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# What is the enthalpy contribution to the stabilization of the Co–Cr–Fe–Mn–Ni faced-centered cubic solid solution?

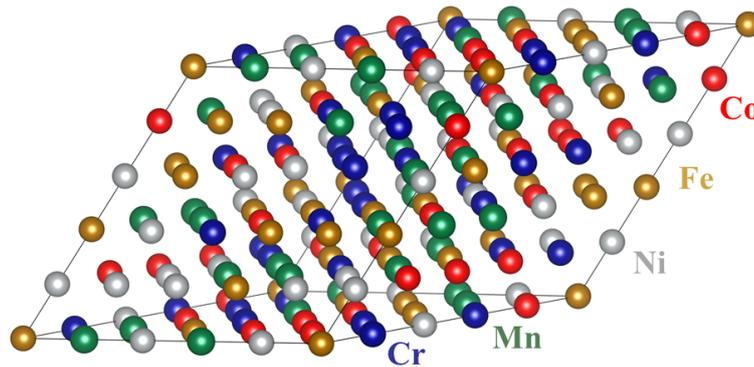
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## Abstract

The aim of this paper is to investigate the contribution of the mixing enthalpy to the stability of the faced-centered cubic (*fcc*) phase of the Co–Cr–Fe–Mn–Ni system. For this purpose, systematic first principles calculations on Special Quasirandom Structures (SQS) were performed in a comprehensive manner on the *fcc* solution in every  $\binom{5}{2} = 10$  binary,  $\binom{5}{3} = 10$  ternary,  $\binom{5}{4} = 5$  quaternary and the quinary systems. The magnetic contributions have been considered carefully *i.e.* including non-collinear spin polarization. An analysis of the different system order interactions to the enthalpy of mixing is detailed. This concludes that, at equiatomic composition, there is no special “cocktail” effect with an increase of components and that the thermodynamic properties can be well anticipated from the lower order systems, essentially binary and ternary systems.



**Keywords:** Multi-component alloys, High entropy alloys, DFT, SQS, solid solution

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## 1. Introduction

Since the report of Yeh [1] and Cantor [2] in 2004, the high entropy alloys (HEA) have received a substantial interest from the scientific community. They are multi-component alloys forming a solid solution and in which all components are very concentrated. A large and growing body of literature has shown that these alloys have promising properties, such as good combination of strength and ductility [3, 4, 5, 6, 7, 8], but also resistance to corrosion [9, 10], improved wear resistance [11, 12] and significant thermal stability [13].

The phase stability has been explained by the large configurational entropy,  $\Delta_{mix}S = -R \sum_i x_i \ln x_i$  expected to play an important role in the solid solution formation, in particular at the equiatomic composition [1]. However, this idea has been challenged by Otto [14] and several studies demonstrate that maximizing configurational entropy alone is not sufficient to form a multi-component solid solution [15, 16]. The phase stability in multi-component alloys is controlled by the Gibbs energy, which includes an enthalpy contribution as well, sometimes difficult to measure and separate from the contribution of the entropy (configurational and other ones [17]).

It is also interesting to deviate from the ideal equiatomic composition, as known as Canthor phase [2], but this makes the large composition range impossible to explore with an experimental approach only. In this respect, the development of predictive tools is necessary. Several empirical models tried to predict the formation of a solid solution phase [18, 19], however they are not very accurate and are proven to be not predictive enough [15]. Another approach, which demonstrated good efficiency to predict the formation of a single solid solution, is based on the thermodynamical analysis of the system using the Calphad methodology [20, 21]. Based on the description of the Gibbs energy, it uses the binary and ternary descriptions to extrapolate higher-order systems. But, the capability to correctly predict the stable phases and the thermodynamic properties is dependent on the quality of the database in which the binary interactions represent the major contribution. Ternary interaction parameters are not always used to optimize the experimental ternary phase diagrams because ternary thermodynamic data are rarely available. Possible special features of HEA compared to conventional solutions open the

question of their need and of the potential need of even higher order interaction parameters. This is why, it appears useful to have both an evaluation and a more physical description of the mixing enthalpy of high entropy alloys.

In the present work, the faced-centered cubic (*fcc*) phase of the Co–Cr–Fe–Mn–Ni system is analyzed as a case study. The aim of this paper is to investigate the contribution of the enthalpy of mixing to the stability of this quinary phase for a better understanding of the “high entropy alloys” concept. For this purpose, systematic density functional theory (DFT) calculations on special quasirandom structures (SQS) were performed in a comprehensive manner on the *fcc* phase in every  $\binom{5}{2} = 10$  binary,  $\binom{5}{3} = 10$  ternary,  $\binom{5}{4} = 5$  quaternary and the quinary systems. The magnetic contributions have been considered carefully.

