



**HAL**  
open science

## Influence of atomic mixing and atomic order on molar volume of the binary sigma phase

Wei Liu, Xiao-Gang Lu, Pascal Boulet, Marie-Christine Record, Hao Wang,  
Qing-Miao Hu

► **To cite this version:**

Wei Liu, Xiao-Gang Lu, Pascal Boulet, Marie-Christine Record, Hao Wang, et al.. Influence of atomic mixing and atomic order on molar volume of the binary sigma phase. *Intermetallics*, 2018, 98, pp.95 - 105. 10.1016/j.intermet.2018.04.008 . hal-01782253

**HAL Id: hal-01782253**

**<https://hal.science/hal-01782253v1>**

Submitted on 10 Feb 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Influence of atomic mixing and atomic order on molar volume of the binary sigma phase

Wei Liu<sup>a</sup>, Xiao-Gang Lu<sup>a,b</sup>, Pascal Boulet<sup>c</sup>, Marie-Christine Record<sup>d</sup>, Hao Wang<sup>b,\*</sup>, Qing-Miao Hu<sup>e</sup>

<sup>a</sup> Materials Genome Institute, Shanghai University, 200444 Shanghai, China

<sup>b</sup> School of Materials Science and Engineering, Shanghai University, 200444 Shanghai, China

<sup>c</sup> Aix-Marseille University, CNRS, MADIREL, Marseille, France

<sup>d</sup> Aix-Marseille University, Université de Toulon, CNRS, IM2NP, Marseille, France

<sup>e</sup> Titanium Alloy Laboratory, Institute of Metal Research, Chinese Academy of Sciences, 110016 Shenyang, China

## ABSTRACT

The present work systematically clarifies the influence of the atomic mixing and the atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal) on the molar volume of the binary sigma phase. We calculated the molar volumes of 21 binary sigma compounds with different atomic order by using EMTO-CPA (Exact Muffin-Tin Orbitals - Coherent Potential Approximation) method. The calculation results follow a similar trend as the experimental data. Moreover, the calculated molar volumes with respect to the composition of the sigma phase in disordered states show that the sigma compounds do not comply with the linear volume-composition relationship. This is due to the influence of the atomic mixing and the deviation can be either negative or positive depending on the tendency of electron loss or gain of the two constituent elements. Additionally, we compared the molar volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) between the hypothetically disordered and ordered states of the binary sigma compounds. The results indicate that the effect of the atomic order on the molar volume of the sigma phase depends on the size difference and the electron configurations of the two constituent elements.

## 1. Introduction

The sigma phase is a nonstoichiometric intermetallic compound with tetragonal structure (space group P42/mnm) containing 30 atoms distributed on five inequivalent sites [1–3] as shown in Table 1. This phase exists in 49 different binary systems, among which Cr-Ni, Ta-V, Ti-Mn, Zr-Ir and Zr-Re are not confirmed. It is a hard brittle phase mostly formed between transition elements and when presenting in stainless and other high-alloy steels as well as Ni-based superalloys, it deteriorates the properties of products [1,2].

As an important physical property, the molar volume (or lattice parameters) of the sigma phase has attracted great interests of investigations [1–5], by using XRD (X-ray diffraction), ND (neutron diffraction), CALPHAD [6–8] or first-principles calculation methods.

From the 1950s–2010s, there are numerous measurements (see e.g. Ref. [5] and references therein) on the lattice parameters of the sigma compounds by using XRD or ND methods. The measured data from the 2000s–2010s are more accurate. Most measured volumes with respect to composition present linear relationship within the homogeneity range [5]. Besides, Crivello et al. [4] calculated the cell volumes of the stoichiometric end-

member compounds (i.e. the complete set of ordered configurations) of Re-X (X = Co, Cr, Fe, Hf, Mn, Mo, Nb, Ni, Os, Ru, Ta, Tc, Ti, V, W and Zr) by using first-principles calculations. They indicated that for most systems, the cell volume with respect to composition present an approximately linear relationship, while for Hf-Re, Nb-Re, Ta-Re, Ti-Re and Zr-Re, a negative deviation from linearity was observed (see Fig.5 in Ref. [4]), which indicates a denser packing with atomic mixing [4]. However, Crivello et al. [4] did not further discuss the origin of the deviation.

In a recent work, Liu et al. [5] modeled and evaluated the molar volume of the binary sigma phase at room temperature and atmospheric pressure by using the CALPHAD method and establishing a CALPHAD-like database. The adopted model expresses the molar volume of a nonstoichiometric sigma phase as a linear average of volumes of the constituent elements in their hypothetical sigma structure [5]. The proposed linear model can well reproduce most experimental data. It has interesting features in developing databases, such as reducing the number of assessed parameters and separating the volume data from the corresponding thermodynamic databases. The proposed linear model works well as a phenomenological method, which however does not present any physical and chemical insights.

In fact, two influencing factors were neglected in the above linear model, namely atomic mixing and atomic order (i.e. atomic constituent distribution or site occupancy preference on inequivalent sites of a crystal). Both the atomic mixing and atomic order may lead to a deviation from the linearity mentioned above. Unlike solution phases, the molar volume of the sigma phase can vary with the atomic order even at a fixed composition. The purpose of the present work is to study how the atomic mixing and atomic order affect the molar volume of the sigma phase.

Hall and Algie [1], Joubert [2] and then Liu et al. [9] systematically investigated the atomic order of the binary sigma phase. Liu et al. [9] indicates that between the two constituent elements, the one with larger size, smaller number of valence electrons or smaller total number of electron shells prefers occupying large coordination number (CN) sites and the other one prefers occupying small CN sites.

In the present work, we calculated the molar volume of the A-B binary sigma phase with different atomic order by using EMT0-CPA approach. The atomic order involves the completely ordered and disordered states as defined in Table 1, as well as the experimental site occupancies. We used the molar volume difference between the A<sub>2</sub>B sigma compounds in the ordered and disordered states to describe the influence of atomic order on molar volume. On the other hand, we describe the influence of atomic mixing on molar volume by studying deviation of the volume of the hypothetically disordered sigma phase from linear volume-composition relationship, which describes volume variations of the hypothetically disordered sigma phase spanning from pure sigma A to pure sigma B. Notably, the disordered state is the closest state to solid solution. Thus, it excludes the influence of atomic order on molar volume.

**Table 1**

Crystal structure of the sigma phase with assignment of the site occupancy of atom A corresponding to the ordered and disordered compounds  $A_2B$  and  $A_xB_{(1-x)}$  ( $V(A) > V(B)$ , where  $V(A)$  and  $V(B)$  are the molar volumes of A and B, respectively, in their hypothetic sigma phase structure from the CALPHAD assessments [5,9]).

Space group	P4 <sub>2</sub> /mm (no. 136)				
Wyckoff position	2a	4f	8i <sub>1</sub>	8i <sub>2</sub>	8j
Coordination number (CN)	12	15	14	12	14
Completely ordered compound ( $A_2B$ ) [2]	0	1	1	0	1
Disordered compound ( $A_xB_{(1-x)}$ )	x	x	x	x	x

To facilitate explanation, all the binary sigma compounds investigated are designated as A-B where atom A always has a larger size than atom B (i.e.  $V(A) > V(B)$ ). The size of atom A or B is determined by the molar volume of pure A or B in their hypothetic sigma phase structure from the CALPHAD assessments [5,9]. Besides, we introduced different categories of the sigma phase divided by Liu et al. [9] as shown in Table 2. It is classified according to the electron configurations of the two constituent elements. There exist six different categories, i.e. SMe, SMs-SMe, LAs, LAs-SMe, LAs-LAe, A-AI (A = Nb, Ta), where SMe or LAe indicates that atom A has smaller or larger number of valence electrons than atom B, respectively; SMs or LAs indicates that atom A has smaller or larger total number of electron shells than atom B, respectively.

**Table 2**

A-B ( $V(A) > V(B)$ ) binary sigma systems in different categories divided by Liu et al [9] according to electron configurations of the two constituent elements. An instance of the electron configurations for each category is given at the bottom. The systems labelled with italic are not confirmed to form the sigma phase.

