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Influence of nearest neighbor atoms and coordination polyhedron on atomic volume of the sigma phase

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Abstract:

We have calculated the atomic volume with respect to the atomic charge of the constituent elements in the complete set of ordered configurations of several binary sigma systems by using VASP and Bader's AIM approach. The calculation results indicate that both the nearest neighbor (NN) atoms and coordination polyhedron (CP) affect the atomic volume of the sigma phase. For a specific element, on a specific site, atoms with more negative atomic charge bear a larger volume; the more the NN large atoms and the higher the symmetry of CP, the larger the space to accommodate the specific atom.

Key words: sigma phase, atomic volume, nearest neighbor (NN) atoms, coordination polyhedron (CP), atomic charge

1. Introduction

The sigma phase, known as Frank Kasper phase, crystallizes in a tetragonal structure with space group $P4_2/mnm$. It is a non-stoichiometric intermetallic compound with large homogeneity range. There are 30 atoms in a unit cell, which distribute on five inequivalent sites, namely 2a, 4f, 8i₁, 8i₂ and 8j. Fig. 1 presents the crystal structure of the sigma phase. As a typical topologically close-packed (TCP) phase, it is stacked by coordination polyhedrons (CP) of coordination number (CN) 12, 14 and 15 around sites 2a, 8i₂; 8i₁, 8j and 4f, respectively, which is clearly displayed in Fig. 2. Table 1 lists the nearest neighbor (NN) sites for each crystal sites of the sigma phase. More details about the crystal chemistry of the sigma phase is recommended to Ref. [1,2].

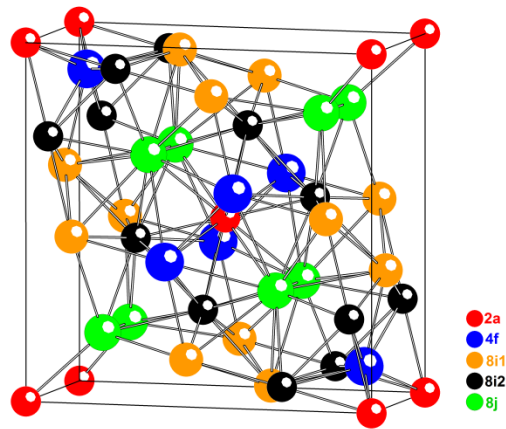


Fig. 1. Crystal structure of the sigma phase with different fillings indicating atoms occupying on different crystal sites, namely 2a, 4f, 8i₁, 8i₂ and 8j. (Color online)

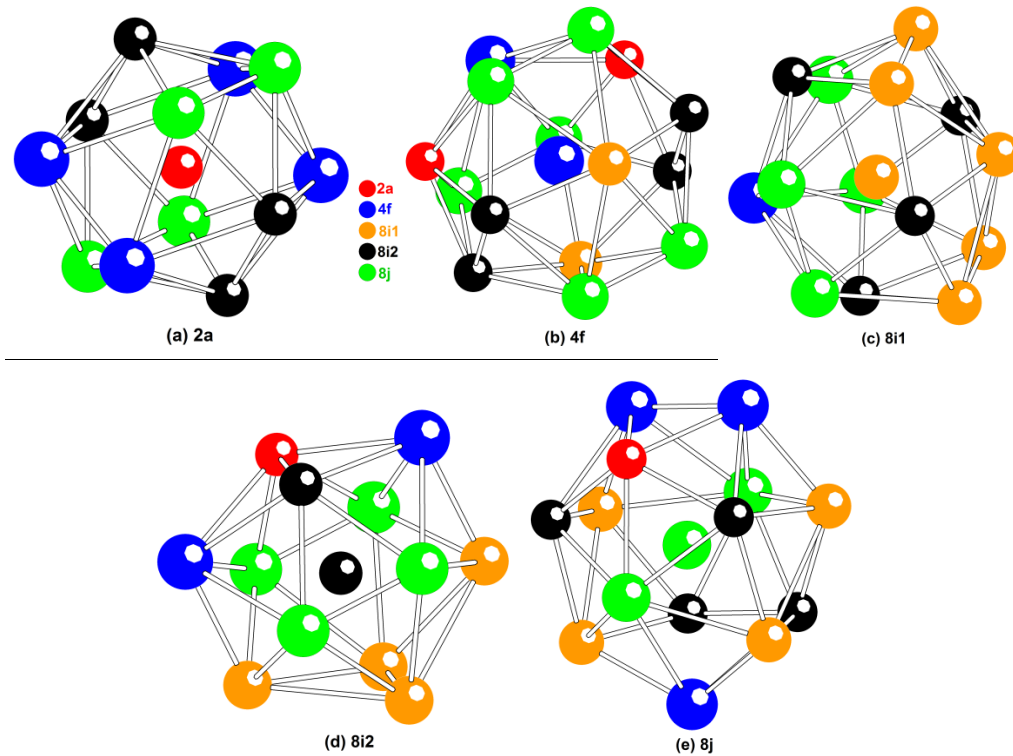


Fig. 2. Coordination polyhedron (CP) around five inequivalent sites of the sigma phase structure with different fillings indicating atoms on different crystal sites, namely 2a (CN12), 4f (CN15), 8i₁ (CN14), 8i₂ (CN12) and 8j (CN14). (Color online)

