

Supplementary of

*First-principles-only CALPHAD phase diagram of the  
solid aluminium-nickel (Al-Ni) system*

Using first-principles data directly in the order-disorder model

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# 1 Introduction

The four substitutional sublattice order-disorder partitioning model offers a convenient way to separately describe both an ordered and a disordered solid solution phase of the same type (e.g. fcc) so that the two descriptions are consistent with one another. Conventionally, data may not be available for both phases at all composition and temperature points, so the parameters describing both types of phases may be optimised simultaneously. However, using first-principles calculations, it is possible to calculate the total energy of fully ordered or disordered phases at all points in temperature and composition space. This document shows how to exactly specify both the energy of the ordered phases and the disordered phase directly from calculated (or available thermodynamic data) in the fcc and bcc four substitutional sublattice order-disorder partitioning model.

The Bragg-Williams-Gorsky pair models for fcc and bcc are first presented in Section 2, and based on those models it is possible to directly assign reciprocal interaction parameters that approximate the effects of short range ordering [1, 2]. Section 3 shows how, based on the connection between the parameters of the ordered and disordered phases constructed from Gibbs energy models using the Bragg-Williams-Gorsky pair models, the energies of the ordered and disordered phases may be specified exactly. The approach may be applied for any choice of interaction parameters that can be expressed as functions of the end member energies.

## 2 Bragg-Williams-Gorsky pair models

Conventional CALPHAD modelling uses the Bragg-Williams [3] point approximation of configurational entropy to describe ideal solution mixing of compounds, and any deviations from the ideal solution behaviour are contained within the excess energy terms that are generally parameterised considering experimental data. However, using only first-principles calculations, such excess energy terms are difficult to obtain. The Bragg-Williams configurational entropy approximation is known to be insufficient to describe the real case, for example in overestimating order-disorder transition temperatures and by excluding any short range ordering [4]. Methods such as the CVM [5] have been used to include higher order cluster contributions to the configurational entropy, which have been shown to improve the theoretical description [6]. However, in real multicomponent systems, the CVM truncation required to provide sufficient accuracy is often computationally infeasible and cannot be easily used directly in computational thermodynamic software. Instead, Kusoffsky *et al.* [1] demonstrated that using the Bragg-Williams-Gorsky (BWG) pair interaction model [7, 3] to obtain interaction parameters creates an approximation to the short range ordering behaviour in the fcc system, approximating the Gibbs energy from an equivalent CVM calculation in the tetrahedron approximation.

### 2.1 Face-centred cubic (fcc) phases

To provide context, the origins of the BWG pair approximation model derived by Kusoffsky *et al.* [1] that relate the energy of each ordered phase to the interaction energies are first reviewed. The fcc crystal may be split into four sublattices which may be represented later using a four-sublattice model. As described by Kusoffsky *et al.*, each of the four sublattices is a cubic sublattice of the fcc cell, which form four corners of a tetrahedron in the unit cell. This is shown in Figure 1. By the crystallographic symmetry of the fcc lattice, each site on the tetrahedron must be equivalent, and the bond length between each atom in the tetrahedron must be equal and of first nearest neighbour

(1nn) type. The next nearest neighbour (2nn) for each atom is its equivalent site on the next tetrahedron. In Figure 1, some of the 1nn bonds are indicated with dashed lines, and some 2nn bonds are shown with solid lines. Each sublattice is equivalent and therefore contains a quarter of the atoms per mole.

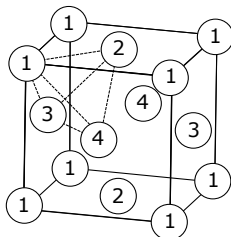


Figure 1: The fcc crystal structure indicating the sites of the four symmetrically equivalent sublattices. 1nn bonds are shown with dashed lines, and 2nn bonds with solid lines.

The model therefore has the possible sublattice occupation end-members (where each sublattice is singularly occupied) fcc-Al (A1),  $\text{Al}_3\text{Ni}$  (L1<sub>2</sub>), AlNi (L1<sub>0</sub>),  $\text{AlNi}_3$  (L1<sub>2</sub>), and fcc-Ni (A1). The sublattice site occupations defining the A1, L1<sub>2</sub>, and L1<sub>0</sub> structures are shown in Table 1, where the white atoms indicate one atomic species in a binary system, and the grey atoms indicate the other. For each case, each species may be either Al or Ni, although in the case of the L1<sub>0</sub> structure, it is equivalent by symmetry regardless of which species occupies the white and grey sites.

Strukturbericht	Formula	Sublattice condition		No. unlike 1nn bonds per tetrahedron
A1	Al/Ni	$y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$		0
L1 <sub>2</sub>	$\text{Al}_3\text{Ni}/\text{AlNi}_3$	$y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)}$		3
L1 <sub>0</sub>	AlNi	$y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)}$		4

Table 1: The ordered end-members that are possible with a four-sublattice description of an fcc phase. The sublattice conditions are defined according to the site occupation probabilities,  $y_i^{(n)}$ , of a species  $i$  on each sublattice  $n$ .

A model is used where it is assumed that there is some energy difference between ordered and disordered fcc phases, the ordering energy. Following Kusoffsky *et al.* [1], Abe and Shimono [8], and Lindahl *et al.* [9], it is further assumed that the ordering energy in a compound is described well when considered as arising from the formation of its unlike nearest-neighbour bonds. This assumption is common in CALPHAD modelling where all energies are given with reference to elemental reference states. Therefore from the tetrahedron construction the fully ordered structures

mentioned above are considered in terms of the number of unlike first nearest neighbour (1nn) bonds. The A1 pure element structures have no unlike bonds, and therefore have a zero energy. This corresponds to our reference state. In the L1<sub>2</sub> structure, there are three A and one B atoms on the four sublattice sites. This corresponds to three A-B bonds. In the L1<sub>0</sub> structure, there are two A and two B atoms on the four tetrahedron sites, corresponding to four equivalent A-B bonds. If the energy of the A-B bond is  $u_{AB}^{\text{fcc}}$ , a general expression for the energy of these intermediate compounds with reference to the A1 states may be written as

$$G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} = 3u_{AB}^{\text{fcc}} + 3\alpha^{\text{fcc}} \quad (1)$$

$$G_{L1_0-A_2B_2}^{\text{fcc:ord}(4\text{SL})} = 4u_{AB}^{\text{fcc}} \quad (2)$$

$$G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} = 3u_{AB}^{\text{fcc}} + 3\beta^{\text{fcc}} \quad (3)$$

where  $\alpha^{\text{fcc}}$  and  $\beta^{\text{fcc}}$  are parameters representing the asymmetry of the A-B system that may occur due to higher-order interactions not considered in this pair model. If total energies of these three ordered compounds are known relative to the pure elements in their fcc state, all of the parameters in this model may be obtained.

Reciprocal interaction parameters defined by Kusoffsky *et al.* [1] are used to relate the Gibbs energies for the end-members above to the 1nn interaction energy,  $L_{i,j:k,l:m:n}^{\text{fcc:ord}(4\text{SL})}$ , where the subscript denotes the interactions described by that interaction parameter. Colons separate each sublattice and commas separate the two species interacting on a given sublattice.  $L_{i,j:k,l:m:n}^{\text{fcc:ord}(4\text{SL})}$  therefore describes the simultaneous interaction of  $i$  and  $j$  on one sublattice and  $k$  and  $l$  on another, while the third and fourth sublattices are occupied by species  $m$  and  $n$  respectively. An approximation is made whereby it is assumed that the 1nn A-B interaction energy (simultaneous interaction on two sublattices) is the same regardless of the occupation of the other sublattices, and such interaction energy is equivalent to the A-B bond energy  $u_{AB}^{\text{fcc}}$  as such reciprocal interaction always changes the number of unlike bonds by one. This can be summarised as:

$$\begin{aligned} u_{AB}^{\text{fcc}} &= L_{A,B:A,B:A:A}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:A,B:A:B}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:A,B:B:A}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:A,B:B:B}^{\text{fcc:ord}(4\text{SL})} \end{aligned} \quad (4)$$

A corresponding approximation for the 2nn interaction parameters may also be made:

$$\begin{aligned} v_{AB}^{\text{fcc}} &= L_{A,B:A:A:A}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:A:A:B}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:A:B:B}^{\text{fcc:ord}(4\text{SL})} \\ &= L_{A,B:B:B:B}^{\text{fcc:ord}(4\text{SL})} \end{aligned} \quad (5)$$

where  $v_{AB}^{\text{fcc}}$  corresponds to the second nearest neighbour A-B bond energy, equivalent to the switching of atoms between the same sublattice site in neighbouring tetrahedra. As in the previous case, as Kusoffsky *et al.* [1], it is assumed that the interaction energy is independent of the species occupying the other sublattices.

