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ZenGen[☆]: a tool to generate ordered configurations for systematic first-principles calculations, example of the Cr–Mo–Ni–Re system

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Abstract

”ZenGen” is a script-tool which helps to automatically generate first-principles input files of all the ordered compounds of a given crystal structure in a given system. The complete set of heats of formation of each end-member can then easily be used in the thermodynamic phase modeling.

”ZenGen” is a free and open source code, which can be downloaded from <http://zengen.cnrs.fr>.

In order to illustrate its possibilities, the quaternary system, Cr–Mo–Ni–Re, has been investigated. The binary solid solution parameters have been estimated from SQS calculations. The σ -phase has been considered according to its crystal structure, *i.e.* with a 5-sublattice model, by the DFT calculation of the $4^5 = 1024$ different ordered quaternary configurations. Several tentative *ab initio* phase diagrams are presented.

Keywords: Calphad, DFT, CEF, intermetallic, sigma-phase

[☆]Fully documented manual and program are available on <http://zengen.cnrs.fr>.

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1. Introduction

The field of thermodynamic modeling has been recently stimulated by the progress of techniques allowing the calculation of thermodynamic quantities from first-principles calculations, such as the Density Functional Theory (DFT) [1]. These methods allow the estimation of formation enthalpies of fully ordered compounds, taking into account their crystal structures. These calculations can be done not only for stable compounds, but also for metastable ones which play an important role in the description of these phases within the Compound Energy Formalism (CEF) [2, 3]. By using the CEF, any intermetallic phase could be described by a sublattice model for which every ordered configuration heat of formation has to be calculated. As an example, a binary phase with five crystal sites, described in a 5-sublattice model generates $2^5 = 32$ different ordered configurations, a ternary $3^5 = 243$... a huge number, but which can be calculated with today's super-computers.

Technically, performing calculations on a large number of end-members may cause two types of problems: (i) a mistake in the distribution of atoms among all different sites; (ii) a too fast relaxation of crystal structure, thus losing the initial symmetry. To avoid these kinds of errors, the "ZenGen" code was created. This code is able to generate all the necessary input files for the DFT calculations of the ordered configurations considering a given system. It has been tested on several phases, such as Laves phases ($C14$, $C15$...), or other topologically close packed phases ($A12$, $A13$, $D8_b$, P , δ , ...). It can also be used to run Special Quasi-random Structures (SQS) calculations [4]. A basic introduction of Zengen workflow is given in section 2.

Then, in order to illustrate the ZenGen capacity, we have investigated the challenging quaternary Cr–Mo–Ni–Re system. Our aim was not to assess thermodynamically this system, but rather to show that systematic DFT calculations **can be run contently in this very complex system, that they allow the calculation of a preliminary *ab initio* computed phase diagram, and that they can be used as an input for a traditional Calphad assessment**. We have demonstrated this approach in our previous works [5, 6]. The results are presented in **the** section 3.

27 **2. The ZenGen workflow**

28 "ZenGen" is a free and open source code, governed by the CeCILL-B license under French
29 law [7], which is officially recognized by Open Source Initiative (OSI). It can be downloaded from
30 <http://zengen.cnrs.fr>. Zengen can be installed on Unix-Linux machines and uses Bash, Perl and
31 Python languages. It has been designed to run VASP program [8, 9] for the DFT calculations, but
32 could be adapted to other first-principles codes.

33 It requires as input the phase φ under consideration the crystallographic structure of which
34 is constituted by m different sites, and the n different elements. Then, ZenGen decomposes the
35 process into four steps:

- 36 1. Automatic generation of the input files for the n^m ordered configurations;
- 37 2. Setup of the convergence criteria and relaxation steps of the φ phase;
- 38 3. Job execution under the same conditions;
- 39 4. Collection of output results (total energy, crystallographic parameters) and generation of a
40 TDB file.

41 These steps are shown schematically in the diagram of Figure 1 and are more detailed in the
42 following paragraphs.

43 *2.1. Generation of ordered configurations*

44 After the command:

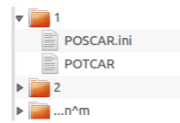
```
$ zengen.pl
```

45 the user should enter the name of the crystal structure ($X= C14, chi$ -phase, SQS type...), and
46 the name the chemical elements. The cut-off energy is also requested. For structures described by
47 more than 2 nonequivalent sites, it is possible to merge sites in order to agree with a simplified sub-
48 lattice description. **Then, `zengen.pl` generates all the ordered configurations based on a simple
49 algorithm which distributes atoms on all the inequivalent sites. The script separates the systems**

1 - generation of ordered configurations

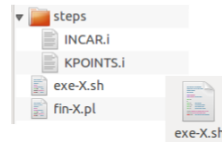
```
$ zengen.pl
```

phase?
elements?
cut-off energy?



2 - setup of calculations

relaxation steps?
configurations?



3 - execution of DFT calculations

```
$ ./exe-X.sh
```

```
FOR i = relaxation steps  
  FOR j = configurations  
    DO VASP
```

4 - post-treatment

```
$ ./fin-X.pl
```

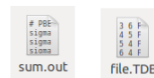


Figure 1: Schematic work flow chart of ZenGen.

50 (unary, binary, ternary...) and sorts the whole configurations by ascending the elemental compo-
51 sition. Finally, `zengen.pl` creates a folder containing all the ordered configurations labeled into
52 subfolders (one by configuration), including all the files (POSCAR and POTCAR) needed to perform
53 DFT calculations.

54 2.2. Setup of calculations

55 The calculation is built into 2 interlinked loops: one on the configurations to be calculated, one
56 on the relaxation step. The `exe-X.sh` file has to be modified by the user regarding the particular
57 demand: **numeration of configuration and relaxation steps to be calculated**. See the manual for
58 more details.