SMe			SMs-SMe		LAs	LAs-SMe		LAs-LAe	A-AI (A=Nb, Ta)
Cr-Co	Nb-Rh	V-Co	Mo-Ir	<i>Zr-Ir</i>	Re-Mn	Mo-Co	Tc-Fe	Os-Cr	Nb-Al
Cr-Fe	Ta-Au	V-Fe	Mo-Os	<i>Zr-Re</i>	<i>Ta-V</i>	Mo-Fe	W-Ru	Re-Cr	Ta-Al
Cr-Mn	Ta-Ir	V-Mn	Mo-Re		Tc-Mn	Mo-Mn	W-Tc	Re-V	
<i>Cr-Ni</i>	Ta-Os	V-Ni	Nb-Ir			Re-Fe		Ru-Cr	
Mo-Ru	Ta-Pt	W-Ir	Nb-Os			Ta-Pd		Tc-Cr	
Mo-Tc	Ta-Re	W-Os	Nb-Pt			Ta-Rh			
Nb-Pd	<i>Ti-Mn</i>	W-Re	Nb-Re						
e.g. Cr-Co: 3d <sup>5</sup> 4s <sup>1</sup> - 3d <sup>7</sup> 4s <sup>2</sup>			e.g. Mo-Ir: 4d <sup>5</sup> 5s <sup>1</sup> - 5d <sup>7</sup> 6s <sup>2</sup>		e.g. Re-Mn: 5d <sup>5</sup> 6s <sup>2</sup> - 3d <sup>5</sup> 4s <sup>2</sup>	e.g. Mo-Co: 4d <sup>5</sup> 5s <sup>1</sup> - 3d <sup>7</sup> 4s <sup>2</sup>		e.g. Os-Cr: 5d <sup>6</sup> 6s <sup>2</sup> - 3d <sup>5</sup> 4s <sup>1</sup>	e.g. Nb-Al: 4d <sup>4</sup> 5s <sup>1</sup> - 3s <sup>2</sup> 3p <sup>1</sup>

## 2. Methodology and calculation details

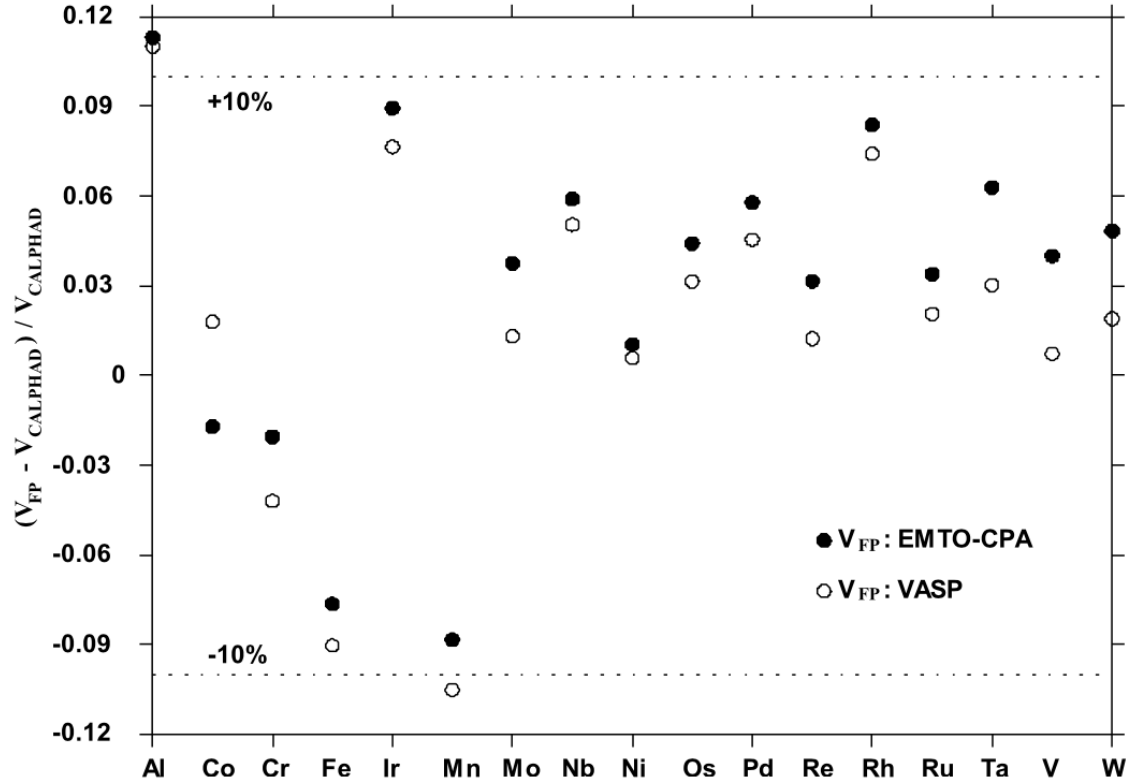
First-principles calculations were performed using the exact muffin-tin orbitals (EMTO) method [10,11] based on the density-functional theory (DFT) [12]. With this method, Green's function technique is used to solve the one electron Kohn-Sham equation. The effective potential in the one-electron equation is treated with the optimized overlapping muffin-tin approximation. Besides, the total energy is corrected with the full charge density (FCD) method [10]. The basis sets of the exact muffin-tin orbitals [10,11] are used to expand the wave function. The coherent potential approximation (CPA) [13–15] is

incorporated within the EMTO code, which facilitates the calculations dealing with chemical disordered alloys. With these techniques, the EMTO-CPA method holds a great higher accuracy than the linear muffin-tin orbital (LMTO) method [16] and ensures the reliability of calculations dealing with atomic and magnetic disordered systems [17].

In the present work, Green's function was calculated for 16 complex energy points distributed exponentially on a semicircular contour. The scalar-relativistic and soft-core approximations were employed. We used the electronic exchange-correlation functional within the generalized-gradient approximation (GGA) parameterized by Perdew et al. [18]. The Brillouin zone was sampled by a uniform k-point mesh without any smearing technique. The k-point mesh was set to  $3 \times 3 \times 6$ . For Cr-Fe and V-Fe, the magnetic parameters for ferro- magnetism were set.

### 3. Results and discussion

The binary sigma compounds chosen to perform EMTO-CPA calculations are Cr-Co, Cr-Fe, Cr-Mn, Mo-Co, Mo-Mn, Mo-Os, Mo-Re, Nb-Al, Nb-Ir, Os-Cr, Re-Cr, Re-Mn, Re-V, Ru-Cr, Ta-Al, Ta-Pd, Ta-Rh, V-Co, V-Fe, V-Mn and V-Ni. The molar volumes of the pure elements in a hypothetical sigma phase structure obtained from first-principle calculations are compared in Fig. 1 with those obtained from the CALPHAD assessments. This figure shows that the volumes calculated by EMTO-CPA and VASP methods follow a similar trend. Besides, it indicates that for most elements, the differences between the first-principles calculations and the CALPHAD assessed ones are within 10%. The small deviations validate our calculations.



**Fig. 1.** Molar volume differences of pure elements in a hypothetical sigma phase structure between data obtained by first-principles calculations (EMTO-CPA and VASP) and from the CALPHAD assessments [5,9]. VASP calculation results are from Crivello et al. [4] and Liu et al. [5]. Dashed lines correspond to 10% deviation.

Fig. 2 shows the calculated molar volumes of the A-B ( $V(A) > V(B)$ ) binary sigma compounds compared with the experimental data. The calculated molar volume data with respect to the composition follow similar changing trends as compared with the measured ones, especially for Cr-Co, Mo-Re, Re-Cr and Ta-Al. In addition, Fig. 2 indicates that for some systems, the changing trends of the calculation results are less obvious than the experimental ones so they have to be magnified as in Fig. 2 (a, q), respectively, for Cr-Co and Re-Cr.

In the present work, the calculations accounting for ferromagnetism were conducted on several sigma compounds of A-Fe ( $A = \text{Cr, V}$ ) to determine the molar volume as shown in Fig. 2 (b, e). The measured magnetic moment for  $V_{39.9}\text{Fe}_{60.1}$  compound is  $0.63 \mu\text{B}$  and the Curie temperature is  $168.4 \text{ K}$  [26]. The calculated magnetic moment by using the corresponding measured site occupancy taken from Ref. [3] is  $0.56 \mu\text{B}$ . The good agreement between these results further validates our calculation results. For the other systems in Fig. 2, ferromagnetism was not considered. It should be noted that since no sigma compounds known to exist in binary alloy systems exhibit magnetic order above room temperature [26], thus during the whole discussion in the present work, no magnetism is considered.