## 2.2 Body-centred cubic (bcc) phases

A similar pair approximation may be applied to tetrahedron cells representing bcc phases, but while fcc phases have a single lattice parameter defining the volume, the asymmetry of the  $a$  and  $c$  lattice parameter in the conventional bcc unit cell means that the six bonds within the tetrahedron are of either 1nn and 2nn type, and the bonds between equivalent sites on neighbouring tetrahedra are of third nearest neighbour (3nn) type. Figures 2 and 3 show examples of the 1nn, 2nn, and 3nn bonds in the bcc unit cell.

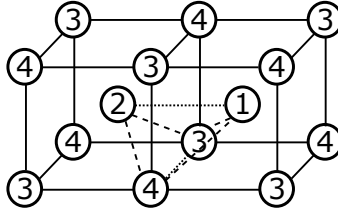


Figure 2: The bcc crystal structure, indicating the sites of the four sublattices. The four sublattice sites make a repeating tetrahedron structure. The 1nn bonds in the tetrahedron are marked with dashed lines, and the 2nn bonds are marked with dotted lines. The solid lines mark the cubic cell, and do not correspond to the 3nn bonds.

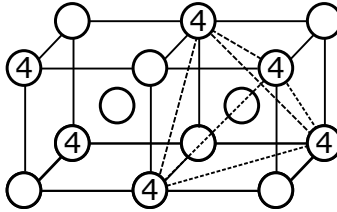


Figure 3: The equivalent sites on each sublattice form a tetrahedron, where the bond between each site is of 3nn type. These bonds are marked with dashed lines. The solid lines demarcate the cubic cell.

The presence of 1nn and 2nn bonds within the tetrahedron construction arising from the asymmetry of the bcc sublattice results in two different possible ordering configurations in an equiatomic binary compound. The end-member ordered phases for the bcc four-sublattice model are therefore Al (A2),  $\text{Al}_3\text{Ni}$  ( $\text{D0}_3$ ), AlNi (B2), AlNi (B32),  $\text{AlNi}_3$  ( $\text{D0}_3$ ), and Ni (A2). The sublattice site occupation conditions defining each phase are given in Table 2, where as before, one species is represented by white atoms, and another by grey.





Strukturbericht	Formula	Sublattice condition		No. unlike 1nn bonds per tetrahedron	No. unlike 2nn bonds per tetrahedron
A2	Al/Ni	$y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$		0	0
B2	AlNi	$y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)}$		4	0
B32	AlNi	$y_i^{(1)} = y_i^{(3)} \neq y_i^{(2)} = y_i^{(4)}$		2	2
D0 <sub>3</sub>	Al <sub>3</sub> Ni/AlNi <sub>3</sub>	$y_i^{(1)} \neq y_i^{(2)} = y_i^{(3)} = y_i^{(4)}$		2	1

Table 2: The ordered end-members that are possible with a four-sublattice description of a bcc phase.

Following Abe and Shimono [8] and Lindahl *et al.* [9], a pair interaction model is constructed to relate the interaction parameters to the energies of the end-member compounds. It is again assumed that all ordering energy in the compound relative to the end-members comes from the unlike bonds. From Lindahl *et al.*, the number of bonds may be averaged over the number of tetrahedra that share the bond, so as to avoid double counting any bonds [9]. Each 1nn bond is shared by six tetrahedra, each 2nn bond is shared by four tetrahedra, and each tetrahedron contains four atoms shared between 24 tetrahedra.

Therefore the Gibbs energy of each of the end-members  $ijkl$  for the above model,  $G_{i:j:k:l}^{\text{bcc:ord}(4\text{SL})}$ , can be expressed in terms of the number of 1nn bonds,  $x$ , and 2nn bonds,  $y$  as

$$G_{i:j:k:l}^{\text{bcc:ord}(4\text{SL})} = \frac{\frac{x}{6}u_{\text{AB}}^{\text{bcc}} + \frac{y}{4}v_{\text{AB}}^{\text{bcc}}}{\frac{4}{24}} = x \cdot u_{\text{AB}}^{\text{bcc}} + \frac{3}{2}y \cdot v_{\text{AB}}^{\text{bcc}} \quad (6)$$

where  $u_{\text{AB}}^{\text{bcc}}$  and  $v_{\text{AB}}^{\text{bcc}}$  are the 1nn and 2nn bond energy respectively.

This gives us the end-member energies relative to the pure elements in the A2 structure:

$$G_{\text{D0}_3\text{-A}_3\text{B}}^{\text{bcc:ord}(4\text{SL})} = 2u_{\text{AB}}^{\text{bcc}} + 1.5v_{\text{AB}}^{\text{bcc}} + \omega_1^{\text{bcc}} \quad (7)$$

$$G_{\text{B2-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} = 4u_{\text{AB}}^{\text{bcc}} \quad (8)$$

$$G_{\text{B32-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} = 2u_{\text{AB}}^{\text{bcc}} + 3v_{\text{AB}}^{\text{bcc}} \quad (9)$$

$$G_{\text{D0}_3\text{-AB}_3}^{\text{bcc:ord}(4\text{SL})} = 2u_{\text{AB}}^{\text{bcc}} + 1.5v_{\text{AB}}^{\text{bcc}} + \omega_2^{\text{bcc}} \quad (10)$$

where, as for the fcc case, parameters  $\omega_1$  and  $\omega_2$  have been introduced to account for the asymmetry that may occur due to higher order interactions.

Reciprocal interaction parameters for the four-sublattice order-disorder partitioning model may be defined using these 1nn and 2nn bond energies as in the fcc case, although not via a simple linear

relation [8]. The 3nn bond energy may also be defined, but does not contribute to the ordering energy in this pair approximation.

To consider the permutations of the interaction parameters, it is important to remember that not all sites are equivalent, and therefore for the case of simultaneous interaction on two sublattices, it is significant which two sublattices are involved in the exchange. By the crystallographic symmetry, there are the following sets of equivalent 1nn interaction energies:

$$\begin{aligned}
L_{A,B:A:A,B:A}^{\text{bcc:ord}(4\text{SL})} &= L_{A,B:A:A:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A:A,B:A,B:A}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A:A,B:A:A,B}^{\text{bcc:ord}(4\text{SL})}
\end{aligned} \tag{11}$$

$$\begin{aligned}
L_{A,B:A:A,B:B}^{\text{bcc:ord}(4\text{SL})} &= L_{A,B:A:B:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A:A,B:A,B:B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A:A,B:B:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A,B:B:A,B:A}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A,B:B:A:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{B:A,B:A,B:A}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{B:A,B:A:A,B}^{\text{bcc:ord}(4\text{SL})}
\end{aligned} \tag{12}$$

$$\begin{aligned}
L_{A,B:B:A,B:B}^{\text{bcc:ord}(4\text{SL})} &= L_{A,B:B:B:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{B:A,B:A,B:B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{B:A,B:B:A,B}^{\text{bcc:ord}(4\text{SL})}
\end{aligned} \tag{13}$$

There are also the following sets of equivalent 2nn interaction energies by symmetry:

$$L_{A,B:A,B:A:A}^{\text{bcc:ord}(4\text{SL})} = L_{A:A:A,B:A,B}^{\text{bcc:ord}(4\text{SL})} \tag{14}$$

$$\begin{aligned}
L_{A,B:A,B:A:B}^{\text{bcc:ord}(4\text{SL})} &= L_{A:B:A,B:A,B}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{A,B:A,B:B:A}^{\text{bcc:ord}(4\text{SL})} \\
&= L_{B:A:A,B:A,B}^{\text{bcc:ord}(4\text{SL})}
\end{aligned} \tag{15}$$

$$L_{A,B:A,B:B:B}^{\text{bcc:ord}(4\text{SL})} = L_{B:B:A,B:A,B}^{\text{bcc:ord}(4\text{SL})} \tag{16}$$

It may be noted that the sublattices may be separated into two sets: the first two sublattices and the second two sublattices. If there is simultaneous interaction on two sublattices in the same set, is it related to the second nearest neighbour interaction parameter. If there is simultaneous

interaction on two sublattices that are not in the same set, it is related to the first nearest neighbour interaction parameter.