## 2. Methodologies

### 2.1. First-principles calculations

The mixing energy and cell volume of the *fcc* solid solutions has been investigated with the SQS methodology [22]. This method allows to reproduce the random disorder of a solid solution at a given composition with a finite number of total atoms per unit cell. The generated SQS-cells are used as input for an additional DFT calculation [23, 24] to estimate the formation or mixing enthalpy: enthalpy is calculated by subtracting the DFT total energy of a SQS-cell to the molar fraction weighted sum of the DFT energies of the pure elements in a *fcc* structure:

$$\Delta_{mix}H = E^{SQS}(x_i; i = \{A, B, C, D, E\}) - \sum_i^{A,B,C,D,E} x_i E^{fcc}(i) \quad (1)$$

In the present work, the 10 binaries have been treated by considering a 16-atom cell in *fcc*-SQS structure for 3 different compositions ( $x_A = \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ ). The SQS structures have been generated from Wolverton’s work [25], with a pair correlation function equal to the random alloy for all pairs up to the 7th nearest-neighbor for  $x_A = \frac{1}{2}$  and to the 4th nearest-neighbor for  $x_A = \frac{1}{4}, \frac{3}{4}$ . In addition, 2 simple dilute solutions ( $x_A = \frac{1}{16}, \frac{15}{16}$ ) have also been considered by substituting a single atom in the same 16-atom supercell.

Furthermore, the *fcc* solution has been studied in the  $\binom{5}{3} = 10$  ternaries. For this, a 24-atom cell and three 32-atom cell SQS structures taken from the literature [26] have been used for the equiatomic composition ( $x_A = x_B = x_C = \frac{1}{3}$ ) and three compositions ( $x_B = x_C = \frac{1}{4}$  and  $x_A = \frac{1}{2}$ ,  $x_A = x_C = \frac{1}{4}$  and  $x_B = \frac{1}{2}$ ,  $x_A = x_B = \frac{1}{4}$  and  $x_C = \frac{1}{2}$ ), respectively. For the quaternaries, the  $\binom{5}{4} = 5$  equiatomic compositions have been calculated with a 64-atom cell, whereas the quinary equiatomic composition has been calculated with a 125-atom cell also taken from the literature [27], where only pair correlation functions up to the third nearest shell are considered to evaluate the SQS generation.

All SQS structures have been calculated using the DFT within a pseudo-potential approach using the Vienna ab initio simulation package (VASP) and projector augmented-wave (PAW) method [28, 29]. The generalized gradient approximation (GGA) described with the Perdew-Burke-Ernzerhof functional (PBE) [30] has been used with a cut-off energy of 400 eV and a high k-mesh density (see details in Supplementary Materials). The convergence criterion is only given on energy argument with difference of 0.01 meV, ie  $\sim 1$  J/mol. The residual force is reduced up to less or the same as the energy difference between two ionic steps.

The estimation of the energy error bars from SQS and DFT with an element permutation test on the different subsystems are given in Supplementary Materials. For equiatomic binaries, there is no effect of the *A/B* permutation since pair correlation functions up to the 7th neighbors are equal (null). For higher order systems, our sample test gives a standard deviation around 0.2 kJ/mol.

While keeping the original crystal symmetry, the structures have been relaxed (volume and internal parameters relaxations) within 3 magnetic states:

- without spin polarization, or non-spin polarization (NSP)
- with collinear spin polarization (CSP)
- with non-collinear spin polarization (NCSP).

Whereas there is no difference for binaries between the calculations done with collinear or non-collinear spin polarization (CSP or NCSP), more stable magnetic states have been obtained with NCSP calculations for ternary, quaternary and quinary systems. Because

of CPU time consumption, only equiatomic compositions have been investigated for NCSP calculations with one additional composition in the Co–Fe–Ni system.

## 2.2. Thermodynamic computations

The Calphad method relies on a self-consistent description of the Gibbs energy of each phase of a given system. This description is made thanks to semi-empirical functions, which depend on temperature and composition. The parameters are optimized on reliable experimental phase diagram and thermodynamic data, and also DFT results. The fitting parameters are stored in dedicated databases.