59 2.3. Execution of DFT calculations

60 After the setup of the `exe-X.sh` file, its execution can be done in blind process mode by:

```
61 $ nohup ./exe-X.sh &
```

61 2.4. Post-treatment

62 After the calculations, the post-treatment is made by the command:

```
63 $ ./fin-X.pl
```

63 This script generates several files: a summary file `sum.out`, and a database file: `X.TDB`. The
64 `sum.out` file contains the total energy, cell parameters, internal positions and magnetic moment of
65 every configuration calculated by `exe-X.sh`. The `X.TDB` file can be used as an input file for ther-
66 modynamic calculation softwares, such as Thermo-Calc [10] or Open-Calphad [11]. **It contains,**
67 **for each configuration C in the φ phase, the corresponding formation energy, called $\Delta_f H^\varphi(C)$,**
68 **given in Joule per formula unit, obtained by the difference between the total energies of $E^\varphi(C)$ and**
69 **those of the weighted pure i elements in their standard element reference state (SER), E_i^{SER} :**

$$\Delta_f H^\varphi(C) = E^\varphi(C) - \sum_i x_i \cdot E_i^{\text{SER}} \quad (1)$$

70 The E_i^{SER} and E_i^φ ($\varphi = A1, A2, A3$) have already been calculated with and without spin-polarization.
71 They are provided for several cut-off energies (5 sets: 300, 400, 500, 600, and 800 eV) in the folder
72 `pure` of the Zengen installation directory. Figure 2 shows the available i elements of the **current**
73 **version**.

74 A user guide is available on the website <http://zengen.cnrs.fr> ("Documentation" page), includ-
75 ing: the installation procedure, a tutorial, additional explanation, **algorithm details**, appendices...

76 Table 1 shows the available intermetallic phases in the current version. The list will probably be
 77 extended in future versions and the user may easily add its own structures.

78 ZenGen is designed to generate all necessary files for the calculation of ordered compounds
 79 described in the CEF formalism. However, it can also be used to prepare and execute SQS calcu-
 80 lations of substitutional solid solutions. The SQS approach considers a random-like distribution
 81 of atoms on equivalent sites of a given lattice at a given composition and with a finite number of
 82 total atoms in the cell. This allows to express the mixing energy of the solid solution, $\Delta_{mix}H^\varphi$:

$$\Delta_{mix}H^\varphi(X) = E^\varphi(X) - \sum_{i=A,B} x_i \cdot E_i^\varphi \quad (2)$$

83
 84 At the moment, only the *fcc*, *bcc*, and *hcp* structures phases for binary systems are imple-
 85 mented. Generated structures have been taken from the literature [12, 13, 14] respectively.

H																	He																														
Li*	Be*											B	C	N	O	F	Ne																														
Na*	Mg*											Al	Si	P	S	Cl	Ar																														
K	Ca*	Sc*	Ti*	V*	Cr*	Mn*	Fe*	Co*	Ni*	Cu*	Zn	Ga	Ge*	As*	Se	Br	Kr																														
Rb	Sr	Y	Zr	Nb	Mo*	Tc*	Ru*	Rh*	Pd*	Ag*	Cd	In	Sn	Sb	Te	I	Xe																														
Cs	Ba		Hf*	Ta*	W*	Re*	Os*	Ir	Pt*	Au	Hg	Tl	Pb*	Bi	Po	At	Rn																														
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo																														
<table border="1"> <tbody> <tr> <td>La</td> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Ac</td> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </tbody> </table>																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																	
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																	
X	Not considered																																														
Y	Investigated for the structures A1, A2, A3 and SER cut off energy: 300, 400, 500, 600, 800 eV & spin polarization																																														
Y*	With and without pseudo-core electrons																																														

Figure 2: Periodic table showing the available elements in Zengen code (see pure folder).

Table 1: List of the available phases for calculation in ZenGen (code of the phase, Strukturbericht, prototype, Space group, Pearson symbol, number of sublattices and additional comments).

Code	Phase	Prototype	Space Group	Pearson	Nb	comments
chi	A12	α -Mn	$I\bar{4}3m$ (217)	cI58	4	FK: χ -phase
betaMn	A13	β -Mn	$P4_132$ (213)	cP20	2	β -Mn
A15	A15	Cr ₃ Si	$Pm\bar{3}n$ (223)	cP8	2	FK: A15-Cr ₃ Si
B2	B2	CsCl	$Pm\bar{3}m$ (221)	cP2	2	bcc ordered AB
B32	B32	NaTl	$Fd\bar{3}m$ (227)	cF16	2	bcc ordered AB
C14	C14	MgZn ₂	$P6_3/mmc$ (194)	hP12	3	FK: Laves AB ₂
C15	C15	Cu ₂ Mg	$Fd\bar{3}m$ (227)	cF24	2	FK: Laves AB ₂
C36	C36	MgNi ₂	$P6_3/mmc$ (194)	hP24	5	FK: Laves AB ₂
D03	D0 ₃	BiF ₃	$Fm\bar{3}m$ (225)	cF16	2	bcc ordered AB ₃
sigma	D8 _b	CrFe	$P4_2/mnm$ (136)	tP30	5	FK: σ -phase
mu	D8 ₅	Fe ₇ W ₆	$R\bar{3}$ (166)	hR13	5	FK: μ -phase
L10	L1 ₀	AuCu	$P4/mmm$ (123)	tP4	2	fcc ordered AB
L11	L1 ₁	CuPt	$R\bar{3}m$ (166)	hR6	2	hex ordered AB
L12	L1 ₂	AuCu ₃	$Pm\bar{3}m$ (221)	cP4	2	fcc ordered AB ₃
L21	L2 ₁	AlCu ₂ Mn	$Fm\bar{3}m$ (225)	cF16	3	bcc ordered ABC ₂ Heusler
Cu3Ti		Cu ₃ Ti, Ni ₃ Ta	$Pm\bar{3}n$ (59)	oP8	3	β -Cu ₃ Ti (LT)
delta		Mo ₇ Ni ₇	$P2_12_12_1$ (19)	oP56	12	FK: δ -MoNi
Dsim		Mo ₇ Ni ₇	$P2_12_12_1$ (19)	oP56	3	delta simplified [CN12,14,15+]
PP		Cr ₁₈ Mo ₄₂ Ni ₄₀	$Pnma$ (62)	oP56	12	FK: P phase
PPsim		Cr ₁₈ Mo ₄₂ Ni ₄₀	$Pnma$ (62)	oP56	3	P simplified [CN12,14,15+]
M		Al ₃ Nb ₁₀ Ni ₉	$Pnma$ (62)	oP52	11	FK: M phase
R		Cr ₁₆ Mo ₃₈ Co ₄₆	$Pnma$ (62)	hR159	11	FK: R phase