The general 1nn and 2nn interaction parameters  $L_{A,B:i:A,B:j}^{\text{bcc:ord}(4\text{SL})}$  and  $L_{A,B:A,B:i:j}^{\text{bcc:ord}(4\text{SL})}$  (where the other sites are occupied by species  $i$  and  $j$ ) are related to the 1nn and 2nn A-B bond energies respectively. For the case of the 3nn interaction on a single sublattice site, e.g.  $L_{A,B:A:A:A}^{\text{bcc-4sl}}$ , there are the same permutations as for the fcc case. The 3nn interaction parameter  $L_{A,B:i:j:k}^{\text{bcc:ord}(4\text{SL})}$  is additionally related to the 3nn A-B bond energy.

Abe and Shimono [8] consider the effect of short range ordering in the 1nn and 2nn shell and obtain approximate expressions for the 1nn and 2nn reciprocal interaction parameters as a function of the 1nn and 2nn bond energy,

$$L_{A,B:*:A,B:*}^{\text{bcc:ord}(4\text{SL})} = -\frac{2(u_{\text{AB}}^{\text{bcc}})^2}{RT} \quad (17)$$

$$L_{A,B:A,B:*:*}^{\text{bcc:ord}(4\text{SL})} = -\frac{3(v_{\text{AB}}^{\text{bcc}})^2}{RT} \quad (18)$$

that are challenging to implement in a thermodynamic database because of the inverse temperature dependence. Therefore, to approximate the short range ordering, Abe and Shimono give the value of the interaction parameters at the A2/B2 critical temperature,

$$L_{A,B:*:A,B:*}^{\text{bcc:ord}(4\text{SL})} = \frac{1}{2}u_{\text{AB}}^{\text{bcc}} \leq 0 \quad (19)$$

$$L_{A,B:A,B:*:*}^{\text{bcc:ord}(4\text{SL})} = \frac{3(v_{\text{AB}}^{\text{bcc}})^2}{4u_{\text{AB}}^{\text{bcc}}} \leq 0 \quad (20)$$

that may be used.

### 3 Four substitutional sublattice order-disorder partitioning model

The order-disorder partitioning model has been widely used to separately describe ordered and corresponding disordered phases that are intrinsically connected by means of an ordering energy. This ensures that the ordered phase is consistent with the disordered phase when certain sublattice occupation conditions are met. In the usual application of this model, the parameters of the ordered and disordered phases are simultaneously optimised considering all available thermodynamic and phase diagram data relating to both phases, where there may not be data relating to both phases available at all points in temperature and composition space. The relationship between the parameters describing the disordered phase and the ordered phases for use in this case are described well by Kusoffsky *et al.* [1] for fcc, and Abe and Shimono [8] for bcc. However in this work, the energy of the fully ordered end-members and the disordered phase are independently specified by calculated data. The following description explains how the four sublattice order-disordering partitioning model may be applied to specify the energies of the disordered phase and the fully ordered phases exactly. The interaction parameters of the ordered and disordered phases are also obtained directly from the calculated Gibbs energies without conventional optimisation. To implement the order-disorder partitioning model in this way, it is necessary to extract the ordering energy which



parameterises the ordered phase relative to the disordered phase. As there is no optimisation in this work beyond fitting single phase calculations of the Gibbs energy to a polynomial, the relations of the model parameters to the calculated Gibbs energy of a specific ordered sublattice configuration and the calculated Gibbs energy of the disordered phase at the same overall composition must be obtained for the specific descriptions used. This means taking into account the number of interaction parameters in the subregular solution model used for the disordered phase and the BWG model used to provide the interaction parameters of the ordered phase as functions of the end-member Gibbs energies. This process of obtaining these relations to exactly parameterise both the ordered and disordered phase in the four-sublattice order-disorder partitioning model is as follows.

### 3.1 Face-centred cubic phases

The disordered fcc phase can be described using a single sublattice model (Al,Ni). The Gibbs energy was described as a function of the molar fraction of species  $i$ ,  $x_i$ , where  $i$  may be Al or Ni. As this is a molar quantity, the sum of the molar fraction of each species must sum to unity.

$$\sum_i x_i = 1 \quad (21)$$

The end-members of this sublattice model are the disordered pure Al and Ni, which have an Al-type structure. The Gibbs energy of the disordered phase may therefore be written as a substitutional solution model in terms of the Gibbs energy of these end-members,  ${}^{\circ}G_i^{\text{fcc-Al}}$ ,

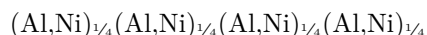
$$G_m^{\text{fcc:dis}}(x_i) = \sum_i x_i {}^{\circ}G_i^{\text{fcc-Al}} + RT \sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j L_{i,j}^{\text{fcc:dis}} \quad (22)$$

where  $L_{i,j}^{\text{fcc:dis}}$  are binary interaction parameters which have a temperature and composition dependence described by a Redlich-Kister polynomial as

$$L_{i,j}^{\text{fcc:dis}} = \sum_{\nu} (x_i - x_j)^{\nu} \cdot {}^{\nu}L_{i,j}^{\text{fcc:dis}} \quad (23)$$

where  $\nu$  indicates the order of the Redlich-Kister polynomial and  ${}^{\nu}L_{i,j}^{\text{fcc:dis}}$  is a polynomial in temperature.

As described in Section 2.1, following Kusoffsky *et al.* [1], each of the four sublattices is a cubic sublattice of the fcc cell, which form four corners of a tetrahedron in the unit cell. By the crystallographic symmetry of the fcc lattice, each site on the tetrahedron must be equivalent. Therefore, the four-sublattice model used to describe the various ordered fcc-based structures is



In order to describe the phase, two compositional quantities are used. As well as the overall molar fraction of species  $i$ ,  $x_i$ , the site fraction  $y_i^{(s)}$  of species  $i$  on sublattice  $s$  is also required. The site fractions of each species  $i$  on each sublattice  $s$  must also sum to unity.

$$\sum_i y_i^{(s)} = 1 \quad (24)$$

These quantities can be related by

$$x_i = \frac{1}{4} \sum_s y_i^{(s)} \quad (25)$$

This model has the end-members fcc-Al (A1), Al<sub>3</sub>Ni (L1<sub>2</sub>), AlNi (L1<sub>0</sub>), AlNi<sub>3</sub> (L1<sub>2</sub>), and fcc-Ni (A1). The conditions for each type of ordering structure are given in terms of sublattice site fractions in Table 1. The disordered case,  $y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)} = x_i$ , is equivalent to the single sublattice case in the disordered phase.

Various other ordered structures may exist based on the fcc lattice, but using only the four-sublattice model, they do not appear as end-members. One example of this is the fcc structure often referred to as the F' phase, which has the condition  $y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} \neq y_i^{(4)}$ . This phase appears in the fcc phase diagram based on the four-sublattice model ([1, 8]), but cannot be represented as an end-member phase with a binary four-sublattice model and so is not considered here. It is worth noting that by using greater numbers of sublattices within the symmetry of the crystal structure, further ordered phases may be considered in the same way.