Thermo-Calc has developed a database dedicated to HEA [31] shown to correctly predict the *fcc* solid solution in this system [16]. It will be used in the present work to compare mixing enthalpies and volumes as a function of composition to our results. 1 K was chosen for the enthalpy of mixing in order to have a full account of the magnetic contribution. We have checked that this is not an issue for the Calphad calculation even if the database has not been evaluated at so low temperature. Excepted the magnetic contribution, no changes of the enthalpy of mixing is observed at so low temperature. 50 K was chosen for the volume calculation since, for several elements, the volume diverges at low temperature. 50 K is a good compromise between this effect and keeping a temperature low enough to allow comparison with DFT results.

In order to be able to compare SQS data of binary and higher order systems and to evaluate the contribution of the higher order interactions compared to the average of binary interactions, we treated our DFT data within a Calphad-like approach. The binary mixing energies were fitted to a first degree polynomial with the Redlich-Kister description [32]:

$$\Delta_{mix}H^{ij}(x_i; x_j) = x_i \cdot x_j ({}^0L + {}^1L(x_i - x_j)) \quad (2)$$

The predicted enthalpy of mixing for higher order systems is estimated by combining the binary descriptions according to the Muggianu extrapolation formula [33], such as in the ternary case:

$$\begin{aligned}
H(x_A, x_B, x_C) = & \frac{4x_A x_B}{(2x_A + x_C)(2x_B + x_C)} \Delta_{mix} H^{AB} \left( x_A + \frac{x_C}{2}; x_B + \frac{x_C}{2} \right) + \\
& \frac{4x_A x_C}{(2x_A + x_B)(2x_C + x_B)} \Delta_{mix} H^{AC} \left( x_A + \frac{x_B}{2}; x_C + \frac{x_B}{2} \right) + \\
& \frac{4x_B x_C}{(2x_B + x_A)(2x_C + x_A)} \Delta_{mix} H^{BC} \left( x_B + \frac{x_A}{2}; x_C + \frac{x_A}{2} \right). \quad (3)
\end{aligned}$$

For higher degree system, the equation can be generalized as given by Hillert's reference handbook [34]:

$$\begin{aligned}
H(\{x_i\}) = & \sum_i \sum_{j>i} \frac{4x_i x_j}{(1+x_i-x_j)(1+x_j-x_i)} \\
& \times H^{ij} \left( \frac{1+x_i-x_j}{2}, \frac{1+x_j-x_i}{2} \right). \quad (4)
\end{aligned}$$

### 3. Results

The calculated enthalpies of mixing for equiatomic compositions are collected in Table 1. The Redlich-Kister parameters fitted from binary SQS-DFT calculations are presented in Table 2.

#### 3.1. Binary compositions

The results for each binary system are collected in the grid of Fig 1. The DFT calculations with spin polarization (CSP equal to NCSP) are represented with red circles with the Redlich-Kister fitted curve also in red. The stability range of the *fcc* phase is also represented. The mixing enthalpies computed using TCHEA4 database [31, 35] are indicated by a blue line. On each graph, is also indicated the volume calculated by DFT (compared with the Zen's law) [36] and from the TCHEA4 database [35].

The mixing enthalpies are generally not found to be very large. They reach -10 kJ/mol only for Co–Cr, Cr–Fe and Cr–Ni. They are always negative except in the case of Co–Mn and Mn–Ni. The values are comparable with other SQS studies of similar systems [37, 38, 39].

For the volume curves, the observed differences between SQS data and TCHEA4 are mainly caused by the differences obtained for the pure elements, in particular Mn. These differences may be explained by the difficulty to assess molar volumes in the database for metastable structures (among the five elements, only *fcc*–Ni is stable at 0 K). Otherwise, the deviation or the absence of deviation to the Zen's law is generally reproduced.

#### 3.2. Ternary compositions

Analyzing and visualizing the enthalpy of mixing in a ternary system is not an easy task. An interesting way is to draw, in an  $A - B - C$  system, the three isopleth sections joining the pure elements with the equiatomic binary compositions, *i.e.*  $A - BC$ ,  $B - AC$ ,  $C - AB$ . The ternary *fcc* SQS cells of four compositions ( $A_{33}B_{33}C_{33}$ ,  $A_{50}B_{25}C_{25}$ ,  $A_{25}B_{50}C_{25}$ ,  $A_{25}B_{25}C_{50}$ ) have been calculated. The three sections are illustrated in three individual plots compiled in Fig. 2 for the Co–Fe–Ni system as an example and in Supplementary Materials for the other systems.

On each graph, the SQS-DFT calculations without magnetism (NSP) and with the two states of magnetic ordering (CSP and NCSP) are indicated. The Muggianu extrapolation obtained from the fit of the binary SQS calculations (Eq. 3) is also shown together with the calculation obtained using TCHEA4 database.