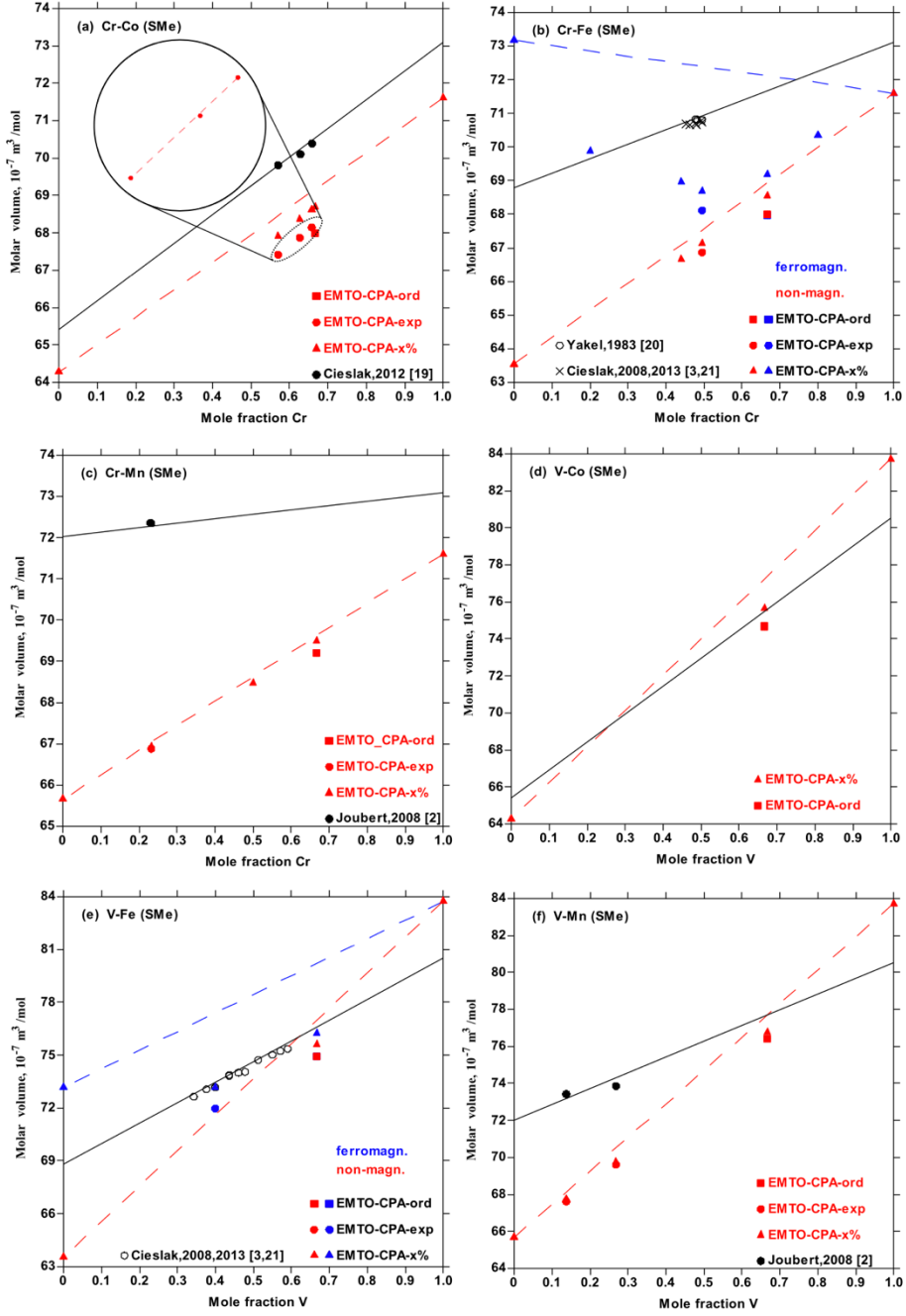


Fig. 2. EMT0-CPA-calculated and CALPHAD assessed molar volumes of A-B (Cr-Co, Cr-Fe, Cr-Mn, Mo-Co, Mo-Mn, Mo-Os, Mo-Re, Nb-Al, Nb-Ir, Os-Cr, Re-Cr, Re-Mn, Re-V, Ru-Cr, Ta-Al, Ta-Pd, Ta-Rh, V-Co, V-Fe, V-Mn and V-Ni) sigma compounds compared with the experimental data [2,3,19–25]. EMT0-CPA-ord, EMT0-CPA-exp and EMT0-CPA-x% represent the calculated volumes, respectively, with site occupancies of ordered states, experimental measurements and disordered states. The full line represents the CALPHAD assessment results [5,9] and the dashed line is a guide to the eye.

### 3.1. Definition of order degree

For an A-B binary ordered phase, the order degree is quantitatively expressed by long-range order parameter  $S$  [27]:

$$S = \frac{P_A - X_A}{1 - X_A} \quad (1)$$

where  $P_A$  is the probability of occurrence of atom A on the right crystal site for atom A (i.e. the crystal site is occupied by atom A when the crystal is in totally ordered state);  $X_A$  is the mole fraction of atom A. When in ordered state,  $P_A = 1$  and thus  $S = 1$ ; When in disordered state,  $P_A = X_A$  and thus  $S = 0$ .

However, Eq. (1) is unable to describe the situation when all the right crystal sites for atom A are occupied by atom A (i.e.  $P_A = 1$ ) but there are extra atom A occupying the wrong site (i.e. the crystal site should be occupied by atom B when the crystal is in totally ordered state). Hence we introduce the following description for long-range order parameter  $S$ :

$$S = \frac{n_A \cdot P_A - X_A}{n \cdot 1 - X_A} + \frac{n_B \cdot P_B - X_B}{n \cdot 1 - X_B} \quad (2)$$

where  $P_A$  and  $P_B$  are the probabilities of occurrence of atoms A and B (i.e. the site occupancies), respectively on their right crystal sites;  $X_A$  and  $X_B$  are the mole fractions of atom A and B, respectively;  $n$ ,  $n_A$  and  $n_B$  are the total number of atoms, the numbers of atom A and B, in a unit cell respectively when the crystal is in totally ordered state. When  $S = 1$ , the compound is totally ordered; when the probabilities  $P_A$  and  $P_B$  equal the mole fractions  $X_A$  and  $X_B$  respectively, the compound is totally disordered with  $S = 0$ .

In the present work, we treat the completely ordered compound  $A_2B$  ( $B_{2a}A_{4f}A_{8i1}B_{8i2}A_{8j}$ ) defined in Table 1 as a reference ordered state of the sigma phase and extend Eq. (2) to the sigma phase as follows:

$$S = \frac{2}{30} \cdot \frac{P_{B_{2a}} - X_B}{1 - X_B} + \frac{4}{30} \cdot \frac{P_{A_{4f}} - X_A}{1 - X_A} + \frac{8}{30} \cdot \frac{P_{A_{8i1}} - X_A}{1 - X_A} + \frac{8}{30} \cdot \frac{P_{B_{8i2}} - X_B}{1 - X_B} + \frac{8}{30} \cdot \frac{P_{A_{8j}} - X_A}{1 - X_A} \quad (3)$$

where atom A has a larger size than atom B;  $P_A$  and  $P_B$  are the probabilities of occurrence (i.e. the site occupancies) on 2a, 4f, 8i1, 8i2 and 8j sites of atoms A and B, respectively;  $X_A$  and  $X_B$  are the mole fractions of atom A and B, respectively. The five terms on the right hand side represent the order degrees of the five inequivalent sites, respectively, designated as  $S_{2a}$ ,  $S_{4f}$ ,  $S_{8i1}$ ,  $S_{8i2}$  and  $S_{8j}$ . The long-range order parameter  $S$  is hereafter considered as the order degree.

When  $S=1$ , the compound is totally ordered; when the probabilities  $P_A$  (i.e.  $P_{A_{2a}}$ ,  $P_{A_{4f}}$ ,  $P_{A_{8i1}}$ ,  $P_{A_{8i2}}$  and  $P_{A_{8j}}$ ) or  $P_B$  (i.e.  $P_{B_{2a}}$ ,  $P_{B_{4f}}$ ,  $P_{B_{8i1}}$ ,  $P_{B_{8i2}}$  and  $P_{B_{8j}}$ ) on the five inequivalent sites equal the mole fractions  $X_A$  or  $X_B$ , respectively, the compound is totally disordered with  $S = 0$ . When the order degree on the five inequivalent sites (i.e.  $S_{2a}$ ,  $S_{4f}$ ,  $S_{8i1}$ ,  $S_{8i2}$  or  $S_{8j}$ ) is negative with  $P_{B_{2a}} < X_B$ ,  $P_{A_{4f}} < X_A$ ,  $P_{A_{8i1}} < X_A$ ,  $P_{B_{8i2}} < X_B$ , or  $P_{A_{8j}} < X_A$ , one deals with an anti-order degree. It should be noted that for a specific value of  $S$ , there are many possible values of site occupancy. However, for a specific sigma compound, the site occupancy on every site changes within a limited range, and thus the values of  $S$  still convey an important piece of information, i.e. compounds with larger values of  $S$  are in more ordered state. The calculated order degrees of several sigma compounds based on experimental site occupancies are listed in Table A.1.