In the order-disorder model, the Gibbs energy of the fcc phase in a given sublattice configuration,  $G_m^{\text{fcc}}(y_i^{(s)})$ , is represented as the energy of the disordered phase at that composition plus the molar ordering energy,  $\Delta G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)})$ ,

$$G_m^{\text{fcc}}(y_i^{(s)}) = G_m^{\text{fcc:dis}}(x_i) + \Delta G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) \quad (26)$$

where

$$\Delta G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) = G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) - G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)} = x_i) \quad (27)$$

These are combined to give

$$G_m^{\text{fcc}}(y_i^{(s)}) = G_m^{\text{fcc:dis}}(x_i) + G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) - G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)} = x_i) \quad (28)$$

When the phase is disordered, the molar ordering energy, or the contribution to the Gibbs energy due to ordering, is zero. This creates the condition

$$\Delta G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) = 0 \quad (29)$$

The Gibbs ordering energy of a phase with a given sublattice configuration can be written with a four-sublattice regular solution model as

$$\begin{aligned} G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) &= \sum_i \sum_j \sum_j \sum_l y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} \circ G_{i;j:k:l}^{\text{fcc:ord(4SL)}} + \frac{1}{4} RT \sum_s \sum_i y_i^{(s)} \ln y_i^{(s)} \\ &+ \sum_i \sum_{j>i} \sum_{k \geq i} \sum_{l>k} \sum_m \sum_n y_i^{(s)} y_j^{(s)} y_k^{(r)} y_l^{(r)} y_m^{(t)} y_n^{(u)} L_{i,j:k,l:m:n}^{\text{fcc:ord(4SL)}} \\ &+ \sum_i \sum_{j>i} \sum_k \sum_l \sum_m y_i^{(s)} y_j^{(s)} y_k^{(r)} y_l^{(t)} y_m^{(u)} L_{i,j:k:l:m}^{\text{fcc:ord(4SL)}} \end{aligned} \quad (30)$$

where the first term describes the mechanical mixing of the stoichiometric end-members in the four-sublattice model described above, and is the composition weighted sum of the Gibbs ordering energy  $\circ G_{i;j:k:l}^{\text{fcc:ord(4SL)}}$  of the ordered end-members  $ijkl$ , where the Gibbs energies are given relative

to the pure elements in the fcc-A1 state. The  $y_i^{(s)} \ln y_i^{(s)}$  term represents the ideal configurational entropy contribution to the Gibbs energy based on the four-sublattice model, and the  $L^{\text{fcc:ord}(4\text{SL})}$  terms represent the interaction parameters that give a contribution to the Gibbs energy depending on the composition. In this notation, species separated by a comma (e.g.  $i, j$ ) are mixing on a sublattice, and each sublattice is separated by a colon. These four-sublattice parameters describe a contribution to the Gibbs energy due to short range ordering [2].

By crystallographic symmetry of the sublattices, the Gibbs energy of the various permutations of the end-member occupations can be expressed as

$$\circ G_{\text{A1-A}_4}^{\text{fcc:ord}(4\text{SL})} = \circ G_{\text{A:A:A:A}}^{\text{fcc:ord}(4\text{SL})} \quad (31)$$

$$\begin{aligned} \circ G_{\text{L1}_2\text{-A}_3\text{B}}^{\text{fcc:ord}(4\text{SL})} &= \circ G_{\text{A:A:A:B}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{A:A:B:A}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{A:B:A:A}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{B:A:A:A}}^{\text{fcc:ord}(4\text{SL})} \end{aligned} \quad (32)$$

$$\begin{aligned} \circ G_{\text{L1}_0\text{-A}_2\text{B}_2}^{\text{fcc:ord}(4\text{SL})} &= \circ G_{\text{A:A:B:B}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{A:B:A:B}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{A:B:B:A}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{B:A:A:B}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{B:A:B:A}}^{\text{fcc:ord}(4\text{SL})} \\ &= \circ G_{\text{B:B:A:A}}^{\text{fcc:ord}(4\text{SL})} \end{aligned} \quad (33)$$

where the same relations may be used for the equivalent compounds  $\circ G_{\text{L1}_2\text{-AB}_3}^{\text{fcc:ord}(4\text{SL})}$  and  $\circ G_{\text{A1-B}_4}^{\text{fcc:ord}(4\text{SL})}$ .

The parameter  $L_{i,j:k:l:m}^{\text{fcc:ord}(4\text{SL})}$  in equation 30 describes the interaction of species  $i$  and  $j$  on sublattice  $s$ , which sublattice  $r$  is occupied with species  $k$ , sublattice  $t$  is occupied with species  $l$ , and sublattice  $u$  is occupied by species  $m$ . This term represents the second nearest neighbour interactions which, as discussed in Section 2.1, are between equivalent sites on the tetrahedron. These terms are not assigned values in this model, as the short range ordering can be described in a first approximation by the reciprocal interaction parameters only [2], with further interactions accounted for by the interaction parameters for the disordered part,  $L_{i,j}^{\text{fcc:dis}}$  [1]. Therefore, it is assumed that all interaction parameters with interaction on a single site are equivalent and equal to zero:

$$L_{i,j:k:l:m}^{\text{fcc:ord}(4\text{SL})} = 0 \quad (34)$$

The parameter  $L_{i,j:k,l:m:n}^{\text{fcc:ord}(4\text{SL})}$  in equation 30 describes the simultaneous interaction of species  $i$  and  $j$  on sublattice  $s$  and species  $k$  and  $l$  on sublattice  $r$ , while sublattice  $t$  is occupied by species  $m$ , and sublattice  $u$  is occupied by species  $n$ . This term represents random mixing among first nearest neighbour atoms, and, from the BWG model in Section 2.1, can be obtained from the  $\circ G_{i,j:k,l}^{\text{fcc:ord}(4\text{SL})}$ . Following Kusoffsky *et al.* [1], it is also assumed that all interaction parameters with simultaneous

interactions on two sites are equivalent and independent of the occupation of the other two sites, e.g.

$$L_{i,j:k,l:m:n}^{\text{fcc:ord(4SL)}} = L_{A,B:A,B:*:*}^{\text{fcc:ord(4SL)}} \quad (35)$$

where \* represents any possible constituent.

Applying these assumptions and symmetry relations,  $G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)})$  may be simplified by gathering terms relating to end-member parameters  ${}^\circ G_{A1-A_4}^{\text{fcc:ord(4SL)}}$ ,  ${}^\circ G_{L1_2-A_3B}^{\text{fcc:ord(4SL)}}$ ,  ${}^\circ G_{L1_0-A_2B_2}^{\text{fcc:ord(4SL)}}$ ,  ${}^\circ G_{L1_2-AB_3}^{\text{fcc:ord(4SL)}}$ , and  ${}^\circ G_{A1-B_4}^{\text{fcc:ord(4SL)}}$ :

$$\begin{aligned} {}^\circ G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)}) &= y_A^{(1)} y_A^{(2)} y_A^{(3)} y_A^{(4)} {}^\circ G_{A1-A_4}^{\text{fcc:ord(4SL)}} \\ &+ \left( y_A^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(4)} + y_A^{(1)} y_A^{(2)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(2)} y_A^{(3)} y_A^{(4)} \right. \\ &\quad \left. + y_B^{(1)} y_A^{(2)} y_A^{(3)} y_A^{(4)} \right) {}^\circ G_{L1_2-A_3B}^{\text{fcc:ord(4SL)}} \\ &+ \left( y_A^{(1)} y_A^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_B^{(2)} y_A^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(3)} y_A^{(4)} \right. \\ &\quad \left. + y_A^{(1)} y_B^{(2)} y_B^{(3)} y_A^{(4)} + y_B^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(4)} \right) {}^\circ G_{L1_0-A_2B_2}^{\text{fcc:ord(4SL)}} \\ &+ \left( y_A^{(1)} y_B^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(4)} \right. \\ &\quad \left. + y_B^{(1)} y_B^{(2)} y_B^{(3)} y_A^{(4)} \right) {}^\circ G_{L1_2-AB_3}^{\text{fcc:ord(4SL)}} \\ &+ y_B^{(1)} y_B^{(2)} y_B^{(3)} y_B^{(4)} {}^\circ G_{A1-B_4}^{\text{fcc:ord(4SL)}} \\ &+ \frac{1}{4} RT \sum_s \sum_i y_i^{(s)} \ln y_i^{(s)} \\ &+ \sum_i \sum_{j>i} \sum_{k \geq i} \sum_{l>k} \sum_m \sum_n y_i^{(s)} y_j^{(s)} y_k^{(r)} y_l^{(r)} y_m^{(t)} y_n^{(u)} L_{A,B:A,B:*:*}^{\text{fcc:ord(4SL)}} \end{aligned} \quad (36)$$