Table 1 Number of nearest neighbor (NN) sites for the five inequivalent sites of the sigma phase [3].

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

The sigma phase is a detrimental precipitation in a lot of technologically important materials, such as duplex stainless steels and Ni-based superalloys. The occurrence of the sigma phase should be carefully avoided or controlled. Thus thermodynamic [4,5] and molar volume [6] databases of the sigma phase have been successively built by using the CALPHAD method [7–9]. Besides, other properties of the sigma phase also attracts lots of interests, like site occupancy preference [2,3,10], enthalpy of formation [11,12] and magnetism [13,14].

In the present work, VASP and Bader’s AIM approach were conducted to elucidate the influencing factors of the atomic volume in the binary sigma phase. To facilitate explanation, for all the A-B binary sigma systems investigated, atom A always holds a larger size than atom B. The size of atom A or B is based on the molar volume assessments of the sigma phase [3,6]. Besides, we follow the divided categories of the A-B sigma phases by Liu et al. [3], which is categorized according to the electron configuration of the two constituent elements, i.e. SMe, SMs-SMe, LAs, LAs-SMe, LAs-LAe, A-Al (A-Nb, Ta), where SMe and LAe indicates that atom A bears smaller or larger number of valence electrons, respectively, than atom B; SMs and LAs indicates that atom A bears smaller or larger total number of electron shells, respectively, than atom B.

2. Methodology and calculation details

2.1. First-principles calculations

The first-principles calculations were performed by using the plane wave method with projector augmented wave (PAW) pseudo-potentials [15] based on density-functional theory (DFT) [16]. The method is implemented in the Vienna ab initio simulation package (VASP) [17]. The exchange-correlation functional within the generalized gradient approximation (GGA) as parameterized by Perdew and Wang (i.e. GGA-PW91) [18] was employed. A large plane-wave cutoff energy of 400 eV was used. The k-point meshes for Brillouin zone sampling were

constructed using the Monkhorst–Pack scheme [19], which were set as $8 \times 8 \times 15$. To facilitate the calculations, ZenGen script-tool [20] was used to automatically generate input files.