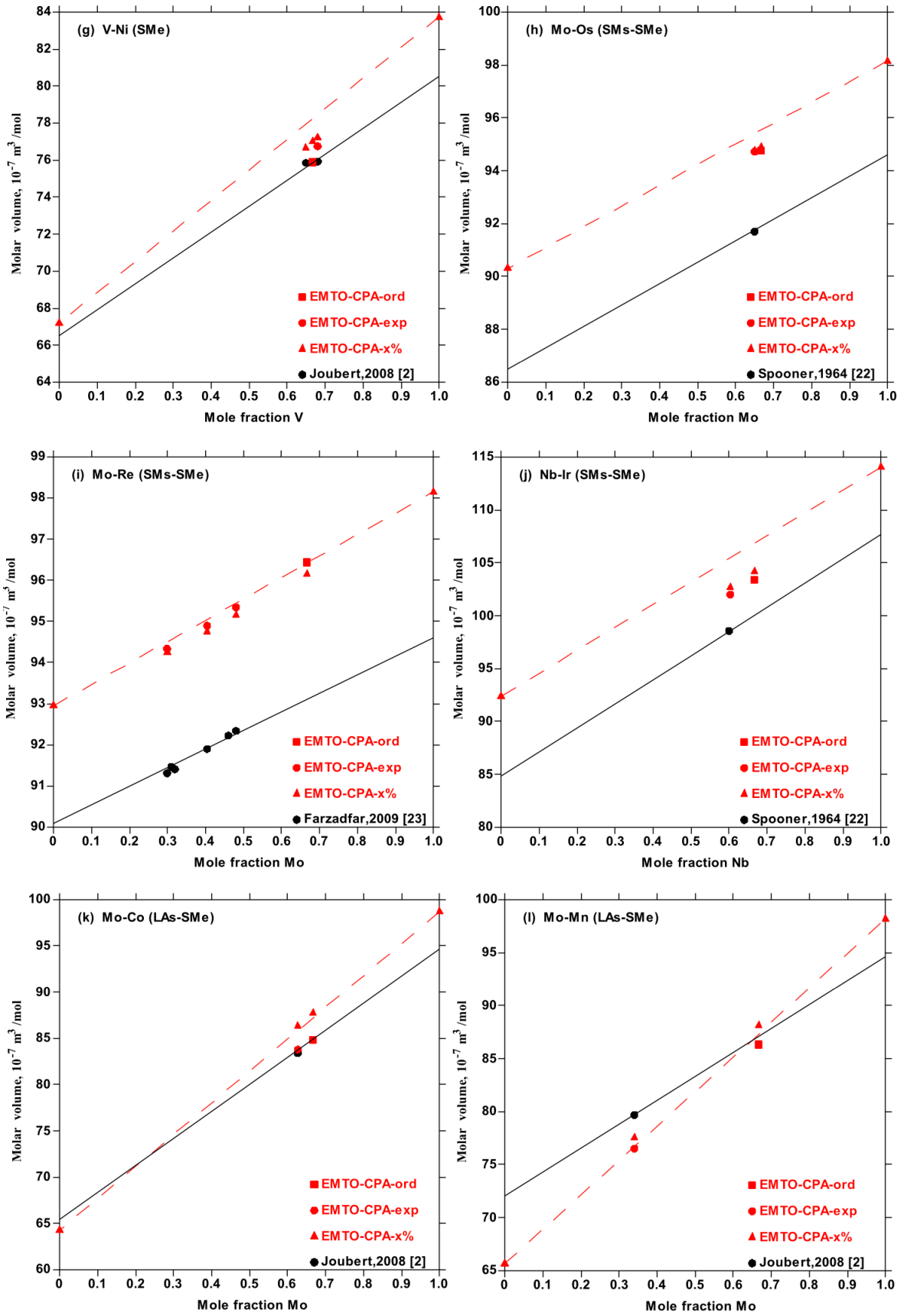


Fig. 2. (continued)

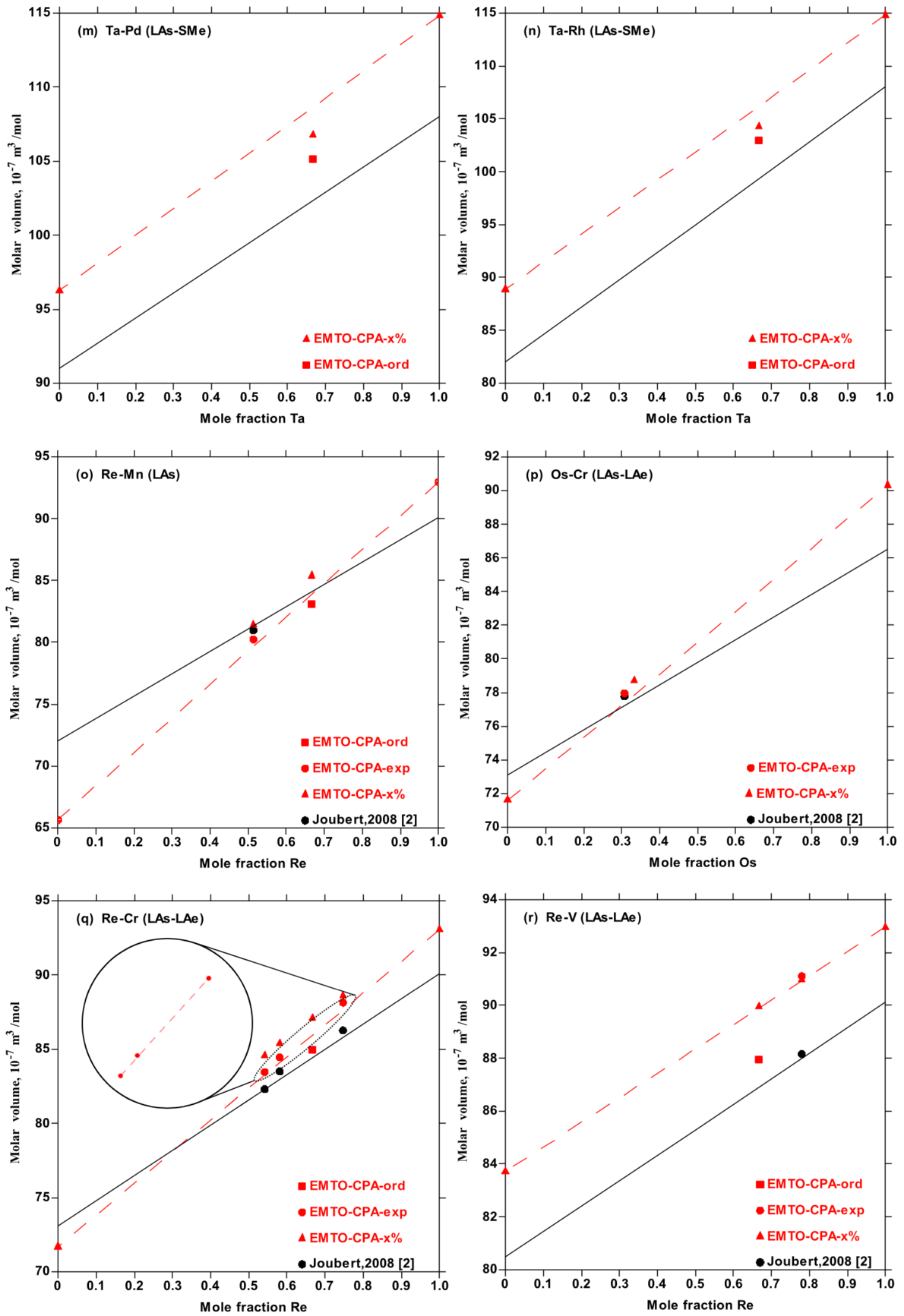


Fig. 2. (continued)

### 3.2. Influence of atomic mixing on molar volume of the sigma phase

The influence of atomic mixing on molar volume is described by the volume deviation of the hypothetically disordered sigma phase from the linear composition-volume relationship. It can be seen from Fig. 2 that the sigma compounds in their disordered states do not comply with the above mentioned linearity and present positive or negative deviations, which is summarized in Table 3.

For A-Al, SMe, SMS-SMe categories and two systems (i.e. Ta-Pd and Ta-Rh) in LAs-SMe category, the disordered calculation results present a negative deviation from the linear composition-volume relationship. For LAs, LAs-LAe categories and two systems (i.e. Mo-Co and Mo-Mn) in LAs-SMe category, a positive deviation is observed. It is expected that the deviation from the linearity is related to the tendency of electron loss or gain between the two constituent elements. The tentative discussion is as follows.

For SMe and SMS-SMe categories, large atom A tends to lose electrons and small atom B tends to gain the corresponding amounts of electrons [9]. The smaller the atomic size, the stronger the bond between the nucleus and the valence electrons [28]. Thus the transferred electrons to atom B are expected to be more bound. This is consistent with the observed negative deviation for the disordered sigma phase in Fig. 2 and Table 3.

Vice versa, for LAs and LAs-LAe categories, large atom A tends to gain electrons and small atom B tends to lose the corresponding electrons [9]. Thus the transferred electrons to atom A are expected to be less bound. This is consistent with the observed positive deviation for the disordered sigma phase in Fig. 2 and Table 3.

With regard to LAs-SMe category, a competition of LAs (i.e. the total number of electron shells of atom A is larger than atom B) and SMe (i.e. the number of valence electrons of atom A is smaller than atom B) factors determines the electron transfer and thus the deviation from the linear composition-volume relationship. For Mo-Co and Mo-Mn, LAs factor is more crucial; for Ta-Pd and Ta-Rh, SMe factor is more crucial. It should be mentioning that the electron transfer behavior for A-Al category is reported to be similar as LAs-SMe category [9].