In the disordered case, where the site occupation is equal to the overall composition,  $y_i = x_i$ , this may be written as

$$\begin{aligned} {}^\circ G_m^{\text{fcc:ord(4SL)}}(y_i^{(s)} = x_i) &= x_A^4 {}^\circ G_{A1-A_4}^{\text{fcc:ord(4SL)}} + 4x_A^3 x_B {}^\circ G_{L1_2-A_3B}^{\text{fcc:ord(4SL)}} + 6x_A^2 x_B^2 {}^\circ G_{L1_0-A_2B_2}^{\text{fcc:ord(4SL)}} \\ &+ 4x_A x_B^3 {}^\circ G_{L1_2-AB_3}^{\text{fcc:ord(4SL)}} + x_B^4 {}^\circ G_{A1-B_4}^{\text{fcc:ord(4SL)}} + RT (x_A \ln x_A + x_B \ln x_B) \\ &+ (6x_A^4 x_B^2 + 12x_A^3 x_B^3 + 6x_A^2 x_B^4) L_{A,B:A,B:*:*}^{\text{fcc:ord(4SL)}} \end{aligned} \quad (37)$$

In Thermo-Calc [10] thermodynamic database (tdb) syntax for the disordered fcc phase, the end-member energies of the disordered phase with sublattice model (A,B) are given by

$$\begin{aligned} \text{PARAMETER G(DIS-FCC,A;0)} &= {}^\circ G_A^{\text{fcc:A1}} + \text{GHSERA} = {}^\circ G_{A1-A_4}^{\text{fcc:ord(4SL)}} + \text{GHSERA} \\ \text{PARAMETER G(DIS-FCC,B;0)} &= {}^\circ G_B^{\text{fcc:A1}} + \text{GHSERB} = {}^\circ G_{A1-B_4}^{\text{fcc:ord(4SL)}} + \text{GHSERB} \end{aligned}$$

where the reference phases **GHSERA** and **GHSERB** are the fcc phase in the Al-Ni case. Therefore  ${}^\circ G_{A1-A_4}^{\text{fcc:ord(4SL)}}$  and  ${}^\circ G_{A1-B_4}^{\text{fcc:ord(4SL)}}$  are necessarily 0, as required for the description of the ordering

contribution to the Gibbs energy. In the case that the SER reference states are not the same phase as the disordered phase being described for instance,  $\text{PARAMETER G(DIS-BCC, A; 0)} = \circ G_{A2-A4}^{\text{fcc:ord}(4\text{SL})} + \Delta G(\text{bcc-fcc}) + \text{GHSERA}$ . This case will be covered further in Section 3.2.

In the fcc four substitutional sublattice order-disorder model, a Gibbs energy contribution due to ordering is added to the disordered phase. The  $\circ G_{A1-A4}^{\text{fcc:ord}(4\text{SL})}$ ,  $\circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})}$ , etc, are the parameters of the four-sublattice description, and represent the contribution due to ordering of a fully ordered phase in the particular sublattice configuration, which is distinct from both the energy of the ordered phase  $\circ G_m^{\text{fcc:ord}(4\text{SL})}(y_i^{(s)})$  at a particular fractional site occupancy, and the energy of the disordered phase,  $G_m^{\text{fcc:dis}}(x_i)$  at a given overall composition.

The tdb syntax is therefore

$$\begin{aligned} \text{PARAMETER G(FCC-4SL, A:A:A:A; 0)} &= \circ G_{A1-A4}^{\text{fcc:ord}(4\text{SL})} \\ \text{PARAMETER G(FCC-4SL, A:A:A:B; 0)} &= \circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} \\ \text{PARAMETER G(FCC-4SL, A:A:B:B; 0)} &= \circ G_{L1_0-A_2B_2}^{\text{fcc:ord}(4\text{SL})} \\ \text{PARAMETER G(FCC-4SL, A:B:B:B; 0)} &= \circ G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} \\ \text{PARAMETER G(FCC-4SL, B:B:B:B; 0)} &= \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \end{aligned}$$

As these are contributions due to ordering, and not end-member energies, no further reference terms are needed as they are already implicitly included.  $\circ G_{A1-A4}^{\text{fcc:ord}(4\text{SL})}$  and  $\circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})}$  are necessarily 0, representing the difference between the pure A or pure B in the fully ordered or disordered states, which are equivalent.

Within this formalism it is possible to separately describe the ordered and disordered phases with various end-member energies and interaction parameters. In such cases as this study, where the required Gibbs energy functions are available from first-principles for both the ordered and disordered phases, one must be careful to correctly include such energies in the database.

From equation 28, the total energy of the fully ordered phases  $G_m^{\text{fcc}}(y_i^{(s)})$  at the  $x_A$  values and sublattice configurations being considered (end members of the four-sublattice model where each sublattice is fully occupied by a single species) is therefore

$$\begin{bmatrix} G_m^{\text{fcc}}(y_A^{(s)} := A1; x_A = 1) \\ G_m^{\text{fcc}}(y_A^{(s)} := L1_2; x_A = \frac{3}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := L1_0; x_A = \frac{1}{2}) \\ G_m^{\text{fcc}}(y_A^{(s)} := L1_2; x_A = \frac{1}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := A1; x_A = 0) \end{bmatrix} = \begin{bmatrix} G_m^{\text{fcc:dis}}(x_A = 1) \\ G_m^{\text{fcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{fcc:dis}}(x_A = 0) \end{bmatrix} + \begin{bmatrix} G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := A1; x_A = 1) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_2; x_A = \frac{3}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_0; x_A = \frac{1}{2}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_2; x_A = \frac{1}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := A1; x_A = 0) \end{bmatrix} - \begin{bmatrix} G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 1) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{3}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{2}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 0) \end{bmatrix} \quad (38)$$

where the notation  $(y_A^{(s)} := L1_2; x_A = \frac{3}{4})$  indicates that the sublattice population fulfils the condition of the  $L1_2$  phase as given in Table 1, while the overall composition is  $x_A = \frac{3}{4}$ . Each of the terms in equation 38 may be written as

$$\begin{bmatrix} G_m^{\text{fcc:dis}}(x_A = 1) \\ G_m^{\text{fcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{fcc:dis}}(x_A = 0) \end{bmatrix} = \begin{bmatrix} \frac{3}{4} \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + \frac{1}{4} \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} + RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) + \left( \frac{3}{4} \right) \left( \frac{1}{4} \right) \sum_{\nu} \left( \frac{3}{4} - \frac{1}{4} \right)^{\nu} \cdot \nu L_{A,B}^{\text{fcc:dis}} \\ \frac{1}{2} \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + \frac{1}{2} \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} + RT \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ \frac{1}{4} \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + \frac{3}{4} \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} + RT \left( \frac{1}{4} \ln \frac{1}{4} + \frac{3}{4} \ln \frac{1}{4} \right) + \left( \frac{1}{4} \right) \left( \frac{3}{4} \right) \sum_{\nu} \left( \frac{1}{4} - \frac{3}{4} \right)^{\nu} \cdot \nu L_{A,B}^{\text{fcc:dis}} \\ \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \end{bmatrix} \quad (39)$$