NCSP calculation results show that the ternary configurations are significantly more stable than those calculated with CSP (sometimes by 7 kJ/mol for Co-Fe-Ni). In rare cases (such as Cr-Fe-Mn), the most stable state was not found using NCSP because of the difficulty to find the magnetic non-collinear ground-state.

The sign of the mixing enthalpy is always negative from a SQS-DFT calculation, involving attractive interaction, with the only exception of the Co-Mn-Ni system. Additionally, in most systems, such as Co-Fe-Ni, where the magnetic contribution is the most significant, the NCSP energies reproduce the extrapolation made from the binary systems extremely well.

At this point, one may conclude several important facts for the ternary systems:

- the magnetic contribution is not negligible and the fundamental state could only be reached by non-collinear spin polarization, NCSP (not only collinear, CSP);
- the good agreement with the Muggianu extrapolation shows that the binary interactions are the main contributions. The additional ternary contribution is always positive except for Co-Fe-Ni where it is almost null;
- the TCHEA data are of same order of the magnetic set of results.

### 3.3. Quaternary and quinary compositions

Only the equiatomic compositions are investigated by SQS-DFT for the quaternary and quinary systems. Thus, 5+1 compositions have been calculated, and the enthalpy of mixing is always negative, as shown in Table 1. The Muggianu extrapolation of the binaries seems to predict correctly the enthalpy for the Co-Cr-Fe-Mn, Co-Cr-Mn-Ni and Co-Fe-Mn-Ni with a difference of less than 1.5 kJ/mol. However, for the Co-Cr-Fe-Ni and Cr-Fe-Mn-Ni, the value of mixing enthalpy is higher than that from the binary prediction. The difference reaches 3 kJ/mol for the quaternary system without manganese.

The difference between CSP and NCSP is very small for quaternary systems compared to the ternary case and null for the quinary. This suggests a maximum of the non-collinear contribution for the ternary case which may cancel out with the increase of complexity of the systems. The heat of mixing of the quinary Cantor alloy Co–Cr–Fe–Mn–Ni was calculated at -5.51 kJ/mol whereas the value from the binaries extrapolation is by 1.4 kJ/mol more stable.

## 4. Discussion

### 4.1. Zen's law

One of the most interesting points in analyzing the volumes obtained from the SQS calculation is the possibility to examine the deviation to the Zen's law in regard with the mixing enthalpies. A negative deviation could be anticipated to accompany negative heats of mixing. The results show that this is neither the case for our SQS nor in the TCHEA4 results. Most often absence of any deviation is noticed which may be related to the weak mixing energies that have been calculated. But the cases for which a larger deviation is observed (Co–Cr, Co–Fe) cannot be related to an energy deviation with larger amplitude.

### 4.2. Binary systems

The analysis of the binary systems shows that the energies of mixing are nearly always negative but are rather weak (in average -4 kJ/mol at the equiatomic composition) as expected from transition metals with comparable electronic structures. Good agreement is obtained between our calculations of the mixing enthalpy and the results from the TCHEA4 database for many systems (Co–Fe, Co–Mn, Co–Ni, Cr–Mn, Fe–Mn, Fe–Ni). Less good agreement is obtained for other systems (Co–Cr, Cr–Fe, Cr–Ni and Mn–Ni). Let us recall that TCHEA4 database is encrypted and that the origin of the thermodynamic parameters originating from the different thermodynamic optimizations that have been used are not known.

Different things should be considered to explain the apparent discrepancies. First, the stable homogeneity range of the *fcc* phase should be taken into account. It has been indicated in Fig. 1. Thermodynamic properties outside this range can be difficult to

establish in a thermodynamic assessment since there are no experimental data that can be used to adjust the description for these compositions. It is interesting to see that the systems in which the *fcc* phase is stable over the complete composition range have a similar description with both approaches (with the exception of Mn–Ni system).