From the above discussion, it is understandable that among all the systems studied by Crivello et al. [4] as mentioned in Section 1, for Hf-Re and Ta-Re (both belonging to the SMe category), and Nb-Re, Ti-Re and Zr-Re (all belonging to the SMS-SMe category), the calculated cell volumes of the 32 ordered configurations present a negative deviation with respect to composition. The calculations involve the full set of ordered configurations, including the ones in anti-ordered states, for which the cell volumes can be very large due to the size mismatch. For the calculated cell volume of each compound, the negative deviation is presented no matter what the atomic order of the compound is. Thus the crucial factor leading to the negative deviation is the atomic mixing rather than the atomic order. Further, we can conclude the negative deviation is due to a significant effect of SMS (i.e. the total number of electron shells of atom A is smaller than atom B) or SMe factor, i.e. the difference of the total number of electron shells or the number of valence electrons of the constituent elements A and B is large. As concerned to W-Re, Re-Os (both belonging to SMe category), Mo-Re (belonging to SMS-SMe category), no obvious negative deviation is observed since for these systems the effects of SMS and SMe factors are less remarkable, i.e. the differences of the total number of electron shells and the number of electrons of the constituent elements A and B are small.

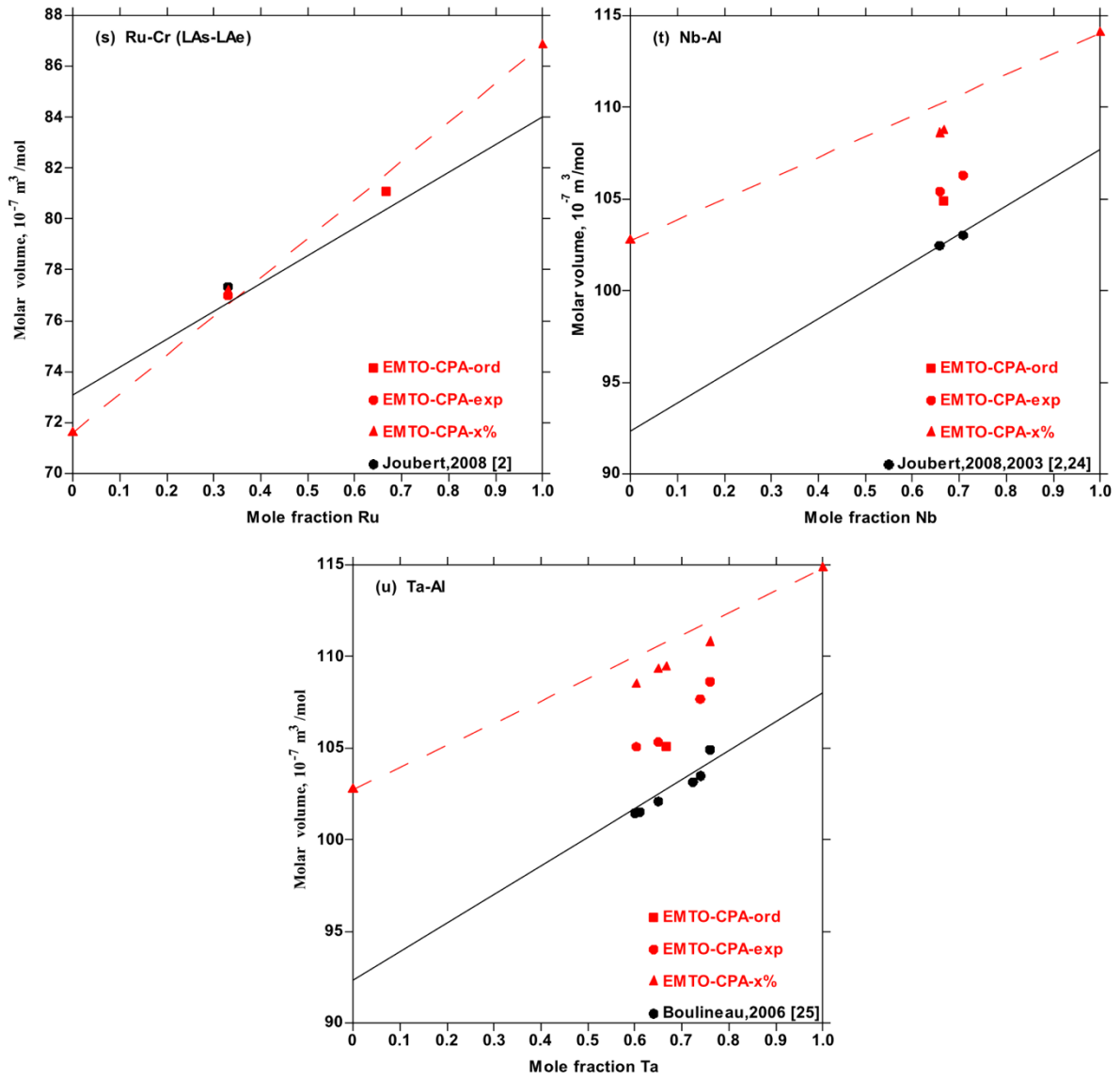


Fig. 2. (continued)

### 3.3. Influence of atomic order on molar volume of the sigma phase

#### 3.3.1. Experimental evidence

In addition to the atomic mixing, the atomic order also affects the molar volume of the sigma phase. Fig. 3 (a) and (b) present the calculated order degree of the sigma phase based on experimental site occupancy and the corresponding measured molar volume of the sigma phase from the literature with respect to the composition. As the measured site occupancy is sensitive to alloy processing, instrument accuracy and systematic error etc., for a specific system, only the data measured by the same authors are selected to conduct the comparison. Cr-Fe and Mo-Re are not presented here as the experimental results [3,20,23] indicate that the influence of atomic order on molar volume is small, which will be discussed in Section 3.3.2.

When the rate of change for order degree increases, the rate of change for molar volume decreases as presented in Fig. 4. The re-processing of data from Figs. 3 to 4 excludes the

influence of atomic mixing on molar volume of the sigma phase. It thus further indicates that for compounds with a specific composition, when the order degree ( $S$ ) increases, the molar volume decreases. This is consistent with the calculation results in Fig. 2, i.e. for most binary systems the compounds with smaller order degree have a larger molar volume. One exception is Mo-Re, which will be discussed in Section 3.3.2. Notably, Fig. 2 (r) indicates that for Re-V, the calculated molar volume based on experimental site occupancy is even larger than the disordered one. It is because the experimental site occupancy leads to an anti-order degree (i.e.  $S = -0.236$ ) and thus causes a large mismatch between atomic size and lattice site.

**Table 3**

Deviation from the linear composition-volume relationship of the binary sigma compounds based on the disordered EMTO-CPA calculations (i.e. EMTO-CPA-x % in Fig. 2).

Categories	Systems					Deviation	
						Negative	Positive
A-Al	Ta-Al	Nb-Al				✓	
SMe	Cr-Mn	Cr-Fe	Cr-Co			✓	
	V-Mn	V-Ni	V-Fe	V-Co			
SMS-SMe	Mo-Re	Mo-Os	Nb-Ir			✓	
LAs-SMe	Ta-Pd	Ta-Rh				✓	
	Mo-Co	Mo-Mn					✓
LAs	Re-Mn						✓
LAs-LAe	Re-Cr	Os-Cr	Ru-Cr	Re-V			✓

### 3.3.2. First-principles calculations

The influence of atomic order on molar volume varies with different sigma systems. Fig. 5 indicates that among all the sigma systems, the volume difference between disordered and ordered compounds is the largest for Ta-Al. It indicates that for Ta-Al the atomic order affects the molar volume more dramatically.

Table 4 and Fig. 5 present the volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) between disordered and completely ordered states of the A-B ( $V(A) > V(B)$ ) binary sigma phase at 66.7 at.% A calculated by EMTO-CPA method. It is found that when increasing the total number of electron shells of atom A,  $s(A)$  as in Fig. 5a (or decreasing  $s(B)$  as in Fig. 5b), or decreasing the number of valence electrons of atom A,  $e(A)$  as in Fig. 5c (or increasing  $e(B)$  as in Fig. 5d), the volume difference increases. Moreover, increasing  $s(A)$  (or decreasing  $s(B)$ ) indicates enhancing LAs factor or weakening SMS factor; decreasing  $e(A)$  (or increasing  $e(B)$ ) indicates enhancing SMe factor or weakening LAe factor; Thus we can deduce that LAs and SMe factors increase the volume difference while SMS and LAe factors decrease the volume difference. It should be noted that for the four systems (Mo-Co, Mo-Mn, Ta-Pd and Ta-Rh) belonging to LAs-SMe categories, LAs factor is the same, i.e.

$s(A)-s(B) = 1$ , and it is expected that the systems (i.e. Ta-Pd and Ta-Rh) with larger SME factor should have larger volume differences ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) based on the deduction in the last paragraph. However, Fig. 5 indicates that the systems (i.e. Mo-Co and Mo-Mn) with smaller SME factor have larger volume differences. This is due to the fact that the volume difference is also affected by the size factor, which in the present work is described by the size difference of the constituent elements, i.e.  $(V_A - V_B)/V_A$ . Fig. 6 (d) indicates that the larger size factors for Mo-Co and Mo-Mn make their volume difference larger than Ta-Pd and Ta-Rh. For the other systems in Fig. 6, either the effect of size factor on the volume difference is consistent with the electronic factors (e.g. Nb-Al vs Ta-Al, Mo-Mn vs Mo-Re) or the size factor is too small to counteract the effect of the electronic factors (i.e. Cr-Co vs Cr-Fe, V-Co vs V-Fe vs V-Ni, Ta-Pd vs Ta-Rh).