$$\begin{bmatrix} G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := A1; x_A = 1) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_2; x_A = \frac{3}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_0; x_A = \frac{1}{2}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := L1_2; x_A = \frac{1}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} := A1; x_A = 0) \end{bmatrix} = \begin{bmatrix} \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{L1_0-A_2B_3}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \end{bmatrix} \quad (40)$$

and

$$\begin{bmatrix} G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 1) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{3}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{2}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{4}) \\ G_m^{\text{fcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 0) \end{bmatrix} = \begin{bmatrix} \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} \\ \left( \frac{3}{4} \right)^4 \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + 4 \left( \frac{3}{4} \right)^3 \left( \frac{1}{4} \right) \circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} + 6 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^2 \circ G_{L1_0-A_2B_2}^{\text{fcc:ord}(4\text{SL})} \\ + 4 \left( \frac{3}{4} \right) \left( \frac{1}{4} \right)^3 \circ G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} + \left( \frac{1}{4} \right)^4 \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \\ + RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \\ + \left[ 6 \left( \frac{3}{4} \right)^4 \left( \frac{1}{4} \right)^2 + 12 \left( \frac{3}{4} \right)^3 \left( \frac{1}{4} \right)^3 + 6 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^4 \right] L_{A,B:A,B:*}^{\text{fcc:ord}(4\text{SL})} \\ \left( \frac{1}{2} \right)^4 \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + 4 \left( \frac{1}{2} \right)^4 \circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} + 6 \left( \frac{1}{2} \right)^4 \circ G_{L1_0-A_2B_2}^{\text{fcc:ord}(4\text{SL})} \\ + 4 \left( \frac{1}{2} \right)^4 \circ G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} + \left( \frac{1}{2} \right)^4 \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \\ + RT \left( \ln \frac{1}{2} \right) \\ + 24 \left( \frac{1}{2} \right)^6 L_{A,B:A,B:*}^{\text{fcc:ord}(4\text{SL})} \\ \left( \frac{1}{4} \right)^4 \circ G_{A1-A_4}^{\text{fcc:ord}(4\text{SL})} + 4 \left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right) \circ G_{L1_2-A_3B}^{\text{fcc:ord}(4\text{SL})} + 6 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^2 \circ G_{L1_0-A_2B_2}^{\text{fcc:ord}(4\text{SL})} \\ + 4 \left( \frac{1}{4} \right) \left( \frac{3}{4} \right)^3 \circ G_{L1_2-AB_3}^{\text{fcc:ord}(4\text{SL})} + \left( \frac{3}{4} \right)^4 \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \\ + RT \left( \frac{1}{4} \ln \frac{1}{4} + \frac{3}{4} \ln \frac{3}{4} \right) \\ + \left[ 6 \left( \frac{1}{4} \right)^4 \left( \frac{3}{4} \right)^2 + 12 \left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right)^3 + 6 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^4 \right] L_{A,B:A,B:*}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{A1-B_4}^{\text{fcc:ord}(4\text{SL})} \end{bmatrix} \quad (41)$$

with  $L_{A,B:A,B:*}^{\text{fcc:ord}(4\text{SL})}$  also being a function of the Gibbs energies via a reciprocal interaction parameter framework from the Bragg-Williams-Gorsky model described in Section 2.1. This gives a temperature-dependent interaction parameter, which along with the disordered interaction parameters, introduces the temperature-dependence of the short range ordering of the fcc phase. The configurational entropy terms cancel, leaving only terms that are functions of the  $\circ G_{i;j:k:l}^{\text{fcc:ord}(4\text{SL})}$  parameters, therefore this can be expressed as

$$\begin{bmatrix} G_m^{\text{fcc}}(y_A^{(s)} := \text{A1}; x_A = 1) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_2; x_A = \frac{3}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_0; x_A = \frac{1}{2}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_2; x_A = \frac{1}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{A1}; x_A = 0) \end{bmatrix} - \begin{bmatrix} G_m^{\text{fcc:dis}}(x_A = 1) \\ G_m^{\text{fcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{fcc:dis}}(x_A = 0) \end{bmatrix} = \underline{\underline{\mathbf{M}^{\text{fcc}}}} \begin{bmatrix} \circ G_{\text{A1-A}_4}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_2\text{-A}_3\text{B}}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_0\text{-A}_2\text{B}_2}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_2\text{-AB}_3}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{A1-B}_4}^{\text{fcc:ord}(4\text{SL})} \end{bmatrix} \quad (42)$$

where  $\underline{\underline{\mathbf{M}^{\text{fcc}}}}$  represents the matrix connecting the total energies of the ordered end-member phases and the total energies of the disordered phase at various compositions (which may be calculated from first-principles) to the parameters in the four-sublattice order-disorder model.

Therefore, if the total energies of the ordered and disordered phase are known from first-principles or assessment, the parameters for the model may be obtained by inverting matrix  $\underline{\underline{\mathbf{M}^{\text{fcc}}}}$  as

$$\begin{bmatrix} \circ G_{\text{A1-A}_4}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_2\text{-A}_3\text{B}}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_0\text{-A}_2\text{B}_2}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{L1}_2\text{-AB}_3}^{\text{fcc:ord}(4\text{SL})} \\ \circ G_{\text{A1-B}_4}^{\text{fcc:ord}(4\text{SL})} \end{bmatrix} = (\underline{\underline{\mathbf{M}^{\text{fcc}}}})^{-1} \left( \begin{bmatrix} G_m^{\text{fcc}}(y_A^{(s)} := \text{A1}; x_A = 1) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_2; x_A = \frac{3}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_0; x_A = \frac{1}{2}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{L1}_2; x_A = \frac{1}{4}) \\ G_m^{\text{fcc}}(y_A^{(s)} := \text{A1}; x_A = 0) \end{bmatrix} - \begin{bmatrix} G_m^{\text{fcc:dis}}(x_A = 1) \\ G_m^{\text{fcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{fcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{fcc:dis}}(x_A = 0) \end{bmatrix} \right) \quad (43)$$

In the case derived from the Bragg-Williams-Gorsky model described in Section 2.1 where

$$L_{\text{A,B:A,B:**}}^{\text{fcc:ord}(4\text{SL})} = \frac{1}{4} \circ G_{\text{L1}_0\text{-A}_2\text{B}_2}^{\text{fcc:ord}(4\text{SL})} \quad (44)$$

and

$$L_{\text{A,B:**}}^{\text{fcc:ord}(4\text{SL})} = 0 \quad (45)$$

the matrix  $\underline{\underline{\mathbf{M}^{\text{fcc}}}}$  is

$$\underline{\underline{\mathbf{M}^{\text{fcc}}}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ -\left(\frac{3}{4}\right)^4 & 1 - 4\left(\frac{3}{4}\right)^3\left(\frac{1}{4}\right) & -6\left(\frac{3}{4}\right)^2\left(\frac{1}{4}\right)^2 - \frac{1}{4}\left[6\left(\frac{3}{4}\right)^4\left(\frac{1}{4}\right)^2 + 12\left(\frac{3}{4}\right)^3\left(\frac{1}{4}\right)^3 + 6\left(\frac{3}{4}\right)^2\left(\frac{1}{4}\right)^4\right] & -4\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)^3 & -\left(\frac{1}{4}\right)^4 \\ -\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & 1 - 6\left(\frac{1}{2}\right)^4 - 24\frac{1}{4}\left(\frac{1}{2}\right)^6 & -4\left(\frac{1}{2}\right)^4 & -\left(\frac{1}{2}\right)^4 \\ -\left(\frac{1}{4}\right)^4 & -4\left(\frac{1}{4}\right)^3\left(\frac{3}{4}\right) & -6\left(\frac{1}{4}\right)^2\left(\frac{3}{4}\right)^2 - \frac{1}{4}\left[6\left(\frac{1}{4}\right)^4\left(\frac{3}{4}\right)^2 + 12\left(\frac{1}{4}\right)^3\left(\frac{3}{4}\right)^3 + 6\left(\frac{1}{4}\right)^2\left(\frac{3}{4}\right)^4\right] & 1 - 4\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)^3 & -\left(\frac{3}{4}\right)^4 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (46)$$

### 3.2 Body-centred cubic phases

The above inverted matrix method of assigning parameters describing both the ordered and disordered phases directly from first-principles calculations is applied to the bcc four substitutional sublattice order-disorder model as derived by Abe and Shimono [8] in a similar way to the fcc phase described in Section 3.1.