2.2. Bader Charge Analysis

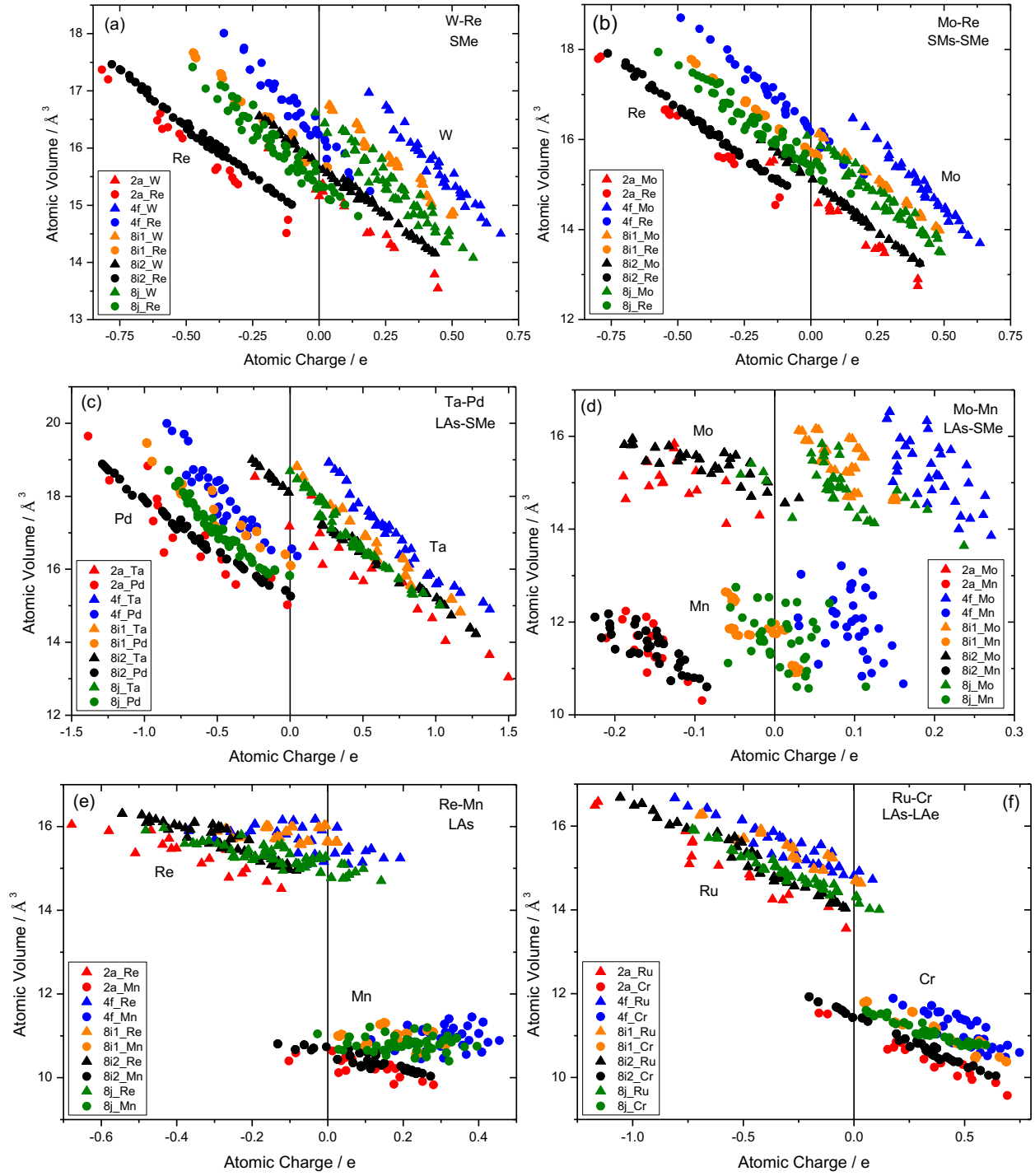
In the present work, we adopted the Bader charge analysis code [21] developed by the Henkelman Group. It is based on Richard Bader's theory of Atoms in Molecules (AIM) [22], which proposes an intuitive way to separate molecules into atoms based purely on the electronic charge density. The code provides an efficient and robust algorithm for the Bader decomposition of charge density [23–26].

During the calculation, the total electron charge was achieved by summing the core charge and the valence charge from the VASP. The Bader analysis was performed on the total charge density and then output the atomic volume and the total charge associated with each atom [21]. To get the atomic charge for each atom, the valence electrons (the valence states set in VASP) minus the obtained electronic charge were conducted. For the atomic charge, the negative value indicates that an atom tends to gain electrons and the positive one indicates that an atom tends to lose electrons.

3. Results and discussion

In the sigma phase structure, for a specific element, the atomic size varies with the change of occupying sites. Normally, the atomic size sequence follows the occupied site size sequence (i.e. $4f_{(CN15)} > 8i_{1(CN14)} > 8j_{(CN14)} > 8i_{2(CN12)} > 2a_{(CN12)}$ [3]) when atomic charges are close, e.g. Fig. 3 (a-c). However, it may not be always true. For some binary sigma compounds, the atomic volumes sometimes may not follow the size sequence of the correspondingly occupied site owing to the influences of NN atoms and CP on atomic volume, e.g. Fig. 3 (d-g).

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, 8i₁, 8i₂ and 8j) and the corresponding CP symmetry. The second concerns the NN atoms around the atom. The effect of the next NN atoms is assumed small that can be neglected.



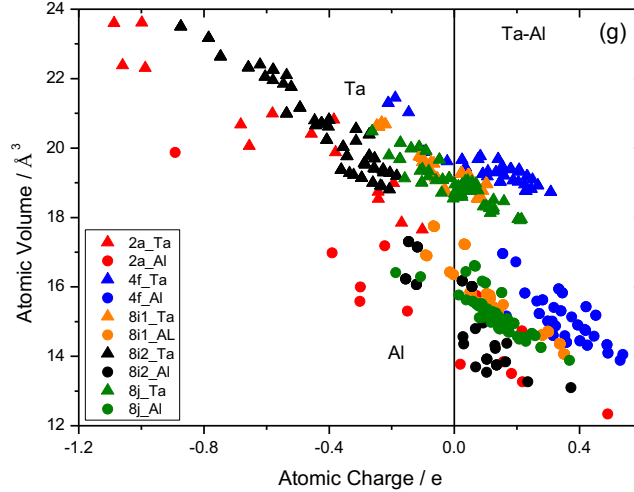


Fig. 3. Atomic volume with respect to atomic charge of the constituent elements in 32 ($2^5=32$) stoichiometric sigma end-member compounds (e.g. $W_2W_4W_8W_8W_8$, $Re_2W_4W_8W_8W_8$ etc.) for W-Re, Mo-Re, Mo-Mn, Ta-Pd, Re-Mn, Ru-Cr and Ta-Al binary systems calculated using VASP and Bader's AIM approach. (Color online).