3. The Cr–Mo–Ni–Re system investigation

3.1. Known phase diagrams

The quaternary Cr–Mo–Ni–Re system is well suited for an automatic investigation of phase stability. Solid solutions with three different structures exist: $A1 - fcc$ (Ni), $A2 - bcc$ (Cr, Mo) and $A3 - hcp$ (Re), and two of the elements are magnetic. The σ -phase is stable in the four ternaries. This phase is a hard brittle intermetallic compound and has a deleterious effect on the mechanical properties of many technologically important systems, like Cr-Mo-Ni-Re, a key system for Ni-based superalloys. The ternary iso-thermal sections have been drawn and compiled in the review of Slyusarenko [15]. Since this work, updates have been published and the most recent ternary phase diagrams are plotted in Figure 3.

3.2. DFT computational details

The σ -phase has been considered with a 5-sublattice model corresponding to its crystal structure and leading to the generation of $4^5 = 1024$ different ordered configurations. Initial crystallographic parameters have been taken from the reported average values [16]. Part of the work on the ternary systems has been published elsewhere (σ -CrMoRe [17], σ -CrNiRe [18], σ -MoNiRe [19]). However, to be sure that all calculations are done with the same parameters (cut-off energy...), they have been run for all the configurations. Solid solutions have been considered with the SQS approach to simulate the mixing of the binary solutions in fcc , bcc and hcp structures, for 0.25, 0.50 and 0.75 compositions with 16-atom supercells.

Thanks to ZenGen, the energy of every σ -phase end-member and SQS structure has been calculated by the DFT calculation approach using the Projector Augmented Wave (PAW) method [20], implemented in the Vienna Ab initio Simulation Package (VASP) [21, 22]. The exchange-correlation energy of electrons is described in the generalized gradient approximation (GGA) using the functional parametrization of Perdew-Burke-Ernzerhof [23]. The energy cut-off for the PAWs was set to 400 eV. All structures have been relaxed, keeping their original symmetries allowing only volume and cell shape evolution for σ and hcp symmetries. An additional step has been done allowing ionic relaxation. The final step included Blöchl corrections [24].

113 3.3. Thermodynamic modeling

114 3.3.1. Configuration energies of the σ -phase at 0 K

115 The σ -phase is described in the structure type FeCr, space group $P4_2/mnm$, 30 atoms per
116 unit cell, with 5 inequivalent sites: $2a$, $4f$, $8i_1$, $8i_2$, $8j$, with coordination numbers (CN) 12, 15,
117 14, 12 and 14, respectively. The main feature of the σ -phase includes its non stoichiometry
118 which is accommodated by substitution on different sites of the crystal structure [16], and its
119 ability to accept wide homogeneity ranges. The main point of interest for the present work is that,
120 qualitatively, in the σ -phase, larger atoms show preference for the sites with high coordination
121 number (CN15 and CN14) whereas smaller atoms occupy the sites with low coordination number
122 (CN12).

123 All the $4^5 = 1024$ configurations of the quaternary σ -phase have been considered by dis-
124 tributing the $n = 4$ atoms (Cr, Ni, Mo, Re) into the $m = 5$ sites (i, j, k, l, m). From the equation 1,
125 the corresponding heat of formation, $\Delta_f H_{ijklm}^\sigma$, has been expressed relatively to the elements in
126 their SER structure. All the results of the 1024 compositions, such as the relaxed crystallographic
127 parameters and heats of formation, are given in a table as a supplementary material o this paper.

128 For each system (binary, ternary...), Table 2 gives selected configurations with smaller values
129 of $\Delta_f H_{ijklm}^\sigma$. In comparison with previous works, slight differences are observed and are explained
130 by the different exchange-correlation functions and cut-off energy. However, the same most stable
131 configurations are found for each system. As an example, the only negative formation enthalpy
132 in the binary systems is obtained in Mo–Ni system, for the Ni:Mo:Mo:Ni:Mo configuration (ideal
133 Mo_2Ni composition) which corresponds to the occupation of low CN sites by Ni, (smaller atom)
134 and high CN sites by Mo (larger atom).

135 This kind of geometric argumentation could be extended to the ternaries, such as in the Mo–
136 Ni–Re system. From the $3^5 = 243$ configurations generated, 90 are unique compositions, and
137 among them, 20 with $\Delta_f H_{ijklm}^\sigma < 0$, like the most stable configuration: Re:Mo:Re:Ni:Mo. They
138 are all explained by the geometric argument. In fact, Ni whose atomic size is significantly smaller
139 than Mo and Re prefers the sites with low coordination numbers *i.e.* $2a$ and $8i_2$ (CN12). On the
140 other hand, Mo atoms being larger in size tend to occupy high coordination sites *i.e.* $4f$, $8i_1$ and
141 $8j$ (CN15, 14, 14) where they find more space. Contrary to the behavior of Mo and Ni, the Re

142 atom, being intermediate in size $r_{\text{Ni}} (\sim 125 \text{ pm}) < r_{\text{Re}} (\sim 137 \text{ pm}) < r_{\text{Mo}} (\sim 139 \text{ pm})$, shows a dual
143 preference depending on the composition.