It can also be seen from Table 4 and Fig. 5 that for Mo-Re (belonging to SMS-SME category), the volume difference is negative, i.e. the ordered volume is larger than the disordered one. However, Mo-Os also belongs to SMS-SME category, has the same SMS factor ( $s(A) - s(B) = -1$ ) as Mo-Re, and the volume difference is positive. The difference is the SME factor ( $e(A) - e(B) = -1$  for Mo-Re and  $-2$  for Mo-Os) and thus increases the volume difference of Mo-Os to be positive. Among all the stable sigma systems, Mo-Re is the only case, for which the volume difference ( $\Delta V = V_{\text{disorder}} - V_{\text{order}}$ ) is negative.

In Section 3.3.1, according to the experimental evidence [3,20,23], we conclude that the influence of atomic order on molar volume is relatively small for Cr-Fe (3d54s1-3d64s2) and Mo-Re (4d55s1-5d56s2) belonging to SME and SMS-SME categories respectively. This is interpretable by considering the small SME (i.e.  $e(A) - e(B) = -2$  for Cr-Fe,  $e(A) - e(B) = -1$  for Mo-Re) and SMS (i.e.  $s(A) - s(B) = -1$  for Mo-Re) factors for these systems, which increase and decrease the volume difference respectively.

To support our arguments, we conducted the calculations for hypothetical Nb-W (4d45s1 - 5d46s2) and Au-W (5d106s1 - 5d46s2) sigma compounds. The two systems belong to SMS-SME and LAe categories respectively. The volume difference for Nb-W is  $-0.496 \times 10^{-7} \text{ m}^3/\text{mol}$  ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}} = 10.959e-6 \text{ m}^3/\text{mol} - 11.008e-6 \text{ m}^3/\text{mol}$ ) and for Au-W is  $-0.779 \times 10^{-7} \text{ m}^3/\text{mol}$  ( $\Delta V_m = 10.726e-6 \text{ m}^3/\text{mol} - 10.804e-6 \text{ m}^3/\text{mol}$ ). Both volume differences present negative value due to the effect of SMS or LAe factors.

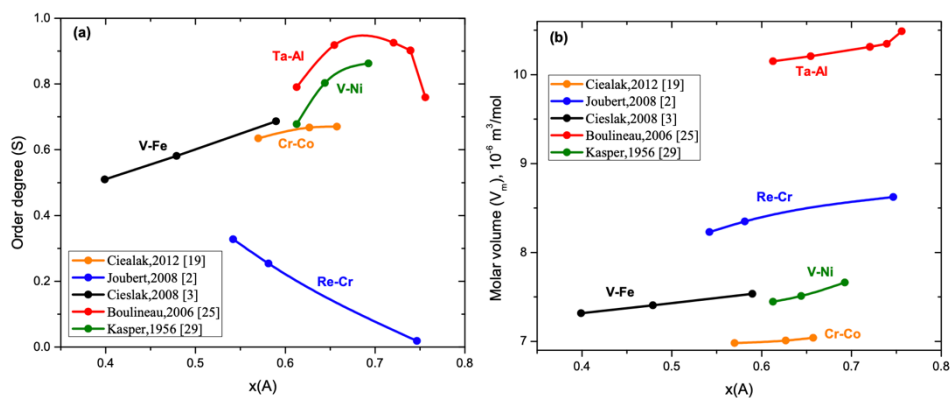
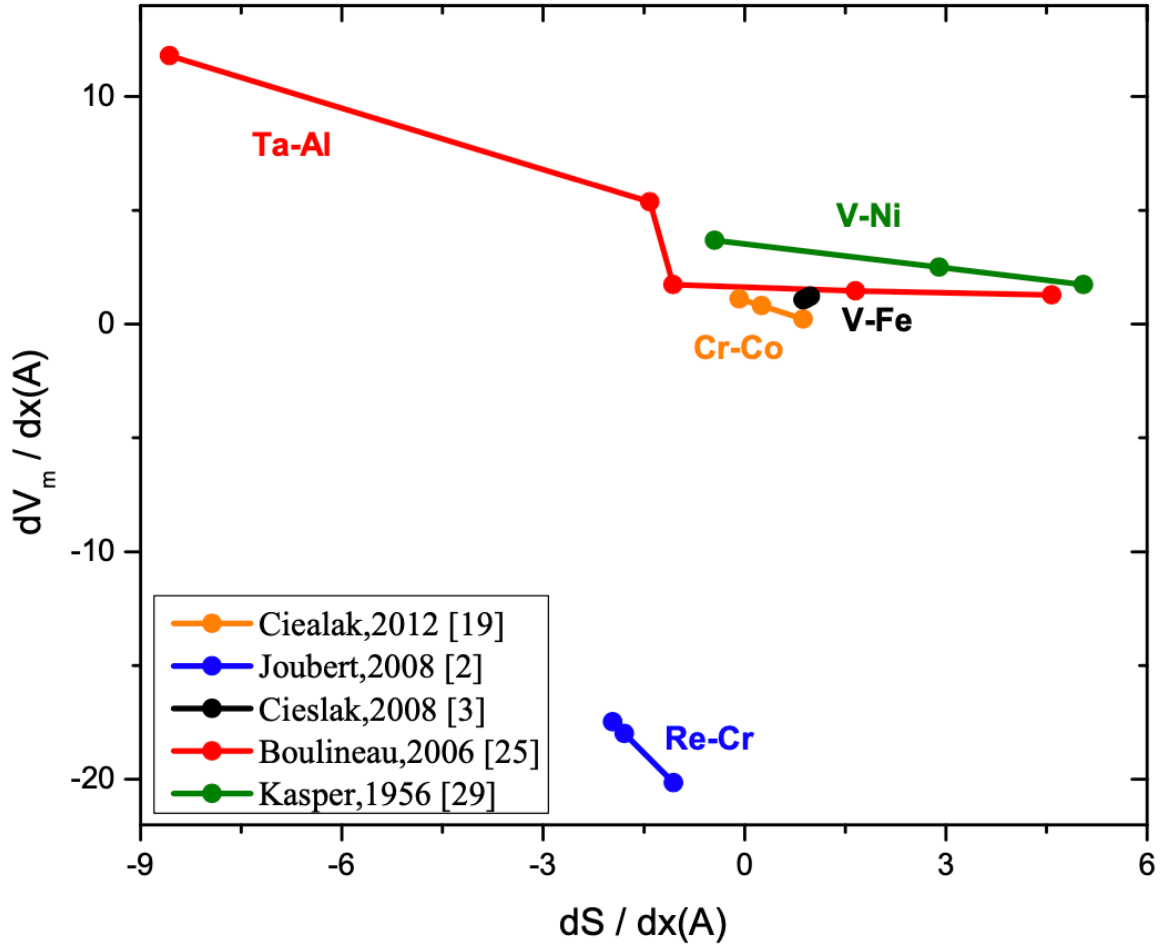


Fig. 3. (a) Calculated order degree of the sigma phase based on experimental site occupancy and (b) corresponding measured molar volume of the sigma phase from the literature [2,3,19,25,29] with respect to composition.



**Fig. 4.** Rate of change for molar volume with respect to mole fraction,  $dV_m/dx(A)$ , versus rate of change for order degree with respect to mole fraction,  $dS/dx(A)$  of the corresponding sigma compounds in Fig. 3.

#### 4. Conclusions

In the present work, the influence of the atomic mixing on molar volume is described by studying the volume deviation of the hypothetical disordered sigma phase from the linear volume-composition relationship; the influence of atomic order on molar volume is described by the molar volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) between the A2B sigma compounds in the ordered and disordered states. To facilitate explanation, the long-range order parameter (i.e. order degree) is redefined, which can describe all the situations of site occupation. The main conclusions can be drawn as follows:

1) The A-B ( $V(A) > V(B)$ ) disordered sigma phase does not follow a linear volume-composition relationship. It presents a negative or positive deviation depending on the tendency of electron loss or gain of the two constituent elements. For SMe and SMs-SMe categories, larger atom A tends to lose electrons leading to a denser packing with atomic mixing, and thus the compounds present a negative deviation; for LAs and LAs-LAe categories, larger atom A tends to gain electrons leading to a looser packing with atomic mixing, and thus the compounds present a positive deviation. For LAs-SMe category, the atomic mixing on the molar volume depends on the competition of the electronic factors (i.e. LAs and SMe factors).

2) The influence of the atomic order on the molar volume depends on the size difference and the electron configurations of the two constituent elements, i.e. large size difference

increases the volume difference; SME and LAs factors increase volume difference ( $\Delta V = V_{\text{disorder}} - V_{\text{order}}$ ); LAe and SMs factors decrease volume difference.

3) For most binary sigma compounds, when increasing the order degree, the molar volume decreases. The only exception is Mo-Re belonging to the SMs-SME category, for which the ordered volume is larger than the disordered one due to the SMs factor causing the volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) to be negative.