3.1. Influence of nearest neighbor (NN) atoms on atomic volume

The NN atoms mainly affect the atomic charge and the space to accommodate the specific atom, and thus affect its atomic volume. In the following section 3.1.1 and 3.1.2, we respectively discussed how the atomic charge and the accommodation space affect the atomic volume of the sigma phase.

3.1.1. Atomic charge

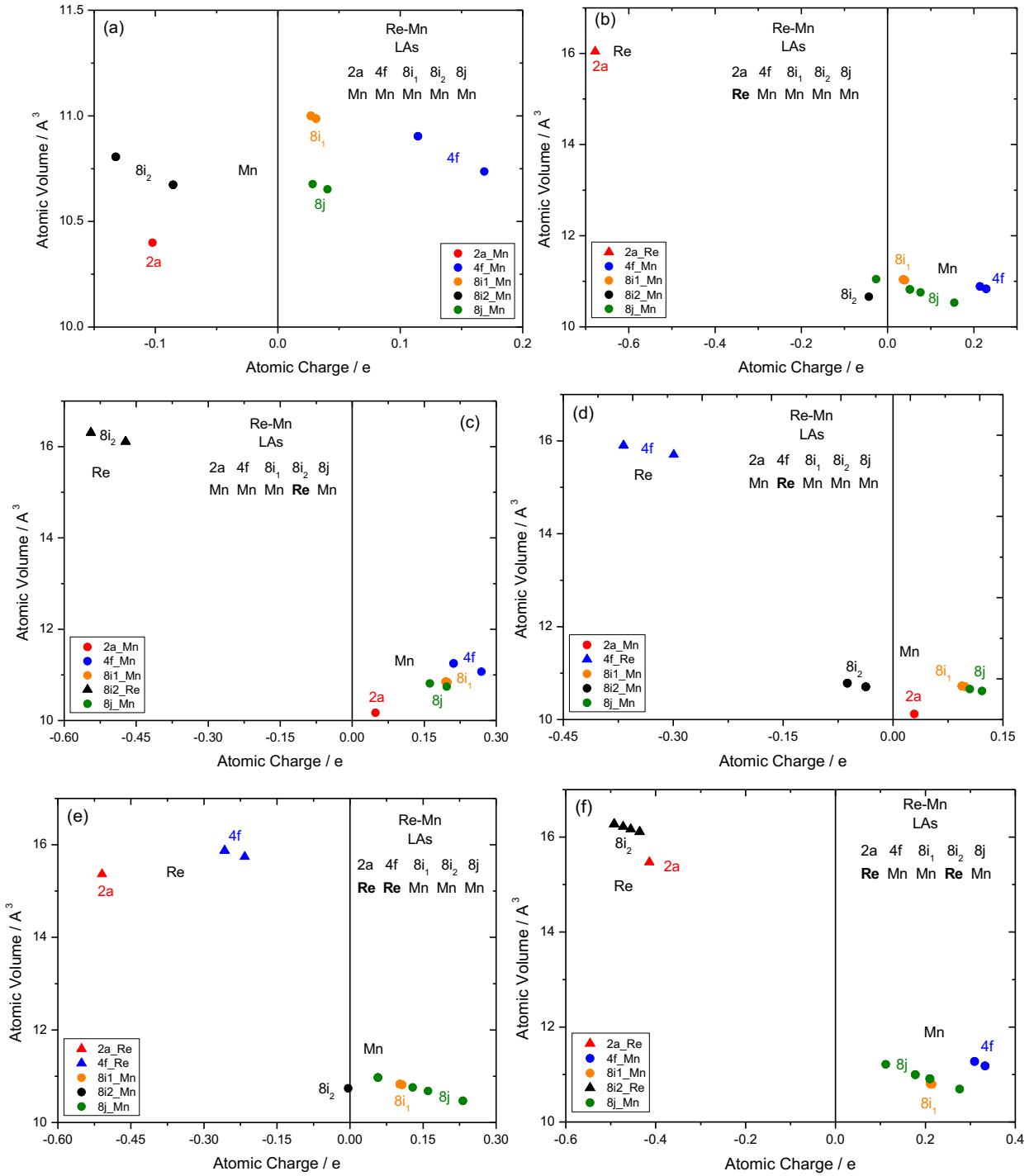
Fig. 3 shows the calculated atomic volume with respect to atomic charge of the constituent elements in the complete set ($2^5=32$) of ordered configurations of the A-B ($V(A) > V(B)$) binary sigma phase. It indicates that for W-Re, Mo-Re and Ta-Pd systems (which belong to SMe, SMS-SMe and LAs-SMe categories respectively), the atomic size and site size follow the same sequence. It can be obviously seen that for a specific element, on a specific site, atoms with more negative atomic charge bear a larger volume.