144 Adding a fourth element makes analyses more complex. Cr size is intermediate between Ni
145 and Re with a radius of about $\sim 128 \text{ pm}$. Only 8 quaternary configurations present a negative
146 heat of formation. The most stable configurations are Cr:Re:Re:Ni:Mo, Cr:Mo:Mo:Ni:Re, or
147 Cr:Mo:Re:Ni:Mo, explained by the discussion given earlier: larger atoms like Mo and Re pre-
148 fer higher coordinated sites (CN14 and CN15), whereas smaller atoms like Ni and Cr prefer lower
149 CN12 sites.

150 The valence electron number \bar{e} has been given in Table 2. It has been discussed elsewhere [16,
151 25, 26] that \bar{e} governs the stability of the σ -phase and has to be between 5.5 and 8 to make the
152 phase stable. Since the less stable quaternary configuration (Re:Ni:Cr:Mo:Cr, $\Delta_f H > 30 \text{ kJ/at}$)
153 presents 6.6 valence electron and satisfies this electronic condition, it clearly shows that, even if
154 the electronic argument may be important, the geometric one dominates strongly the σ -phase
155 stability.

156 3.3.2. *Ideal ternaries phase diagram*

157 For the first calculation, ideal solid solutions have been considered. The Bragg-Williams-
158 Gorsky approximation [29] has been applied using the CEF formalism to describe the σ -phase.
159 Without any adjustable parameter and with DFT lattice stability of pure elements (only enthalpies
160 no entropy terms), the four ternary phase diagrams have been calculated using the Thermo-Calc
161 software package. They are represented in Figure 4. With the exception of Cr-Mo-Ni, all the
162 expected σ -phases appear in a reasonable range of compositions.

163 3.3.3. *Additional interaction parameters*

164 Using the SQS results, the mixing enthalpy of binary solid solutions is obtained. As an ex-
165 ample, the results on the three phases of Mo-Re are shown in Figure 5 The six binary systems
166 will not be discussed in this work. From the mixing energy obtained after full relaxation, solu-
167 tions have been treated as regular solutions with a fit done using a unique L^0 parameter. Results
168 are summarized in Table 3, they have been considered for the computed ternary phase diagrams
169 shown in Figure 6. The terminal solid solutions at each corner better match now the experimental

Table 2: Selected σ -phase configurations with average valence electron number \bar{e} and their heat of formation $\Delta_f H_{ijklm}^\sigma$ (in kJ/at) calculated in the present study or in a previous works.

	System	2a	4f	8i ₁	8i ₂	8j	\bar{e}	$\Delta_f H_{ijklm}^\sigma$ calculated	$\Delta_f H_{ijklm}^\sigma$ previous works	Ref.
		CN12	CN15	CN14	CN12	CN14				
binaries	Cr-Mo	Cr	Mo	Mo	Cr	Mo	6.00	12.62	8.65	[17]
	Cr-Ni	Cr	Ni	Ni	Ni	Cr	8.67	7.63	5.65	[18]
	Cr-Re	Cr	Re	Re	Cr	Cr	6.40	0.60	1.00	[27]
		Cr	Re	Re	Cr	Re	6.67	0.79	1.30	[27]
	Mo-Ni	Ni	Mo	Mo	Ni	Mo	7.33	-0.67	-0.70	[19]
	Mo-Re	Re	Mo	Re	Re	Mo	6.60	0.96	1.07	[28]
	Ni-Re	Ni	Re	Re	Ni	Re	8.00	0.54	0.75	[18]
ternaries	Cr-Mo-Ni	Cr	Mo	Mo	Ni	Mo	7.07	0.65		
	Cr-Mo-Re	Cr	Mo	Re	Cr	Re	6.53	0.36	0.75	[17]
		Cr	Mo	Mo	Re	Re	6.53	-0.07	0.16	[17]
	Cr-Re-Ni	Cr	Re	Re	Ni	Cr	7.47	-2.11	-2.02	[18]
		Re	Re	Re	Ni	Cr	7.53	-1.28	-1.16	[18]
		Ni	Re	Re	Ni	Cr	7.73	-1.87	-1.80	[18]
	Mo-Ni-Re	Re	Mo	Re	Ni	Re	7.67	-0.85	-0.73	[19]
		Ni	Mo	Re	Ni	Re	7.87	-1.53	-1.42	[19]
		Ni	Re	Mo	Ni	Re	7.73	-0.14	-0.04	[19]
		Re	Re	Mo	Ni	Re	7.53	-0.73	-0.62	[19]
		Ni	Re	Re	Re	Mo	6.93	-0.50	-0.35	[19]
		Ni	Re	Re	Ni	Mo	7.73	-3.34	-3.25	[19]
		Re	Re	Re	Ni	Mo	7.53	-3.26	-3.15	[19]
		Mo	Re	Re	Ni	Mo	7.47	-1.44	-1.33	[19]
		Ni	Mo	Mo	Re	Re	6.80	-0.64	-0.50	[19]
		Ni	Mo	Mo	Ni	Re	7.60	-2.17	-2.09	[19]
		Re	Mo	Mo	Ni	Re	7.40	-2.93	-2.83	[19]
		Ni	Mo	Re	Ni	Mo	7.60	-3.52	-3.43	[19]
		Ni	Mo	Re	Re	Mo	6.80	-1.20	-1.06	[19]
		Re	Mo	Re	Ni	Mo	7.40	-3.50	-3.40	[19]
Mo	Mo	Mo	Ni	Re	7.33	-1.10	-1.01	[19]		
Mo	Mo	Re	Ni	Mo	7.33	-0.53	-0.44	[19]		
Ni	Re	Mo	Ni	Mo	7.47	-0.60	-0.52	[19]		
Re	Re	Mo	Ni	Mo	7.27	-1.38	-1.29	[19]		
Re	Mo	Mo	Ni	Mo	7.13	-1.25	-1.18	[19]		
Ni	Mo	Mo	Re	Mo	6.53	-0.86	-0.74	[19]		
quaternary	Cr-Mo-Ni-Re	Cr	Mo	Re	Ni	Re	7.60	-1.11		
		Ni	Mo	Re	Ni	Cr	7.60	-0.25		
		Re	Mo	Re	Ni	Cr	7.40	-0.24		
		Cr	Re	Mo	Ni	Re	7.47	-1.27		
		Cr	Re	Re	Ni	Mo	7.47	-3.07		
		Cr	Mo	Mo	Ni	Re	7.33	-2.37		
		Cr	Mo	Re	Ni	Mo	7.33	-2.01		
		Cr	Re	Mo	Ni	Mo	7.20	-0.49		
	Re	Ni	Cr	Mo	Cr	6.60	31.16			