### Acknowledgements

This work was supported by National Key R&D Program of China (Grant number: 2017YFB0701502). W. Liu gratefully acknowledges the financial support from the China Scholarship Council. X.-G. Lu acknowledges the High Performance Computing Center of Shanghai University for providing the calculation facility.

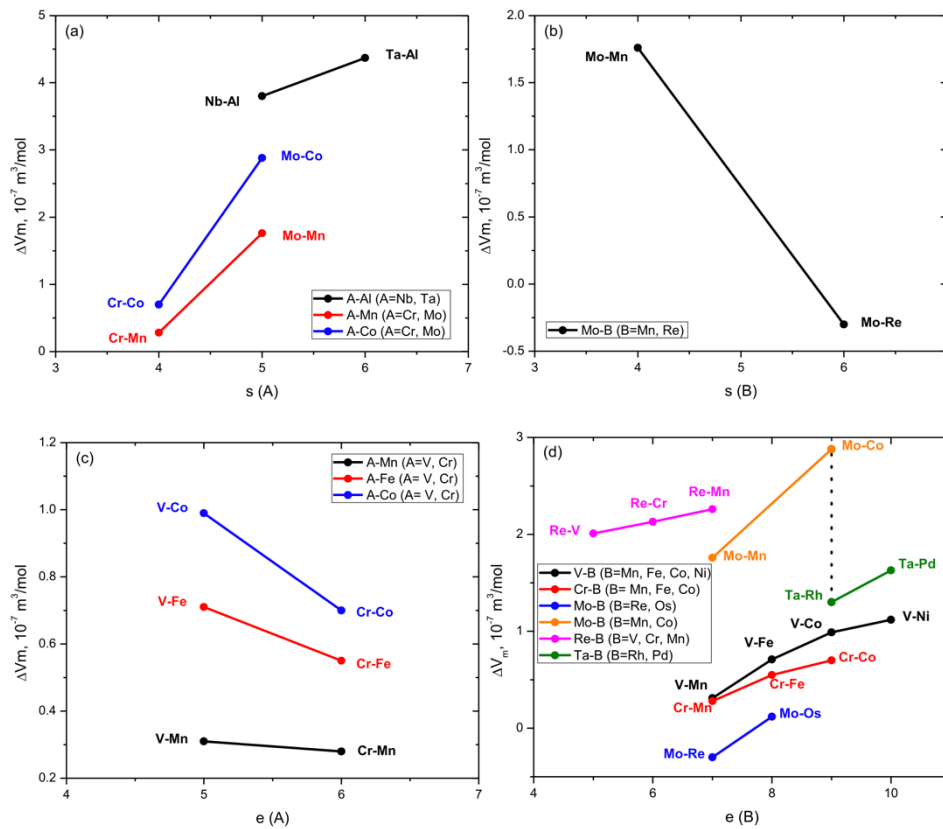
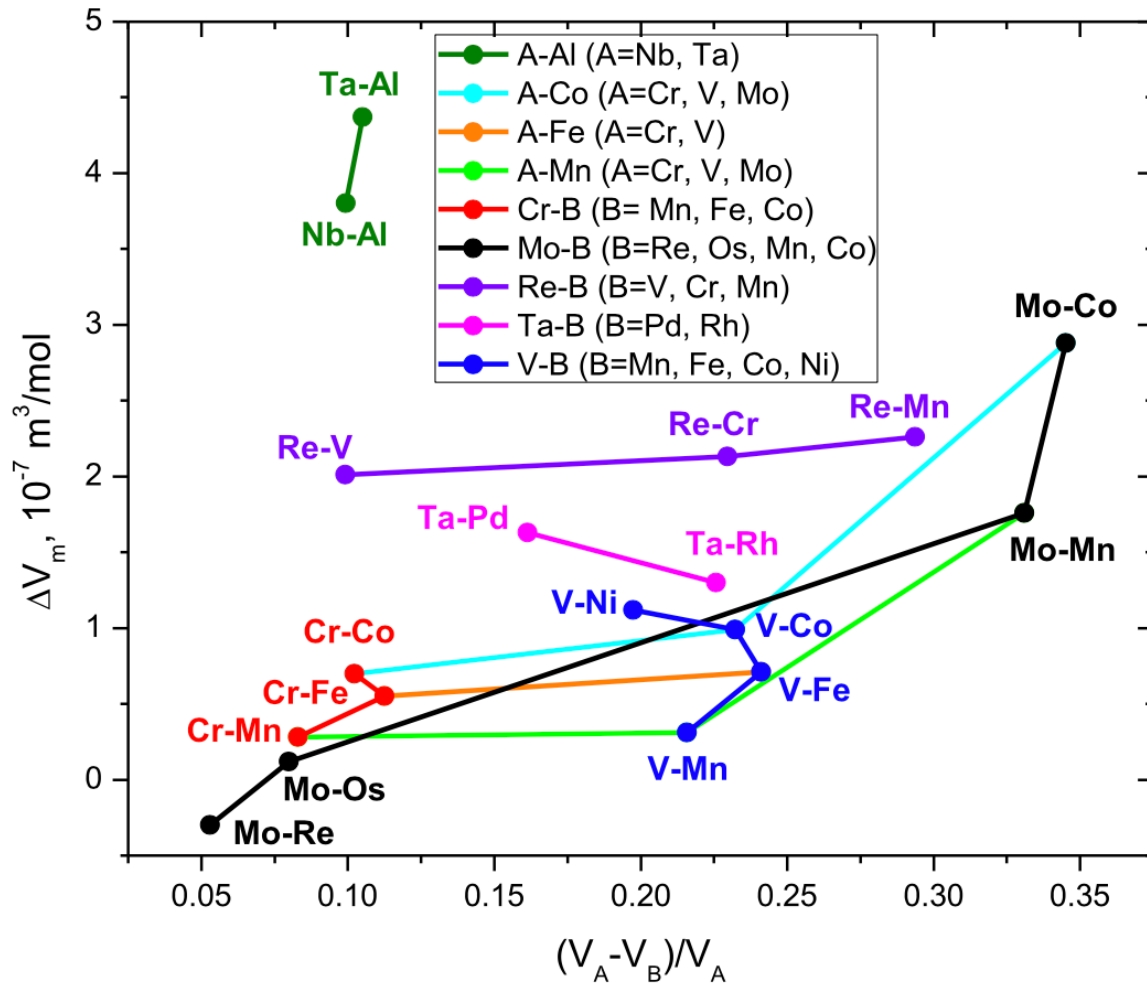


Fig. 5. Molar volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) between disordered and ordered states of the A-B ( $V(A) > V(B)$ ) binary sigma phase at 66.7 at.% A calculated by EMTO-CPA method with respect to: (a) the total number of electron shells of atom A,  $s(A)$ ; (b) the total number of electron shells of atom B,  $s(B)$ ; (c) the number of valence electrons of atom A,  $e(A)$ ; (d) the number of valence electrons of atom B,  $e(B)$ .





**Fig. 6.** Molar volume difference ( $\Delta V_m = V_{\text{disorder}} - V_{\text{order}}$ ) between disordered and ordered states of the A-B ( $V(A) > V(B)$ ) binary sigma phase at 66.7 at.% A calculated by EMT0-CPA method with respect to size difference between the constituent elements (A and B).  $V_A$  and  $V_B$  are the molar volumes of element A and B in their hypothetical sigma phase structure from the EMT0-CPA calculations.

## Appendix A

Table A.1

Order degree of selected sigma compounds calculated based on the experimental site occupancy from the literature.