For Re-Mn, Ru-Cr, Mo-Mn (which belong to LAs, LAs-LAe and LAs-SMe categories respectively) and Ta-Al systems, for the same or a small variation of the atomic charge, the atomic volume difference for a specific element on a specific site can be very large. This is due to the fact that for these systems, the atomic volume is more sensitive to the accommodation space. For LAs,

LAs-LAe categories and some system in LAs-SMe category, large atom A tend to gain electrons and the atomic size further increases; small atom B tend to lose electrons and the atomic size further decreases [3]. Thus the size difference between the two constituent elements becomes very large, which makes the factor of accommodation space crucial. Properties of A-Al (A-Nb, Ta) category behaves similarly as LAs-SMe category [3], such as the tendency of electron loss or gain, and the site occupancy preference.

3.1.2. Accommodation space

As mentioned in the last section, for LAs, LAs-LAe categories, the atomic volume is more sensitive to accommodation space. Thus we selected Re-Mn and Ru-Cr systems, and analyzed the atomic volume among the 32 stoichiometric end-member compounds, compound-by-compound. Fig. 4 and Fig. 5 show the atomic volume with respect to atomic charge of the constituent elements in several stoichiometric sigma end-member compounds for Re-Mn and Ru-Cr system, respectively. Table 2 shows the number of NN atom A around the δ_{i1} , δ_j and δ_{i2} sites of the corresponding compounds in Fig. 4 and Fig. 5, which can be conveniently achieved from Fig. 1 and Table 1. It was found that when large atom A ($V(A) > V(B)$) occupy δ_{i1} and δ_j sites, and in the meanwhile the number of the NN atom A surrounding δ_j site is large enough as indicated in Table 2, the atomic sizes of B on δ_{i1} and δ_j follows $\delta_j > \delta_{i1}$ (normally the atomic size sequence for a specific element follows the occupied site size sequence, i.e. $\delta_{i1(CN14)} > \delta_{j(CN14)}$ [3]) as seen in Fig. 4 (e-h) and Fig. 5 (e-h). Hence we can conclude that the more the NN large atoms, the larger the space to accommodate the specific atom. There are more evidences to support this, but to avoid redundance, we will not state.



