$; $8i_1$ and $8j$). The above observations are because of a compromise among the three influencing factors. Besides, the measurements present that $Y_{8i_1}(A)/Y_{8j}(A) > Y_{4f}(A)$, which is caused by the effects of both LAs and SMe factors.

3.3. Discussion

In view of the size and electron configuration of the constituent elements, we have classified all the binary sigma phase systems into different categories. With this classification approach, it is possible to study the tendency of electrons loss or gain of the constituent elements and obtain the regularity of atomic order as investigated in the present work

The present findings can not only explain various results for stable sigma phase but also the calculation results for hypothetically unstable sigma phase. As mentioned in Section 1, Crivello et al.⁵ calculated the site occupancies of the sigma phase in binary Re-X (X= Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Os, Ru, Ta, Tc, Ti, V, W and Zr) systems including stable sigma compounds (Re-V, Re-Cr, Re-Mn, Re-Fe, Nb-Re, Mo-Re, Ta-Re and W-Re) as well as some hypothetically unstable ones (Ti-Re, Zr-Re, Hf-Re, Re-Co, Re-Ni, Re-Tc, Re-Ru and Re-Os). Some calculation results cannot be well explained in that work as already mentioned in Section 1 but are interpretable by using the analysis method in the present work as follows.

Among the sigma phase studied by Crivello et al.⁵ Hf-Re, Ta-Re, W-Re and Re-Os systems belong to SMe category and Ti-Re, Zr-Re, Nb-Re and Mo-Re systems belong to SMS-SMe category. For SMe and SMS-SMe categories, both size and electronic factors cause the atomic order follow $4f/8i_1/8j > 8i_2/2a$, that is why the site occupancies of Nb-Re, Mo-Re, Ta-Re, W-Re, Ti-Re, Zr-Re and Hf-Re systems behave more-ordered⁵. As respect to Re-Os system, the site occupancies present relative less-ordered at the finite temperature of 2000K (see Fig. 9 in Ref. 5), which is because that the effects of the size and electronic factors are both small for this system.

Re-Mn and Re-Tc systems belong to LAs category, while Re-V and Re-Cr belong to LAs-LAe category and Re-Fe, Re-Co, Re-Ni and Re-Ru belong to LAs-SMe category. A competition of the

influencing factors makes a less-ordered state in these categories. Besides, Crivello et al.⁵ indicated that site occupancy behavior for the sites with the same CN (i.e. $2a$ vs $8i_2$; $8i_1$ vs $8j$) is different. Taking Re-Os vs Re-Tc and Re-V systems as an example, for Re-Os (belongs to SMe category) system, the site occupancies present the order of $8j > 8i_1$ which is because of the effect of SMe factor. For Re-Tc (belongs to LAs) and Re-V (belongs to LAs-LAe) systems, the site occupancies present the order of $8i_1 > 8j$ which is because of the effects of size, LAs and LAe factors.

In addition, we are also expecting to use the present method to investigate the atomic order for other non-stoichiometric intermetallic compounds, like Chi phase and Mu phase, etc.

4. CONCLUSIONS

The experimental site occupancies are results of competition and cooperation of the size factor and electronic factors (i.e. the number of valence electrons and the total number of electron shells). The present work dissociated the effect of individual influencing factor on the atomic order for the binary sigma phase. All accurately measured site occupancies can be well explained by using the following conclusions.

1. Both the coordination number (CN) and nearest neighbor crystal sites affect the size of the five crystal sites of the sigma phase. The size of the five inequivalent crystal sites of the sigma phase follows $4f_{(CN15)} > 8i_{1(CN14)} > 8j_{(CN14)} > 8i_{2(CN12)} > 2a_{(CN12)}$.

2. In the binary sigma compounds, between the two constituent elements, the one with a smaller total number of electron shells or smaller number of valence electrons tend to lose electrons and thus the atomic size decreases; the one with a larger total number of electron shells or larger number of valence electrons tend to gain electrons and thus the atomic size increases. On the other

hand, atoms on 2a and 8i₂ sites tend to gain electrons and those on 4f, 8i₁ and 8j sites tend to lose electrons. Hence between the two constituent elements, the one with a larger size, smaller number of valence electrons or smaller total number of electron shells prefer occupying large CN sites (i.e. 4f, 8i₁, 8j) and the one with a smaller size, larger number of valence electrons or larger total number of electron shells preferring occupy small CN sites (i.e. 2a, 8i₂). The site occupancy for a specific system is a compromise of the three influencing factors.