170 **measurements.** However, the σ -phase does not appear in the Cr–Mo–Ni system, contrary to the
171 experimental evidence [30]. Some adjusting parameters are needed to fix this point.

172 Using the same hypothesis, the quaternary phase diagram is plotted in Figure 7 in the form of
173 several constant Ni-composition sections. This plot allows to evaluate the quaternary extension of
174 the σ -phase. The most striking feature is the shrinking of the homogeneity range as a function
175 of the Ni-content. In fact, Ni is the element richest in valence electrons (10 electrons). Thus,
176 our result is in agreement with the empirical rule stating that the σ -phase forms for an average
177 electron concentration range below the value of 8 [16, 26]

178 **4. Conclusions**

179 Zengen is a tool to automate the construction of the input files for the systematic DFT calcu-
180 lation of all the ordered configurations of a multicomponent phase. This approach can be used
181 in parallel with a thermodynamic assessment of the system by the Calphad method. It has been
182 illustrated by the calculation of the quaternary Cr–Mo–Ni–Re system for which all the binary solid
183 solutions and every end-member of the quaternary σ -phase have been calculated for the first time.

184 Many improvements will be made in future versions of Zengen: creation of tools to easily add
185 new structures, facilitate the site merging for sublattice description... At the present time, about
186 fifty different users have downloaded the code, and Zengen has already been used by external peo-
187 ple for different purposes, such as the study of the molar volume of the σ -phase involving transi-
188 tion elements [31], or the phase stability and mechanical properties of σ -phase in Co–Mo [32].

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195 **Appendix A. Supplementary material**

- 196 • DFT results of the σ -phase configurations (relaxed crystallographic parameters and heats
197 of formation)
- 198 • Thermodynamic database file of Cr–Mo–Ni–Re (TDB format), including SQS results

199 **References**

- 200 [1] W. Kohn, Nobel lectures, chemistry 1996-2000, in: World Scientific Publishing, Singapore, 2003.
- 201 [2] B. Sundman, B. J. Ågren, A regular solution model for phases with several components and sublattices, suitable
202 for computer applications, *J. Phys. Chem. Solids* 42 (1981) 297–301.
- 203 [3] J.-O. Andersson, A. Guillermet, M. Hillert, B. Jansson, B. Sundman, A compound-energy model of ordering in
204 a phase with sites of different coordination numbers, *Acta Metall.* 34 (3) (1986) 437–445.
- 205 [4] A. Zunger, S. H. Wei, L. G. Ferreira, J. E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.* 65 (3)
206 (1990) 353.
- 207 [5] J.-M. Joubert, J.-C. Crivello, M. Andasmas, P. Joubert, Phase stability in the ternary Re–W–Zr system, *Acta*
208 *Mater.* 70 (0) (2014) 56–65.
- 209 [6] A. Breidi, M. Andasmas, J.-C. Crivello, N. Dupin, J.-M. Joubert, Experimental and computed phase diagrams
210 of the Fe–Re system, *J. Phys.: Condens. Matter* 26 (48) (2014) 485402 (13p).
- 211 [7] CEA, CNRS, INRIA, CeCill-B license information, zengen IDDN.FR.001.280024.000.S.P.2015.000.10600,
212 french Free Software license, compatible with the GNU GPL.
- 213 URL <http://www.cecill.info>
- 214 [8] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* 47 (1) (1993) 558–561.
- 215 [9] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave
216 basis set, *Phys. Rev. B* 54 (16) (1996) 11169–11186.
- 217 [10] B. Sundman, B. Jansson, J.-O. Andersson, The thermo-calc databank system, *Calphad* 9 (1985) 153–190.
- 218 [11] B. Sundman, U. Kattner, M. Palumbo, S. Fries, OpenCalphad - a free thermodynamic software, *Integrating*
219 *Materials and Manufacturing Innovation* 4 (1) (2015) 1.
- 220 [12] C. Wolverton, Crystal structure and stability of complex precipitate phases in Al-Cu-Mg(Si) and Al-Zn-Mg
221 alloys, *Acta Mater.* 49 (16) (2001) 3129–3142.
- 222 [13] C. Jiang, C. Wolverton, J. Sofo, L.-Q. Chen, Z.-K. Liu, First-principles study of binary bcc alloys using special
223 quasirandom structures, *Phys. Rev. B* 69 (2004) 214202.
- 224 [14] D. Shin, R. Arróyave, Z.-K. Liu, A. Van de Walle, Thermodynamic properties of binary hcp solution phases
225 from special quasirandom structures, *Phys. Rev. B* 74 (2006) 024204.