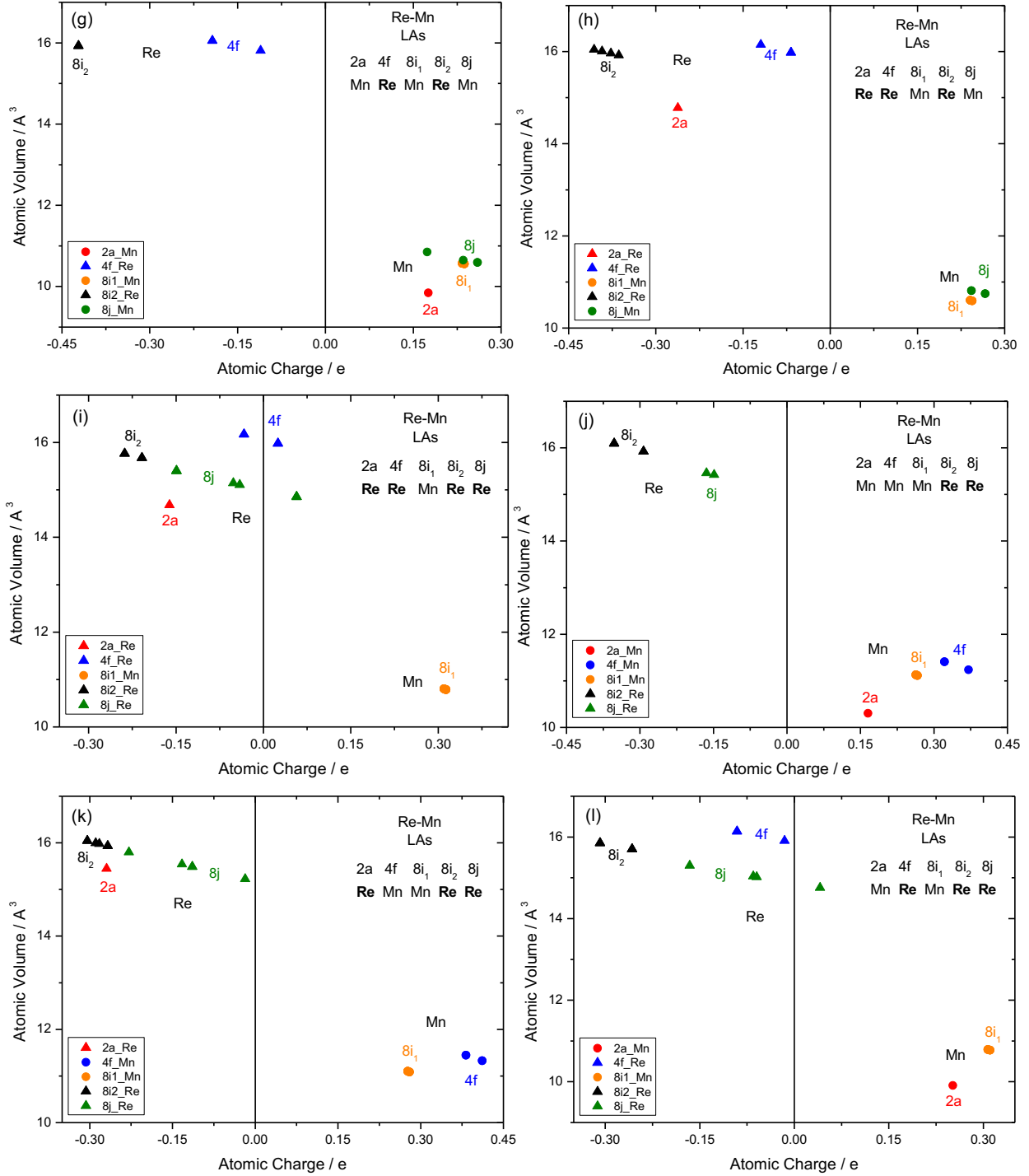
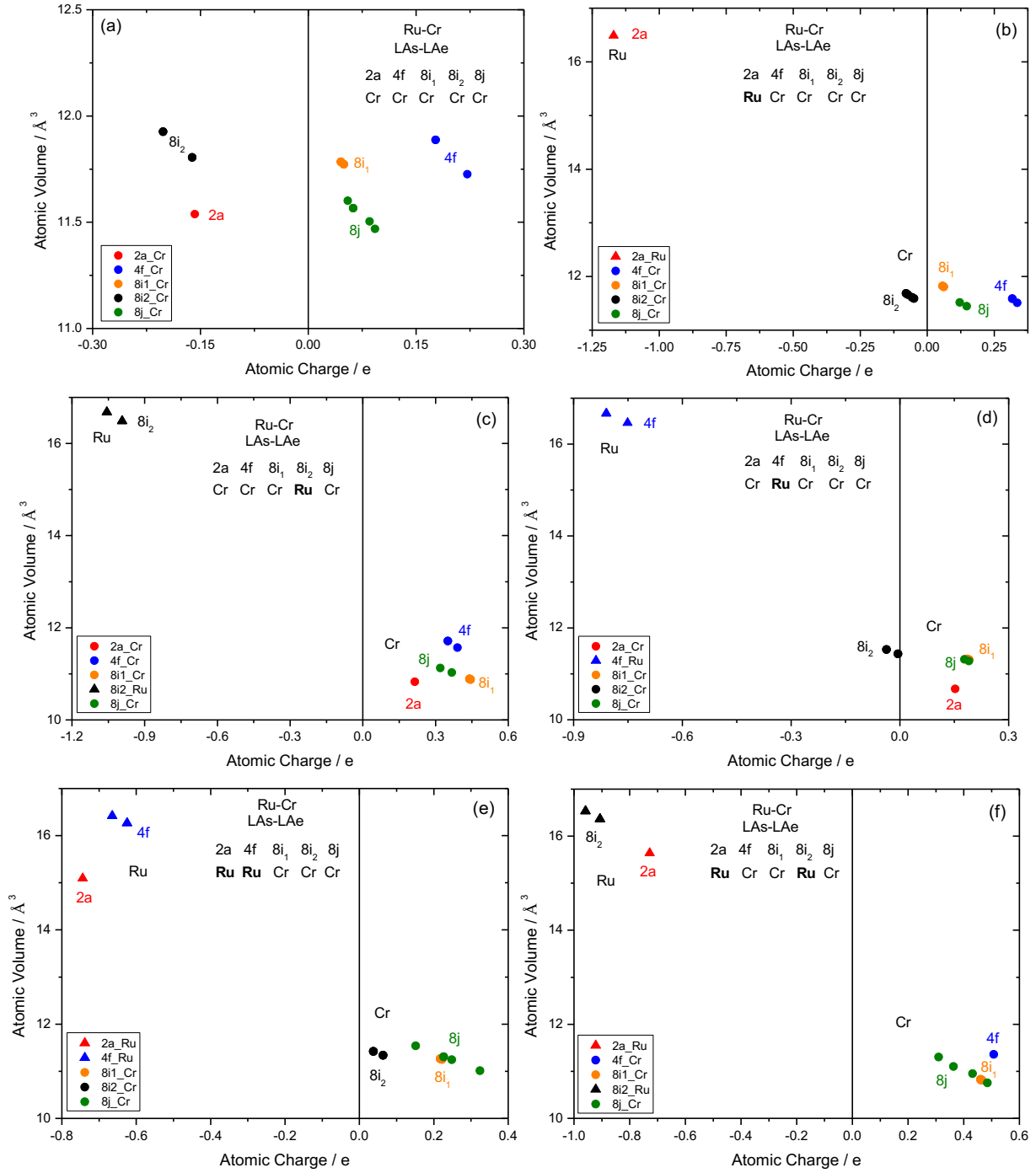