AxBy	X(A)	A site occupancies					Order degree						Reference
		2a	4f	8i <sub>1</sub>	8i <sub>2</sub>	8j	S <sub>2a</sub>	S <sub>4f</sub>	S <sub>8i1</sub>	S <sub>8i2</sub>	S <sub>8j</sub>	S	
<b>SMe</b>													
V <sub>59</sub> Fe <sub>41</sub>	0.590	0.141	0.936	0.814	0.079	0.815	0.051	0.113	0.146	0.231	0.146	0.686	[3]
V <sub>47.9</sub> Fe <sub>52.1</sub>	0.479	0.072	0.838	0.662	0.037	0.660	0.057	0.092	0.094	0.246	0.093	0.581	[3]
V <sub>39.9</sub> Fe <sub>60.1</sub>	0.399	0.047	0.739	0.543	0.029	0.543	0.059	0.075	0.064	0.247	0.064	0.509	[3]
V <sub>68</sub> Ni <sub>32</sub>	0.680	0.000	1.000	0.840	0.500	0.710	0.067	0.133	0.133	0.071	0.025	0.429	[2]
V <sub>65</sub> Ni <sub>35</sub>	0.649	0.320	0.970	0.700	0.200	0.970	0.034	0.122	0.039	0.185	0.244	0.623	[2]
Cr <sub>57</sub> Co <sub>43</sub>	0.570	0.070	0.797	0.801	0.111	0.809	0.058	0.070	0.144	0.215	0.148	0.635	[19]
Cr <sub>62.7</sub> Co <sub>37.3</sub>	0.627	0.107	0.823	0.852	0.172	0.889	0.055	0.070	0.161	0.194	0.187	0.667	[19]
Cr <sub>65.7</sub> Co <sub>34.3</sub>	0.657	0.240	0.816	0.903	0.196	0.898	0.042	0.062	0.191	0.187	0.188	0.670	[19]
<b>LAs-LAe</b>													
Re <sub>54</sub> Cr <sub>46</sub>	0.542	0.210	0.860	0.780	0.320	0.450	0.041	0.093	0.139	0.109	-0.054	0.328	[2]
Re <sub>58</sub> Cr <sub>42</sub>	0.581	0.180	0.870	0.780	0.450	0.470	0.046	0.092	0.127	0.060	-0.071	0.254	[2]
Re <sub>69</sub> Cr <sub>31</sub>	0.747	0.320	0.940	0.860	0.840	0.550	0.038	0.102	0.119	-0.033	-0.207	0.019	[2]
Re <sub>78</sub> V <sub>22</sub>	0.777	0.86	0.78	0.83	0.91	0.57	-0.007	0.002	0.063	-0.046	-0.248	-0.236	[2]
<b>A-Al</b>													
Ta <sub>60</sub> Al <sub>40</sub>	0.603	0.060	0.810	0.900	0.050	0.890	0.060	0.070	0.200	0.245	0.193	0.767	[25]
Ta <sub>61</sub> Al <sub>39</sub>	0.613	0.050	0.790	0.920	0.050	0.920	0.061	0.061	0.212	0.245	0.212	0.790	[25]
Ta <sub>65</sub> Al <sub>35</sub>	0.655	0.040	0.950	0.980	0.030	0.960	0.063	0.114	0.251	0.254	0.236	0.918	[25]
Ta <sub>72.4</sub> Al <sub>27.6</sub>	0.721	0.170	1.000	1.000	0.160	1.000	0.051	0.133	0.267	0.207	0.267	0.925	[25]
Ta <sub>74</sub> Al <sub>26</sub>	0.739	0.210	1.000	1.000	0.220	1.000	0.048	0.133	0.267	0.187	0.267	0.902	[25]
Ta <sub>76</sub> Al <sub>24</sub>	0.756	0.320	0.970	0.960	0.340	0.970	0.038	0.117	0.223	0.147	0.234	0.759	[25]

## References

- [1] E.O. Hall, S.H. Algie, The sigma phase, *Metall. Rev.* 11 (1966) 61–88.
- [2] J.-M. Joubert, Crystal chemistry and Calphad modeling of the  $\sigma$  phase, *Prog. Mater. Sci.* 53 (2008) 528–583, <http://dx.doi.org/10.1016/j.pmatsci.2007.04.001>.
- [3] J. Cieślak, M. Reissner, S.M. Dubiel, J. Wernisch, W. Steiner, Influence of composition and annealing conditions on the site-occupation in the  $\sigma$ -phase of Fe–Cr and Fe–V systems, *J. Alloy. Comp.* 460 (2008) 20–25, <http://dx.doi.org/10.1016/j.jallcom.2007.05.098>.
- [4] J.-C. Crivello, A. Breidi, J.-M. Joubert,  $\chi$  and  $\sigma$  phases in binary rhenium–transition metal systems: a systematic first-principles investigation, *Inorg. Chem.* 52 (2013) 3674–3686, <http://dx.doi.org/10.1021/ic302142w>.
- [5] W. Liu, X.-G. Lu, Y.-L. He, L. Li, Modeling of molar volume of the sigma phase involving transition elements, *Comput. Mater. Sci.* 95 (2014) 540–550, <http://dx.doi.org/10.1016/j.commatsci.2014.08.015>.
- [6] L. Kaufman, H. Bernstein, *Computer Calculations of Phase Diagrams*, Academic Press, New York, 1970.
- [7] N. Saunders, A.P. Miodownik, *CALPHAD (Calculation of Phase Diagrams): a Comprehensive Guide*, Pergamon, Oxford; New York, 1998.
- [8] H.L. Lukas, S.G. Fries, B. Sundman, *Computational Thermodynamics: the CALPHAD Method*, Cambridge University Press, Cambridge; New York, 2007.
- [9] W. Liu, X.-G. Lu, P. Boulet, M.-C. Record, Influencing factors of atomic order in the binary sigma phase, *Intermetallics* 93 (2018) 6–19 <https://doi.org/10.1016/j.intermet.2017.11.006>.
- [10] L. Vitos, *Computational Quantum Mechanics for Materials Engineers: the EMTO Method and Applications*, Springer, London, 2007.
- [11] L. Vitos, Total-energy method based on the exact muffin-tin orbitals theory, *Phys. Rev. B* 64 (2001), <http://dx.doi.org/10.1103/PhysRevB.64.014107>.
- [12] R.M. Dreizler, E.K.U. Gross, *Density Functional Theory*, Springer, Berlin, 1998 <http://www.springer.com/br/book/9783642861055> (accessed May 18, 2017).
- [13] P. Soven, Coherent-potential model of substitutional disordered alloys, *Phys. Rev.* 156 (1967) 809.
- [14] B.L. Gyorffy, Coherent-potential approximation for a nonoverlapping-muffin-tin-potential model of random substitutional alloys, *Phys. Rev. B* 5 (1972) 2382.
- [15] L. Vitos, I.A. Abrikosov, B. Johansson, Anisotropic lattice distortions in random alloys from first-principles theory, *Phys. Rev. Lett.* 87 (2001), <http://dx.doi.org/10.1103/PhysRevLett.87.156401>.
- [16] O.K. Andersen, *Linear methods in band theory*, *Phys. Rev. B* 12 (1975) 3060–3083.
- [17] Q.-M. Hu, L. Vitos, R. Yang, Theoretical investigation of the  $\omega$ -related phases in TiAl – Nb/Mo alloys, *Phys. Rev. B* 90 (2014), <http://dx.doi.org/10.1103/PhysRevB.90.054109>.
- [18] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868, <http://dx.doi.org/10.1103/PhysRevLett.77.3865>.
- [19] J. Cieślak, S.M. Dubiel, M. Reissner, Site occupancy and lattice parameters in sigma-phase Co–Cr alloys, *Acta Crystallogr. B* 68 (2012) 123–127, <http://dx.doi.org/10.1107/S0108768112006234>.
- [20] H.L. Yakel, Atom distributions in sigma phases. I. Fe and Cr atom distributions in a binary sigma phase equilibrated at 1063, 1013 and 923 K, *Acta Crystallogr. B* 39 (1983) 20–28, <http://dx.doi.org/10.1107/S0108768183001974>.
- [21] J. Cieślak, S.M. Dubiel, J. Tobola, J. Zukrowski, Experimental and theoretical study of the  $\sigma$ -phase Fe–Re alloys, *Mater. Chem. Phys.* 139 (2013) 590–595, <http://dx.doi.org/10.1016/j.matchemphys.2013.01.061>.
- [22] F.J. Spooner, C.G. Wilson, Ordering in binary  $\sigma$  phases, *Acta Crystallogr.* 17 (1964) 1533–1538, <http://dx.doi.org/10.1107/S0365110X64003826>.
- [23] S.A. Farzadfar, M. Levesque, M. Phejar, J.-M. Joubert, Thermodynamic assessment of the molybdenum–rhenium system, *Calphad* 33 (2009) 502–510, <http://dx.doi.org/10.1016/j.calphad.2009.02.001>.
- [24] J.-M. Joubert, C. Pommier, E. Leroy, A. Percheron-Guégan, Hydrogen absorption properties of topologically close-packed phases of the Nb–Ni–Al system, *J. Alloy. Comp.* 356–357 (2003) 442–446, [http://dx.doi.org/10.1016/S0925-8388\(02\)01238-0](http://dx.doi.org/10.1016/S0925-8388(02)01238-0).
- [25] A. Boulineau, J.-M. Joubert, R. Černý, Structural characterization of the Ta-rich part of the Ta–Al system, *J. Solid State Chem.* 179 (2006) 3385–3393, <http://dx.doi.org/10.1016/j.jssc.2006.07.001>.
- [26] J. Cieślak, B.F.O. Costa, S.M. Dubiel, M. Reissner, W. Steiner, Magnetic ordering above room temperature in the sigma-phase of Fe<sub>66</sub>V<sub>34</sub>, *J. Magn. Magn. Mater.* 321 (2009) 2160–2165, <http://dx.doi.org/10.1016/j.jmmm.2009.01.005>.
- [27] G.-X. Hu, X. Cai, Y.-H. Rong, *Fundamentals of Materials Science*, third ed., Shanghai Jiao Tong University Press, Shanghai, 2010.
- [28] J.-F. Wang, *Solid State Physics*, eighth ed., Shandong University press, 2013.
- [29] J.S. Kasper, R.M. Waterstrat, Ordering of atoms in the  $\sigma$  phase, *Acta Crystallogr.* 9 (1956) 289–295, <http://dx.doi.org/10.1107/S0365110X56000802>.