The second point concerns the evaluation of the so-called lattice stability of the *fcc* phase *i.e.* the energy difference between the *fcc* and the stable phase for elements that are not stable in the *fcc* structure. It is very well known that DFT calculations give different results compared to Calphad estimations [40, 41]. This has been attributed to the instability of some elements in the *fcc* structure yielding inconsistent DFT estimations. This is particularly true for body-centered cubic (*bcc*) elements and, in our case, Cr. Within this framework, it is striking to see that the systems giving the worse agreement are those containing Cr and, in particular, in the Cr-rich region. Problems on the reported enthalpies of mixing may arise from the fact that the pure Cr reference is wrongly calculated, that SQS may be or may not be also mechanically unstable and that atomic relaxation of mechanically unstable structures may result in wrong estimation of the total energy (maximum estimated error of 2 kJ for Cr<sub>0.5</sub>Mn<sub>0.5</sub>). We however choose to keep the raw data without a correction such as that proposed for pure components in Ref. [41] because the procedure is too complex for SQS structures and the detection of the instability would necessitate phonon calculations for all the 50 structures presented in this work. The error should affect the Cr-rich compositions only. We believe it is negligible (less than 1 kJ) in the range of composition investigated for the HEA in which Cr composition is not higher than 33 at.% and for which the binary compositions at 50 at.% Cr at most are used for Muggianu’s extrapolation. Using mixing energies rather than total energies also diminishes partly the risk of errors. On the hand, in cases like the Cr–Mn system where the calculated mixing enthalpies tend not to converge to zero as we approach pure Cr, the error is also suppressed by using the SQS values for a fitting function which is forced to zero for the pure components.

Another feature that should be considered is the fact that the Calphad data have been evaluated at temperatures where the systems are no longer magnetic. Of course, magnetism is considered in the modeling and the reported Calphad are computed at low temperature. But, the overall results may differ from the ground state that is calculated

by SQS and DFT approaches.

#### 4.3. Ternary systems

We would like to emphasize the importance of magnetism for the calculation of ternary configurations. It appears that binary alloys can be fairly well calculated using CSP and no major difference was observed when calculated with NCSP. This is not the case for ternary configurations for which NCSP yields significantly more stable states than CSP. Note that the NCSP calculation is much more complex and that one is never completely sure that convergence is obtained toward the most stable magnetic configuration. In few cases, more stable states are found for CSP meaning that the global minimum has not been reached for NCSP. The lower values will be considered for the rest of the discussion.

On the other hand, NCSP results are found much closer than CSP to the prediction of ternary mixing energies using Muggianu extrapolation and the fit of the SQS binary data. The difference is always positive corresponding to a positive ternary interaction (opposite to the binary interactions), except for Co–Fe–Ni where it is almost null. The maximum is obtained for Cr–Fe–Ni system in which the difference between calculated and the extrapolated mixing enthalpies reaches 4.7 kJ/mol.

The comparison with the extrapolation made with TCHEA4 shows relatively good agreement for the ternary systems for which the binary sub-systems were in agreement (in general without chromium).

#### 4.4. Quaternary and quinary systems

For quaternary and quinary alloys, the difference between CSP and NCSP states vanishes. As shown in Fig. 3, we find again in both quaternaries and the quinary the positive interaction already shown for the ternary alloys, *i.e.* the calculated values are not as negative as expected from the only extrapolation of the calculated binary systems (lines in Fig. 3). We show that the mixing enthalpy of the quinary Cantor alloy could have been estimated from the only binary contributions to within 1.9 kJ/mol. The TCHEA4 results for the Cantor alloy deviate somewhat from our calculation.

Additionally, we present in Fig. 4, for each system order  $n$ , the difference between its enthalpies of mixing (Eq. 2) with circle symbols and those calculated from the extrapolation of  $n - 1$  systems order with empty triangle symbols. It shows that the contribution

of the  $n - 1$  systems to the enthalpy of mixing decreases with  $n$  and is almost null for  $n = 5$  (*i.e.* the quinary alloy can be perfectly calculated from the quaternary systems). This is an indication that there is no special “cocktail” effect for this composition and that its thermodynamic properties can be well anticipated from the lower order systems, essentially binary and ternary systems, as usually observed in any system.

Note also that the stability of the quinary alloy is not very large because, if elements are no longer taken in the *fcc* state but rather in their reference state, the formation enthalpy becomes positive (+7.2 kJ/mol, in agreement with +7.6 kJ/mol in [27]) indicating that the solid solution is not stable at 0K relative to its pure components. Entropy contribution at high temperature is therefore necessary to stabilize the phase.

## 5. Summary and conclusions

Using the SQS+DFT methods, the mixing enthalpy of the *fcc* phase has been investigated for the all sub-systems of the quinary Co–Cr–Fe–Mn–Ni, they are found almost always negative suggesting attractive interactions. It was shown that magnetism is not negligible. For ternary systems, consideration of non-collinear spin polarization is necessary, but is tricky to calculate. All the calculated energies were compared with the results obtained with TCHEA4 database. There is no obvious correlation between the sign of mixing enthalpy and the cell volume in the solid solution. The study of higher-order systems shows that the binary interactions are dominant and that higher-order interactions diminish progressively with the system order and cancel for the quinary system. In spite of a negative mixing energy, the quinary equiatomic alloy has a positive formation energy and needs an entropy contribution to be stable at high temperature.