Fig. 4. Atomic volume with respect to atomic charge of the constituent elements in stoichiometric sigma end-member compounds for Re-Mn system calculated using VASP and Bader's AIM approach. (a-h): $X_2X_4Mn_8X_8Mn_8$; (i-l) $X_2X_4Mn_8Re_8Re_8$ (X=Re or Mn). Every figure contains 30 points but some of them are overlapped (Color online).



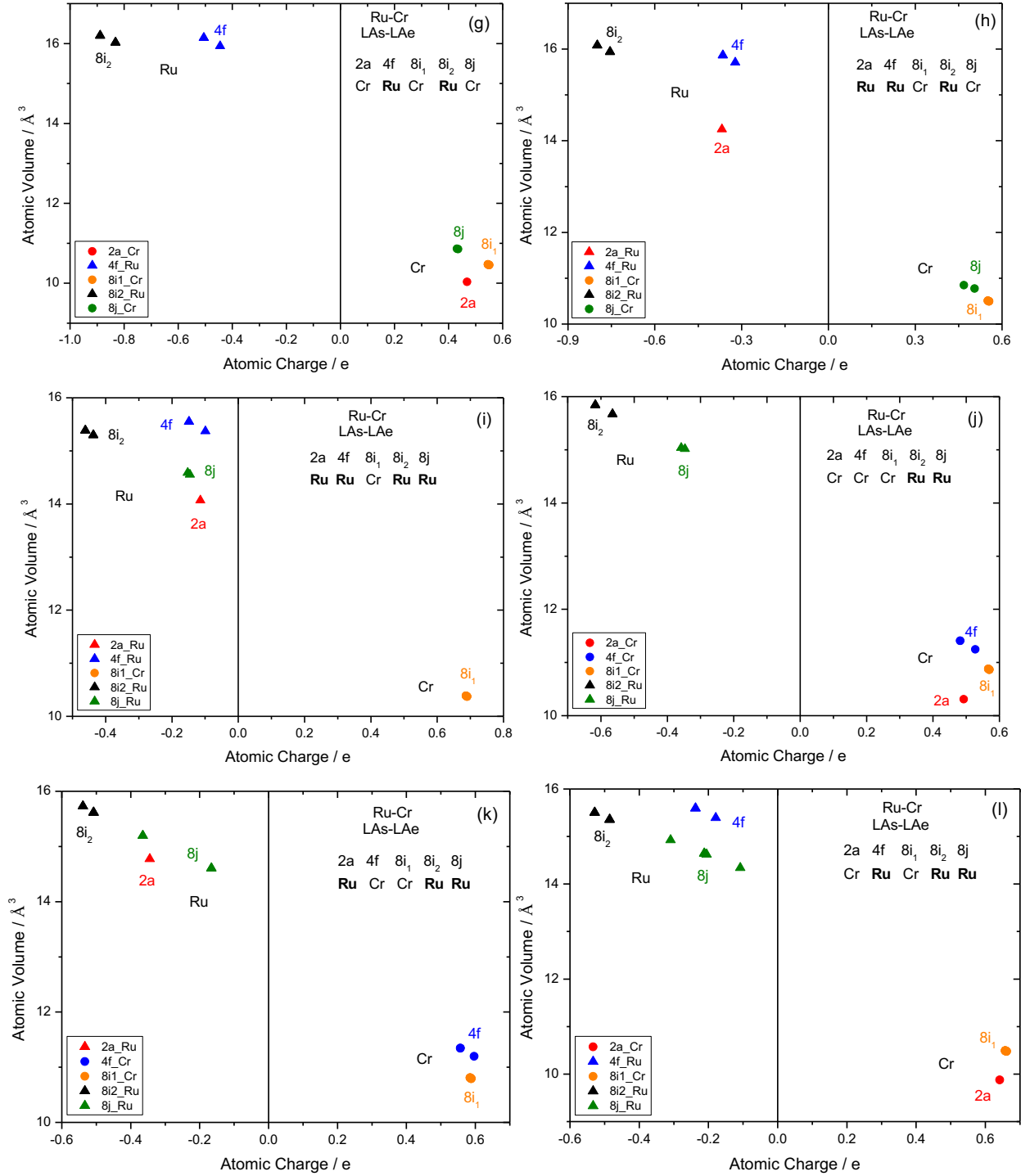


Fig. 5. Atomic volume with respect to atomic charge of the constituent elements in stoichiometric sigma end-member compounds for Ru-Cr system calculated using VASP and Bader's AIM approach. (a-h): $X_2X_4Cr_8X_8Cr_8$; (i-l) $X_2X_4Cr_8Ru_8Ru_8$ ($X=Ru$ or Cr). Every figure contains 30 points but some of them are overlapped (Color online).

Table 2 Number of nearest neighbor (NN) atom A for the $8i_1$, $8j$ and $8i_2$ sites of the corresponding A-B ($V(A)>V(B)$) binary sigma compounds in Fig. 4 and Fig. 5.

Site	2a	4f	$8i_1$	$8i_2$	$8j$	NN atom A around the site		
						$8i_1(\text{CN}14)$	$8j(\text{CN}14)$	$8i_2(\text{CN}12)$
(a)	B	B	B	B	B	0	0	
(b)	A	B	B	B	B	0	1	
(c)	B	B	B	A	B	4	4	
(d)	B	A	B	B	B	1	3	
(e)	A	A	B	B	B	1	4	
(f)	A	B	B	A	B	4	5	
(g)	B	A	B	A	B	5	7	
(h)	A	A	B	A	B	5	8	
(i)	A	A	B	A	A		10	8
(j)	B	B	B	A	A		6	5
(k)	A	B	B	A	A		7	6
(l)	B	A	B	A	A		9	7

3.2. Influence of coordination polyhedron (CP) on atomic volume

The CP mainly affects the space to accommodate the specific atom, and thus affect its atomic volume. Fig. 4 (i-l) and Fig. 5 (i-l) show that when larger atom A ($V(A)>V(B)$) occupy $8i_2$ and $8j$ sites, and smaller atom B occupy $8i_1$ site, 4f and 2a sites occupied by either A or B, the atomic sizes of A on $8i_2$ and $8j$ sites become close (normally it follows $8j(\text{CN}14)>8i_2(\text{CN}12)$ [3]). Since atom B occupy $8i_1$ site, it makes the NN