The disordered bcc phase is described using a single sublattice model (Al,Ni) with disordered bcc pure Al and Ni end-members, which have an A2-type structure. The Gibbs energy of the

disordered phase may therefore be written as a substitutional solution model in terms of the Gibbs energy of these end-members,  ${}^\circ G_i^{\text{bcc-A2}}$ , where  $i$  may be either Al or Ni.

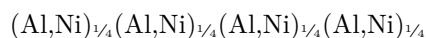
$$G_m^{\text{bcc:dis}}(x_i) = \sum_i x_i {}^\circ G_i^{\text{bcc:A2}} + RT \sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j L_{i,j}^{\text{bcc:dis}} \quad (47)$$

where the binary interaction parameters  $L_{i,j}^{\text{fcc:dis}}$  are expanded as a Redlich-Kister polynomial as

$$L_{i,j}^{\text{bcc:dis}} = \sum_\nu (x_i - x_j)^\nu \cdot {}^\nu L_{i,j}^{\text{bcc:dis}} \quad (48)$$

where  $\nu$  indicates the order of the Redlich-Kister polynomial and  ${}^\nu L_{i,j}^{\text{bcc:dis}}$  is a polynomial in temperature.

A four-sublattice model is used to describe the four sublattices of the bcc structure,



where there are two sets of two equivalent sites as described in Section 2.2, providing six end-members that are different bcc ordered structures.

The order-disorder partitioning model that was applied to the fcc phases in Section 3.1 is used again for the bcc case.

The molar ordering energy  $\Delta G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)})$  relates the molar Gibbs energy of a given sublattice configuration,  $G_m^{\text{bcc}}(y_i^{(s)})$ , and the molar Gibbs energy of the disordered phase at the same overall composition,  $G_m^{\text{bcc:dis}}(x_i)$ ,

$$G_m^{\text{bcc}}(y_i^{(s)}) = G_m^{\text{bcc:dis}}(x_i) + \Delta G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)}) \quad (49)$$

where the molar ordering energy can be expanded as

$$\Delta G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)}) = G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)}) - G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)} = x_i) \quad (50)$$

These are combined as

$$G_m^{\text{bcc}}(y_i^{(s)}) = G_m^{\text{bcc:dis}}(x_i) + G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)}) - G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)} = x_i) \quad (51)$$

When the phase is disordered, the molar ordering energy,  $\Delta G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)})$ , or the contribution to the Gibbs energy due to ordering, is zero.

The Gibbs energy due to ordering at a given sublattice configuration can be written with a regular solution model within the four-sublattice model for the bcc phase as

$$\begin{aligned} G_m^{\text{bcc:ord(4SL)}}(y_i^{(s)}) &= \sum_i \sum_j \sum_j \sum_l y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} {}^\circ G_{i:j:k:l}^{\text{bcc:ord(4SL)}} + \frac{1}{4} RT \sum_s \sum_i y_i^{(s)} \ln y_i^{(s)} \\ &+ \sum_i \sum_{j>i} \sum_{k \geq i} \sum_{l>k} \sum_m \sum_n y_i^{(s)} y_j^{(s)} y_k^{(r)} y_l^{(r)} y_m^{(t)} y_n^{(u)} L_{i,j:k,l:m:n}^{\text{bcc:ord(4SL),0}} \\ &+ \sum_i \sum_{j>i} \sum_k \sum_l \sum_m y_i^{(s)} y_j^{(s)} y_k^{(r)} y_l^{(t)} y_m^{(u)} L_{i,j:k:l:m}^{\text{bcc:ord(4SL),0}} \end{aligned} \quad (52)$$

where the the Gibbs formation energies indicated with a  ${}^\circ$  are given relative to the pure elements in the bcc-A2 state.



The type of interaction parameter may be given by the symmetry of the bcc lattice with the conditions

$$s = \{1, 2\}, r = \{3, 4\} \text{ or } s = \{3, 4\}, r = \{1, 2\} \rightarrow 1\text{nn}$$

$$s = \{1, 2\}, r = \{1, 2\} \text{ or } s = \{3, 4\}, r = \{3, 4\} \rightarrow 2\text{nn}$$

By crystallographic symmetry of the sublattices, the contribution to the Gibbs energy due to ordering from the various permutations of the end-member occupations can be expressed as

$${}^{\circ}G_{\text{A:A:A:A}}^{\text{bcc:ord}(4\text{SL})} = G_{\text{A}_2\text{-A}_4}^{\text{bcc-4sl}} \quad (53)$$

$$\begin{aligned} {}^{\circ}G_{\text{A:A:B:B}}^{\text{bcc:ord}(4\text{SL})} &= {}^{\circ}G_{\text{B:B:A:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{B}_2\text{-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} \end{aligned} \quad (54)$$

$$\begin{aligned} {}^{\circ}G_{\text{A:B:A:B}}^{\text{bcc:ord}(4\text{SL})} &= {}^{\circ}G_{\text{A:B:B:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{B:A:A:B}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{B:A:B:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{B}_3\text{2-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} \end{aligned} \quad (55)$$

$$\begin{aligned} {}^{\circ}G_{\text{A:A:A:B}}^{\text{bcc:ord}(4\text{SL})} &= {}^{\circ}G_{\text{A:A:B:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{A:B:A:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{B:A:A:A}}^{\text{bcc:ord}(4\text{SL})} \\ &= {}^{\circ}G_{\text{D0}_3\text{-A}_3\text{B}}^{\text{bcc:ord}(4\text{SL})} \end{aligned} \quad (56)$$

where A and B may be either Al or Ni.

It is assumed that the interaction parameters  $L_{i,j:k:l,m:n}^{\text{bcc:ord}(4\text{SL})}$  and  $L_{i,j:k,l:m:n}^{\text{bcc:ord}(4\text{SL})}$  are independent of the occupation of the remaining sites, and may be obtained from the BWG model in Section 2.2.

It is assumed that the interaction parameters of 1nn and 2nn type with simultaneous interactions on two sites obey the symmetry relations in Section 2.2 and are independent of the occupation of the other two sites, e.g.

$$L_{i,j:k:l,m:n}^{\text{bcc:ord}(4\text{SL})} = L_{\text{A,B:}*:\text{A,B:}*}^{\text{bcc:ord}(4\text{SL})} \quad (57)$$

$$L_{i,j:k,l:m:n}^{\text{bcc:ord}(4\text{SL})} = L_{\text{A,B:A,B:}*:*}^{\text{bcc:ord}(4\text{SL})} \quad (58)$$

where \* represents any possible constituent.