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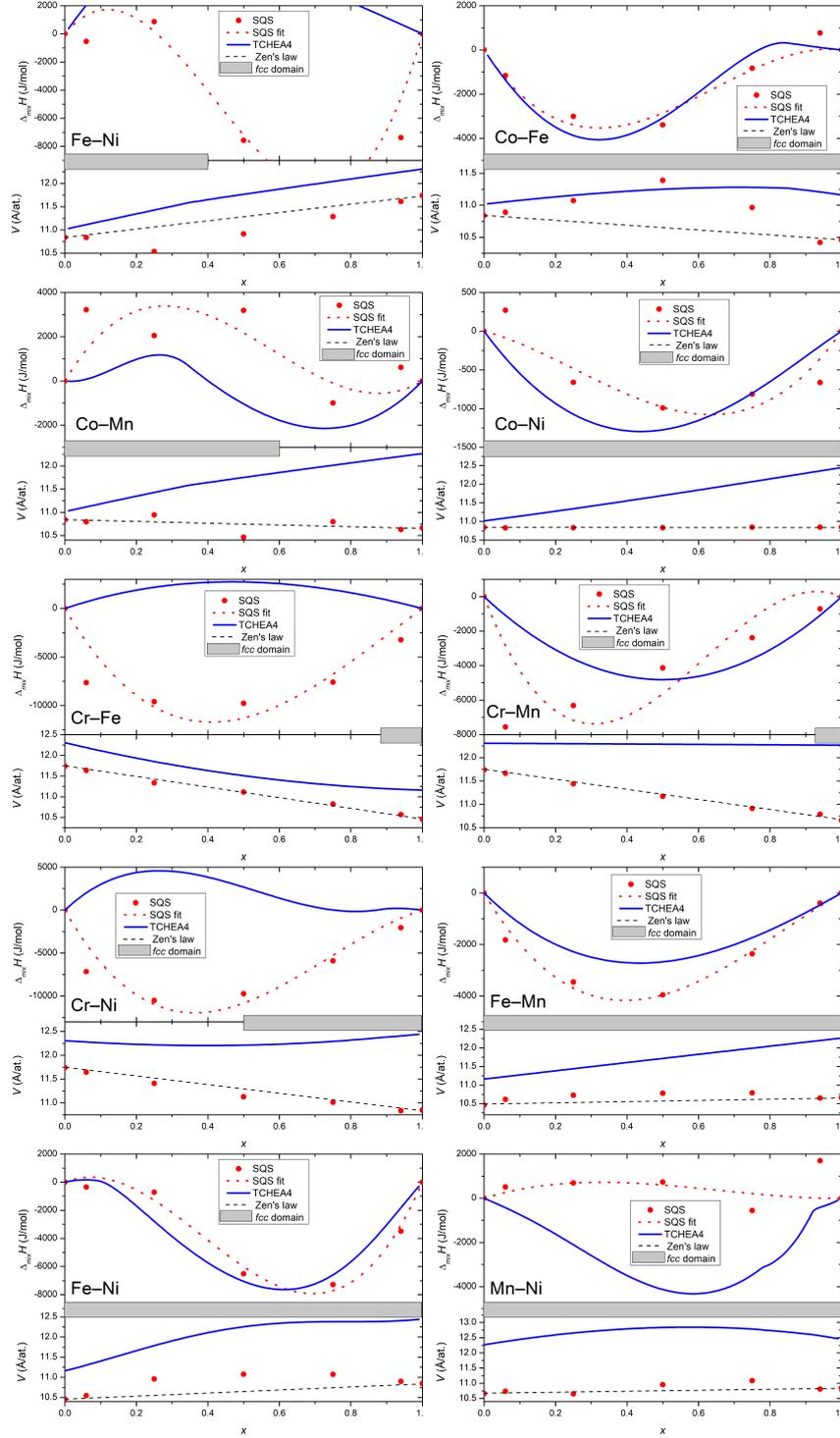


Figure 1: Enthalpy of mixing (J/mol) and volume ( $\text{\AA}^3/\text{at}$ ) for the *fcc* phase in the 10 of Co-Cr-Fe-Mn-Ni binary sub-system.