atom A around $8j$ and $8i_2$ sites less. Thus the space of $8j$ and $8i_2$ sites cannot loosely accommodate the large atom A, and the CP symmetry becomes a primary factor determining the atomic size on $8j$ and $8i_2$ sites. The symmetry of CN12 sites is higher than that of CN14 sites [27], which can be clearly observed in Fig. 2. Thus even though, $8j$ site is with larger CN and more NN atom A as compared to $8i_2$ site as indicated in Table 2, for compounds (i-l) in Table 2, the atomic sizes of A on $8j$ and $8i_2$ sites are close.

4. Conclusion

In the present work, the influencing factors of the atomic volume in the A-B ($V(A) > V(B)$) binary sigma systems were investigated. The main conclusion can be summarized as follows:

1. Both the nearest neighbor (NN) atoms and coordination polyhedron (CP) affect the atomic volume of the sigma phase and cause the atomic volumes sometimes unfollow the size sequence of the correspondingly occupied site.
2. The CP mainly affects the accommodate space, the NN atoms mainly affect the atomic charge and the accommodate space, and thus affect the atomic volume. For a specific element, on a specific site, the greater the ability of an atom to gain electrons, the larger the volume of the atom; the more the NN large atoms (atom A), the larger the space to accommodate the specific atom.
3. For SMe and SMs-SMe categories, the atomic volume of the sigma phase is mainly affected by the atomic charge; For LAs, LAs-LAe categories, the atomic volume is more sensitive to the accommodation space. For LAs-SMe category, it is ultimately determined by the compromised effect of LAs and SMe factors on the tendency of electron loss or gain of the two constituent elements.

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