3. The dissociated effect of the electronic factors leads to the following atomic order:

LAs: 8i₂ > 2a > 8i₁ > 4f/8j; SMs: 4f/8j > 8i₁ > 2a > 8i₂; LAe: 8i₂ > 2a > 4f > 8i₁ > 8j; SMe: 8j > 8i₁ > 4f > 2a > 8i₂.

APPENDIX A: MOLAR VOLUME ASSESSMENTS FOR THE SIGMA PHASE IN THE MN-X (X=CR, MO, RE, TC, TI, V) BINARY SYSTEMS

By using the CALPHAD approach, Liu et al ¹⁸ have assessed the molar volume of the sigma phase at room temperature and atmospheric pressure for binary systems concerning 20 elements Al, Au, Co, Cr, Fe, Ir, Mo, Nb, Ni, Os, Pd, Pt, Re, Rh, Ru, Ta, Tc, V, W and Zr. As a supplement of that work, we assessed Mn-X (X=Cr, Mo, Re, Tc, Ti, V) sigma binary systems by using the same model (for details see Ref. 18). Besides, the assessed results for element Cr, Mo, Re, Tc and V were adopted from Ref. 18 directly.

During the assessments, the recent data from Joubert ² are given more considerations and the assessed results are shown in Fig. A. 1. The assessment results for element Mn is 7.203×10⁻⁶ m³/mol. The agreements between different data are fairly good except for Mn-Ti system. Only measurements with molar volume of 7.19×10⁻⁶ m³/mol (a=8.88 Å, c=4.54 Å, at about 48.6 at.%)

Mn) from Elliott ⁴³ is available. The predicted molar volume of the Mn-Ti sigma compound is much higher than the measurements, which is presented in Fig A. 1.

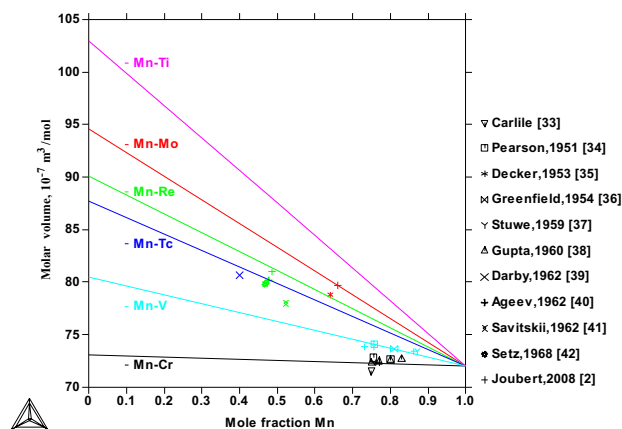


Fig. A. 1. Calculated molar volumes of Mn-X (X=Cr, Mo, Re, Tc, Ti, V) sigma phase compared with the experimental data. Note that for one sigma phase, the same color is assigned to both the calculated line and the experimental data ^{2, 33-42}.

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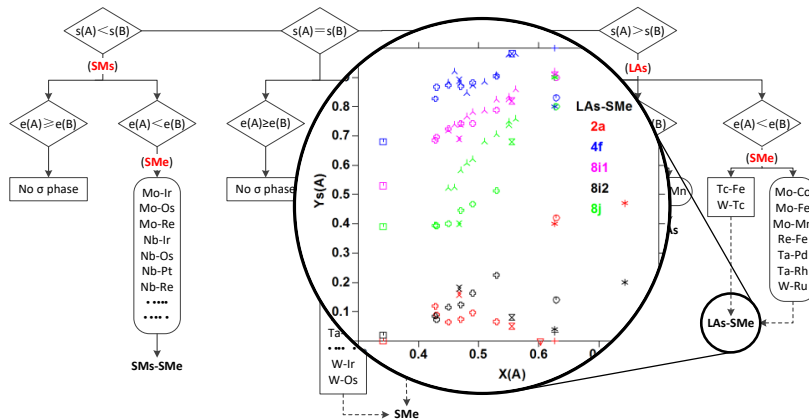
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Synopsis

The atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal structure) of the sigma phase is driven by both size and electronic (the number of valence electrons and the total number of electron shells) factors. By classifying the binary sigma systems into different categories according to the size and electron configuration of the two constituent elements, the site occupancy regularity of the sigma phase can be observed and analyzed.