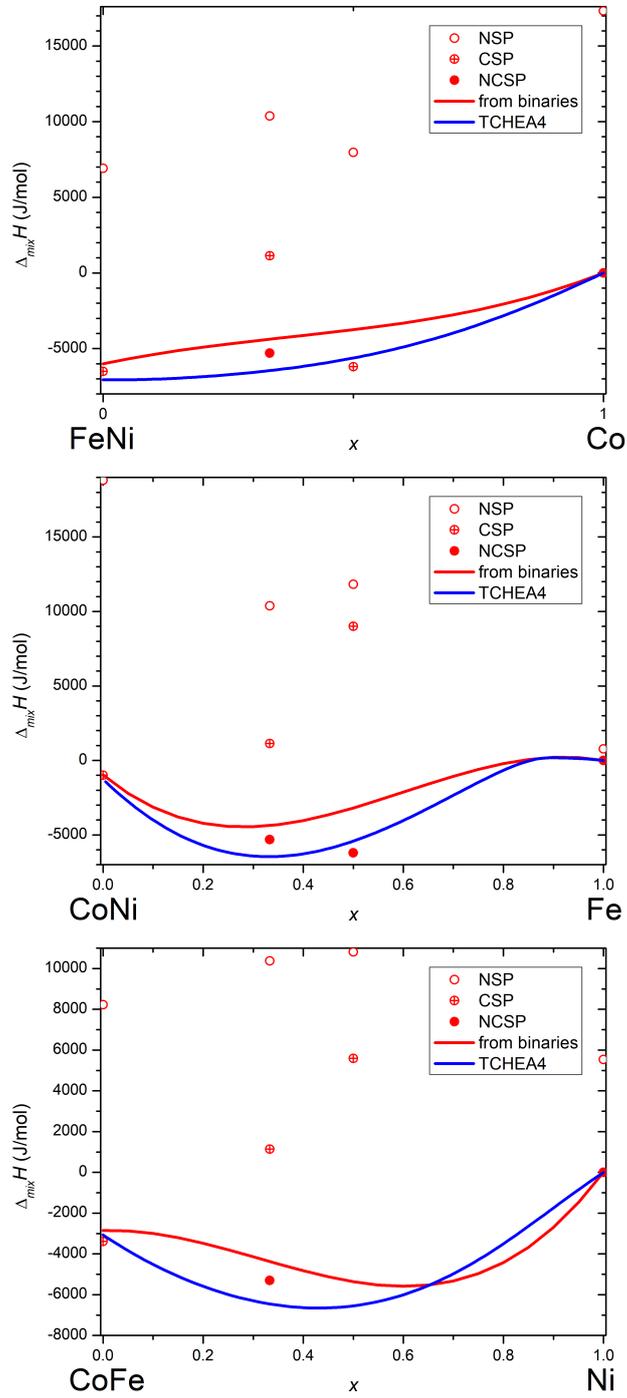


Figure 2: Enthalpy of mixing (J/mol) for the *fcc* phase in three isopleth sections of Co-Fe-Ni system

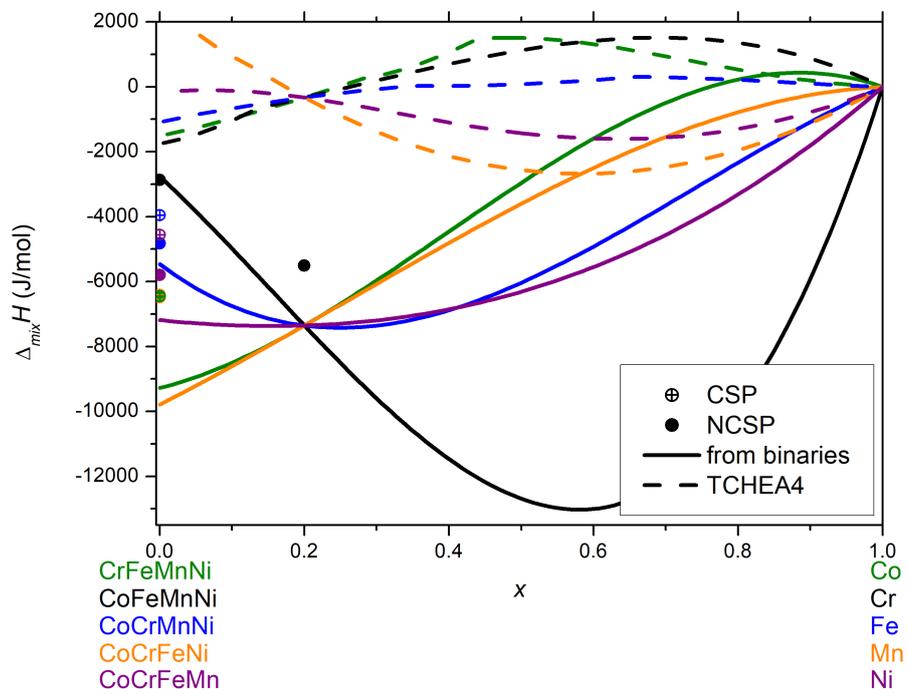


Figure 3: Enthalpy of mixing (J/mol) for the  $fcc$  phase in the isopleth section  $BCDE$  to  $A$  for different  $A$  elements from the Co-Cr-Fe-Mn-Ni system.

