ZenGen, a tool to generate ordered configurations for systematic first-principles calculations: The Cr–Mo–Ni–Re system as a case study ☆

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ABSTRACT

"ZenGen" is a script-tool which helps us 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-members 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 test its applicability, we have chosen the quaternary system, Cr–Mo–Ni–Re as a case study to be investigated. The binary solid solution parameters have been estimated from special quasirandom structures (SQS) calculations. The σ-phase has been fully described without any adaptation to its crystal structure, i.e. with a 5-sublattice model, through first-principles calculation of the $4^5 = 1024$ different ordered quaternary configurations. Several tentative *ab initio* phase diagrams are presented.

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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 supercomputers.

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 problematics, "ZenGen" code was created. This code is able to generate the necessary input files required to start DFT calculations of the corresponding ordered configurations for a given system. It has been tested on several phases, such as Laves phases ($C14$, $C15$, etc.), or other topologically close packed phases ($A12$, $A13$, $D8_b$, P, δ, etc.). It can also be used to run Special Quasi-random Structures (SQS) calculations [4]. A basic introduction of ZenGen workflow is given is Section 2.

Thereafter, in order to illustrate 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 Section 3.

2. The ZenGen workflow

"ZenGen" is a free and open source code, governed by the CeCILL-B license under French law [7], which is officially recognized by Open Source Initiative (OSI). It can be downloaded from http://zengen.cnrs.
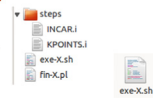
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1 - generation of ordered configurations

```
$ 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
```

Fig. 1. Schematic work flow chart of ZenGen.

fr. ZenGen can be installed on Unix–Linux machines and uses Bash, Perl and Python languages. In its present version, it is compatible with VASP program [8,9] for DFT calculations; however it can be adapted to be compatible with other first-principles codes, as well.

φ, the conventional name of the considered phase, and n, the number of involved elements, are the main inputs needed to be entered by the user as prompted by the code. Consequently, ZenGen decomposes the process into four steps:

1. Automatic generation of the input files for the n^m ordered configurations, where m is the number of the inequivalent sites of the φ phase.
2. Setup of the convergence criteria and relaxation steps of the φ phase.
3. Job execution under the same conditions.
4. Collection of output results (total energy, crystallographic parameters) and generation of a TDB file.

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

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_3Si	$Pm\bar{3}n$ (223)	$cP8$	2	FK: $A15$-Cr_3Si
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_2Mg	$Fd\bar{3}m$ (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_7W_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	$L2_1$	$AlCu_2Mn$	$Fm\bar{3}m$ (225)	$cF16$	3	bcc ordered ABC_2 Heusler
Cu3Ti		Cu_3Ti, Ni_3Ta	$Pmmn$ (59)	$oP8$	3	β-Cu_3Ti (LT)
delta		Mo_7Ni_7	$P2_12_12_1$ (19)	$oP56$	12	FK: δ MoNi
Dsim		Mo_7Ni_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		$Al_3Nb_{10}Ni_9$	$Pnma$ (62)	$oP52$	11	FK: M phase
R		$Cr_{16}Mo_{38}Co_{46}$	$Pnma$ (62)	$hR159$	11	FK: R phase

2.1. Generation of ordered configurations

After the command

```
$ zengen.pl
```

Fig. 2. Periodic table showing the available elements in ZenGen code (see `pure` folder).