- 226 [15] E. M. Slyusarenko, V. A. Borisov, M. V. Sofin, E. Y. Kerimov, A. E. Chastukhin, Determination of phase
227 equilibria in the system Ni-V-Cr-Mo-Re at 1425 K using the graph method, *J. Alloys Comp.* 284 (1-2) (1999)
228 171–189.
- 229 [16] J.-M. Joubert, Crystal chemistry and calphad modeling of the σ phase, *Prog. Mater. Sci.* 53 (2008) 528–583.
- 230 [17] J.-C. Crivello, M. Palumbo, T. Abe, J.-M. Joubert, *Ab initio* ternary σ -phase diagram: the Cr-Mo-Re system,
231 *Calphad* 34 (2010) 487–494.
- 232 [18] M. Palumbo, T. Abe, S. G. Fries, A. Pasturel, First-principles approach to phase stability for a ternary sigma
233 phase: Application to Cr-Ni-Re, *Phys. Rev. B* 83 (14) (2011) 144109.
- 234 [19] K. Yaqoob, J.-C. Crivello, J.-M. Joubert, Study of site occupancies in Mo-Ni-Re sigma-phase by both experi-
235 mental and ab initio methods, *Inorg. Chem.* 51 (2012) 3071–3078.
- 236 [20] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50 (24) (1994) 17953.
- 237 [21] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*
238 59 (3) (1999) 1758.
- 239 [22] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using
240 a plane-wave basis set, *Comput. Mater. Sci.* 6 (1) (1996) 15–50.
- 241 [23] J. P. Perdew, K. Burke, M. Ernzerhof, Erratum: Generalized gradient approximation made simple, *Phys. Rev.*
242 *Lett.* 78 (7) (1997) 1396.
- 243 [24] P. E. Blöchl, O. Jepsen, O. K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, *Phys.*
244 *Rev. B* 49 (23) (1994) 16223.
- 245 [25] B. Seiser, T. Hammerschmidt, A. N. Kolmogorov, R. Drautz, D. G. Pettifor, Theory of structural trends within
246 4d and 5d transition metal topologically close-packed phases, *Physical Review B* 83 (2011) 224116.
- 247 [26] B. Seiser, R. Drautz, D. Pettifor, TCP phase predictions in ni-based superalloys: Structure maps revisited, *Acta*
248 *Mater.* 59 (2) (2011) 749–763.
- 249 [27] M. Palumbo, T. Abe, C. Kocer, H. Murakami, H. Onodera, Ab initio and thermodynamic study of the Cr-Re
250 system, *Calphad* 34 (4) (2010) 495–503.
- 251 [28] J.-C. Crivello, J.-M. Joubert, First principles calculations of the σ and χ phases in the Mo-Re and W-Re systems,
252 *J. Phys.: Condens. Matter* 22 (2010) 035402.
- 253 [29] W. L. Bragg, E. J. Williams, The effect of thermal agitation on atomic arrangement in alloys, *Proceedings of the*
254 *Royal Society of London. Series A* 145 (855) (1934) 699–730.
- 255 [30] P. Turchi, L. Kaufman, Z.-K. Liu, Modeling of Ni-Cr-Mo based alloys: Part I- phase stability, *Calphad* 30 (1)
256 (2006) 70 – 87.
- 257 [31] W. Liu, X.-G. Lu, Y.-L. He, L. Li, Modeling of molar volume of the sigma phase involving transition elements,
258 *Computational Materials Science* 95 (0) (2014) 540–550.
- 259 [32] S. Li, J. Liu, B. Liu, Phase stability and mechanical properties of sigma phase in Co–Mo system by first princi-

- 260 ples calculations, *Computational Materials Science* 98 (0) (2015) 424–429.
- 261 [33] S. Saito, T. Takashima, K. Miyama, K. Kurokawa, T. Narita, Tie-lined compositions of the σ and (γ,δ) phases
262 in the Re–Cr–Ni system at 1573 K, *J. Japan Inst. Metals* 75 (6) (2011) 361–365.
- 263 [34] K. Yaqoob, J.-M. Joubert, Experimental investigation of the Mo–Ni–Re system, *J. Alloys Comp.* 559 (2013)
264 101–111.

Table 3: Regular 0L interaction parameter term (kJ/mol) obtained by SQS calculation. They are given for the six binary systems in the three structures : *fcc*, *bcc*, *hcp*.

	<i>fcc</i>	<i>bcc</i>	<i>hcp</i>
Cr–Mo	+9.8	+34.9	+42.3
Cr–Ni	-54.0	+26.3	-55.5
Cr–Re	-0.6	-17.2	+10.0
Mo–Ni	-54.2	+25.8	-54.0
Mo–Re	-18.1	-20.0	+2.9
Ni–Re	+7.2	-11.2	1.4