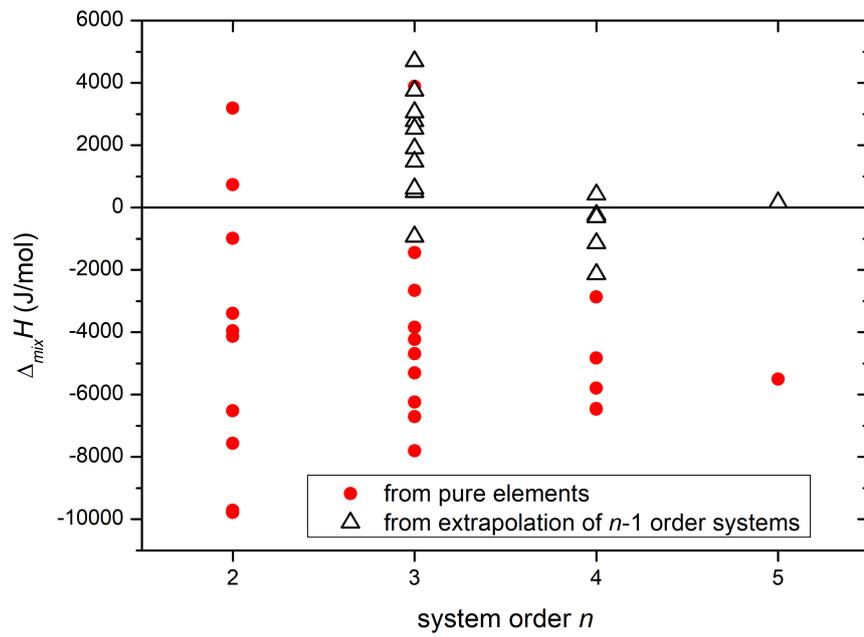


Figure 4: Enthalpy of mixing of each system order  $n$  (J/mol) calculated from the pure elements or from the extrapolation of the  $n - 1$  order systems in the  $fcc$  phase of Co-Cr-Fe-Mn-Ni system.

Table 1: Heat of mixing  $\Delta_{mix}H^{SQS}$ , for binary to quinary systems at the equiatomic composition, using non-collinear spin polarization NCSP SQS-DFT calculations. A comparison with the extrapolated  $\Delta_{mix}H^{extrapolation}$ , from the Muggianu extrapolation, computed from the fit of binary SQS calculations is also given.

System	$\Delta_{mix}H^{SQS}$ (J/mol-at)	$\Delta_{mix}H^{extrapolation}$ (J/mol-at)
Co-Cr	-7568	
Co-Fe	-3392	
Co-Mn	3193	
Co-Ni	-991	
Cr-Fe	-9782	
Cr-Mn	-4128	
Cr-Ni	-9719	
Fe-Mn	-3952	
Fe-Ni	-6517	
Mn-Ni	732	
Co-Cr-Fe	-6706	-9484
Co-Cr-Mn	-4227	-4729
Co-Cr-Ni	-4694	-8443
Co-Fe-Mn	-1450	-2060
Co-Fe-Ni	-5308	-4376
Co-Mn-Ni	3331	798
Cr-Fe-Mn	-7372	-9275
Cr-Fe-Ni	-7801	-12497
Cr-Mn-Ni	-3982	-7043
Fe-Mn-Ni	-2690	-4163
Co-Cr-Fe-Mn	-5794	-7185
Co-Cr-Fe-Ni	-6475	-9786
Co-Cr-Mn-Ni	-4827	-5463
Co-Fe-Mn-Ni	-2865	-2759
Cr-Fe-Mn-Ni	-6447	-9274
Co-Cr-Fe-Mn-Ni	-5506	-7403

Table 2:  ${}^0L$  and  ${}^1L$  Redlich-Kister parameters fitted from the SQS-DFT binary calculations (J/mol).

System	${}^0L$	${}^1L$
Co-Cr	-28776	59319
Co-Fe	-11424	-13309
Co-Mn	8708	18420
Co-Ni	-3925	2693
Cr-Fe	-45153	-18069
Cr-Mn	-22492	-31471
Cr-Ni	-43287	-30483
Fe-Mn	-15827	-7695
Fe-Ni	-24036	34278
Mn-Ni	2395	2566