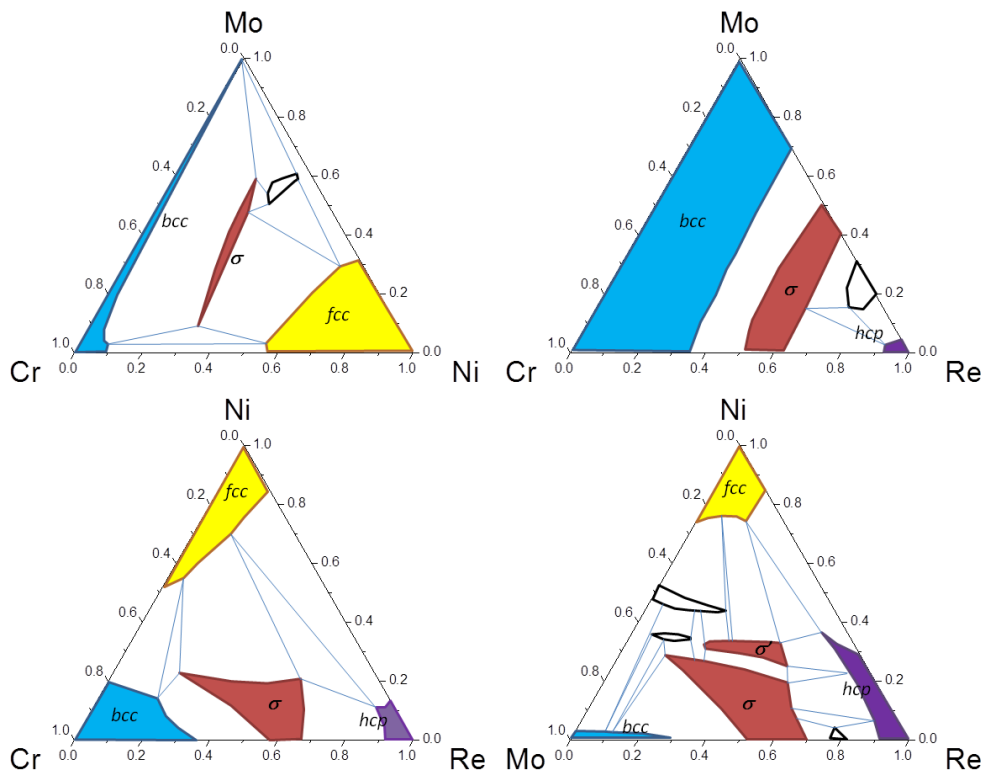


Figure 3: Literature ternary phase diagrams of Cr–Mo–Ni at 1323 K [30], Cr–Mo–Re at 1425 K [15], Cr–Ni–Re at 1573 K [33], Mo–Ni–Re at 1473 K [34]. Only solid solutions and the σ -phase are colored.

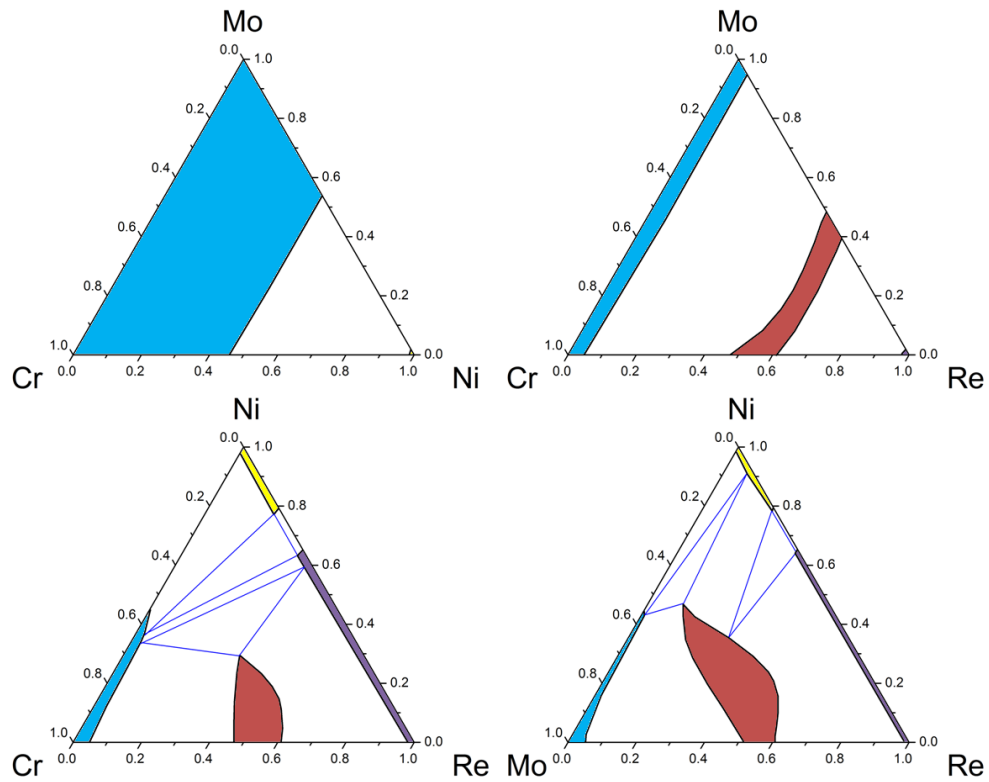


Figure 4: Using the BWG approximation, computed ternary phase diagrams of Cr–Mo–Ni, Cr–Mo–Re, Cr–Ni–Re and Mo–Ni–Re at 1423 K. The solid solutions are considered as ideal.

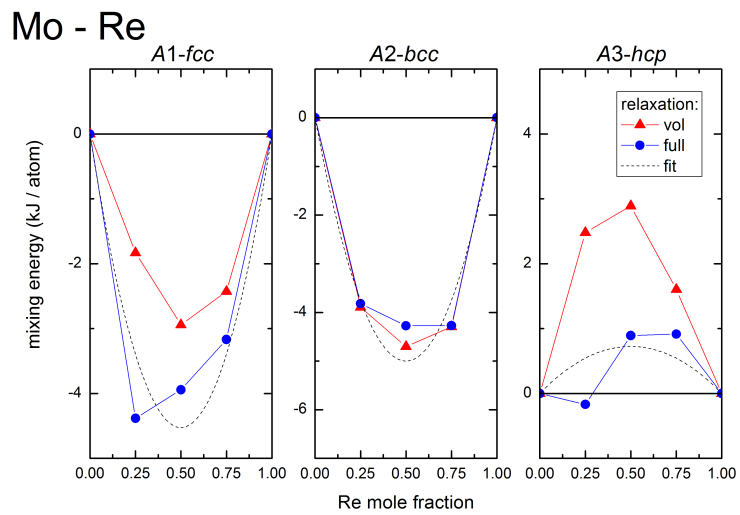


Figure 5: Enthalpy of mixing in the Mo–Re solid solutions calculated using SQS methodology of the three phases *fcc*, *bcc* and *hcp*. Dash line represents the fitted excess energy considered for the computed phase diagram.

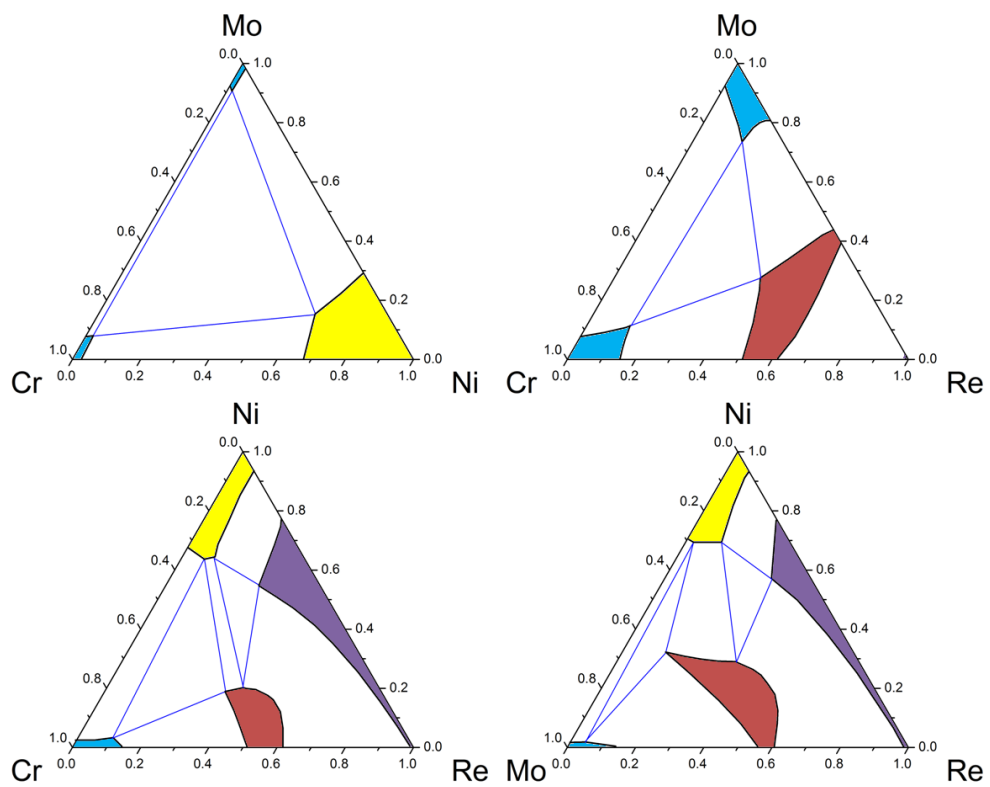


Figure 6: Computed ternary phase diagrams of Cr–Mo–Ni, Cr–Mo–Re, Cr–Ni–Re and Mo–Ni–Re at 1423 K. The solid solutions are considered as regular from the SQS results of Table 3.

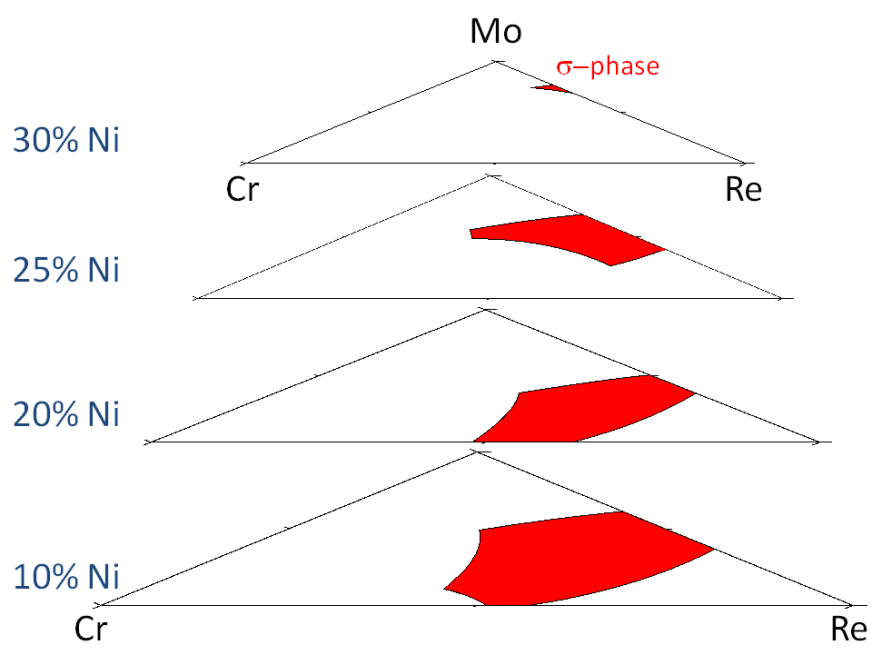


Figure 7: Computed quaternary Ni-isocomposition sections at 1423 K of Cr–Mo–Ni–Re phase diagrams for 10, 20, 25 and 30 at %-Ni.