Applying these assumptions and symmetry relations,  $G_m^{\text{bcc:ord}(4\text{SL})}(y_i^{(s)})$  may be simplified by gathering terms relating to end-member parameters  ${}^{\circ}G_{\text{A}_2\text{-A}_4}^{\text{bcc:ord}(4\text{SL})}$ ,  ${}^{\circ}G_{\text{D0}_3\text{-A}_3\text{B}}^{\text{bcc:ord}(4\text{SL})}$ ,  ${}^{\circ}G_{\text{B}_2\text{-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})}$ ,  ${}^{\circ}G_{\text{B}_3\text{2-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})}$ ,  ${}^{\circ}G_{\text{D0}_3\text{-AB}_3}^{\text{bcc:ord}(4\text{SL})}$ , and  ${}^{\circ}G_{\text{A}_2\text{-B}_4}^{\text{bcc:ord}(4\text{SL})}$ .

$$\begin{aligned}
\circ G_m^{\text{bcc:ord}(4\text{SL})}(y_i^{(s)}) &= y_A^{(1)} y_A^{(2)} y_A^{(3)} y_A^{(4)} \circ G_{A_2-A_4}^{\text{bcc:ord}(4\text{SL})} \\
&+ \left( y_A^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(4)} + y_A^{(1)} y_A^{(2)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(2)} y_A^{(3)} y_A^{(4)} \right. \\
&\quad \left. + y_B^{(1)} y_A^{(2)} y_A^{(3)} y_A^{(4)} \right) \circ G_{D_{0_3-A_3}B}^{\text{bcc:ord}(4\text{SL})} \\
&+ \left( y_A^{(1)} y_A^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_B^{(2)} y_A^{(3)} y_A^{(4)} \right) \circ G_{B_2-A_2B_2}^{\text{bcc:ord}(4\text{SL})} \\
&+ \left( +y_A^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(2)} y_B^{(3)} y_A^{(4)} \right. \\
&\quad \left. + y_B^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(4)} \right) \circ G_{B_{32-A_2}B_2}^{\text{bcc:ord}(4\text{SL})} \\
&+ \left( y_A^{(1)} y_B^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(4)} \right. \\
&\quad \left. + y_B^{(1)} y_B^{(2)} y_B^{(3)} y_A^{(4)} \right) \circ G_{D_{0_3-AB_3}}^{\text{bcc:ord}(4\text{SL})} \\
&+ y_B^{(1)} y_B^{(2)} y_B^{(3)} y_B^{(4)} \circ G_{A_2-B_4}^{\text{bcc:ord}(4\text{SL})} \\
&+ \frac{1}{4} RT \sum_s \sum_i y_i^{(s)} \ln y_i^{(s)} \\
&+ \left( \left[ y_A^{(1)} y_B^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(3)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} \right. \right. \\
&\quad \left. \left. + y_A^{(1)} y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_B^{(4)} \right] + \left[ y_A^{(1)} y_B^{(1)} y_A^{(2)} y_A^{(3)} y_A^{(4)} y_B^{(4)} + y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(3)} y_A^{(4)} y_B^{(4)} \right. \right. \\
&\quad \left. \left. + y_A^{(1)} y_B^{(1)} y_B^{(2)} y_A^{(3)} y_A^{(4)} y_B^{(4)} + y_A^{(1)} y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(4)} y_B^{(4)} \right] + \left[ y_A^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} \right. \right. \\
&\quad \left. \left. + y_A^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_B^{(4)} \right] \right. \\
&\quad \left. + \left[ y_A^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_A^{(4)} y_B^{(4)} + y_A^{(1)} y_A^{(2)} y_B^{(2)} y_B^{(3)} y_A^{(4)} y_B^{(4)} + y_B^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_A^{(4)} y_B^{(4)} \right. \right. \\
&\quad \left. \left. + y_B^{(1)} y_A^{(2)} y_B^{(2)} y_B^{(3)} y_A^{(4)} y_B^{(4)} \right] \right) \cdot L_{A,B:*:A,B:*}^{\text{bcc:ord}(4\text{SL})} \\
&+ \left( \left[ y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(2)} y_A^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(2)} y_B^{(3)} y_A^{(4)} + y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(2)} y_B^{(3)} y_B^{(4)} \right. \right. \\
&\quad \left. \left. + y_A^{(1)} y_B^{(1)} y_A^{(2)} y_B^{(2)} y_B^{(3)} y_B^{(4)} \right] + \left[ y_A^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} y_B^{(4)} + y_A^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} y_B^{(4)} \right. \right. \\
&\quad \left. \left. + y_B^{(1)} y_A^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} y_B^{(4)} + y_B^{(1)} y_B^{(2)} y_A^{(3)} y_B^{(3)} y_A^{(4)} y_B^{(4)} \right] \right) \cdot L_{A,B:*:A,B:*}^{\text{bcc:ord}(4\text{SL})} \\
\end{aligned} \tag{59}$$

In the disordered case, where the site occupation is equal to the overall composition,  $y_i = x_i$ , this may be written as

$$\begin{aligned}
\circ G_m^{\text{bcc:ord}(4\text{SL})}(y_i^{(s)} = x_i) &= x_A^4 \circ G_{A_2-A_4}^{\text{bcc:ord}(4\text{SL})} + 4x_A^3 x_B \circ G_{D_{0_3-A_3}B}^{\text{bcc:ord}(4\text{SL})} + 2x_A^2 x_B^2 \circ G_{B_2-A_2B_2}^{\text{bcc:ord}(4\text{SL})} \\
&+ 4x_A^2 x_B^2 \circ G_{B_{32-A_2}B_2}^{\text{bcc:ord}(4\text{SL})} + 4x_A x_B^3 \circ G_{D_{0_3-AB_3}}^{\text{bcc:ord}(4\text{SL})} + x_B^4 \circ G_{A_2-B_4}^{\text{bcc:ord}(4\text{SL})} \\
&+ RT (x_A \ln x_A + x_B \ln x_B) + (4x_A^4 x_B^2 + 8x_A^3 x_B^3 + 4x_A^2 y_B^4) L_{A,B:*:A,B:*}^{\text{bcc:ord}(4\text{SL})} \\
&+ (2x_A^4 x_B^2 + 4x_A^3 x_B^3 + 2x_A^2 y_B^4) L_{A,B:A,B:*:*}^{\text{bcc:ord}(4\text{SL})} \\
\end{aligned} \tag{60}$$

In Thermo-Calc tdb syntax for the disordered bcc phase, the end-member energies of the disordered phase with sublattice model (A,B) are given by

$$\begin{aligned} \text{PARAMETER } G(\text{DIS-BCC}, \text{A}; 0) &= {}^\circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} + {}^\circ G_{\text{A}}^{\text{bcc:A2}} + \text{GHSERA} = {}^\circ G_{\text{A}}^{\text{bcc:A2}} + \text{GHSERA} \\ \text{PARAMETER } G(\text{DIS-BCC}, \text{B}; 0) &= {}^\circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} + {}^\circ G_{\text{B}}^{\text{bcc:A2}} + \text{GHSERB} = {}^\circ G_{\text{B}}^{\text{bcc:A2}} + \text{GHSERA} \end{aligned}$$

where the reference phases **GHSERA** and **GHSERB** are the fcc phase in the Al-Ni case. As  ${}^\circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})}$  and  ${}^\circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})}$  are zero, as required for the description of the ordering contribution to the Gibbs energy, the Gibbs energy of each element relative to the fcc phases,  ${}^\circ G_{\text{A}}^{\text{bcc:A2}} = \Delta G_{\text{A}}(\text{bcc-fcc})$  and  ${}^\circ G_{\text{B}}^{\text{bcc:A2}} = \Delta G_{\text{B}}(\text{bcc-fcc})$ , must be included.

The  ${}^\circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})}$ ,  ${}^\circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})}$ , etc, are the parameters of the four-sublattice description, and represent the contribution due to ordering of a fully ordered phase in the particular sublattice configuration.

This is included in the tdb as

$$\begin{aligned} \text{PARAMETER } G(\text{BCC-4SL}, \text{A:A:A:A}; 0) &= {}^\circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} \\ \text{PARAMETER } G(\text{BCC-4SL}, \text{A:A:A:B}; 0) &= {}^\circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} \\ \text{PARAMETER } G(\text{BCC-4SL}, \text{A:A:B:B}; 0) &= {}^\circ G_{\text{B2-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ \text{PARAMETER } G(\text{BCC-4SL}, \text{A:B:A:B}; 0) &= {}^\circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ \text{PARAMETER } G(\text{BCC-4SL}, \text{A:B:B:B}; 0) &= {}^\circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ \text{PARAMETER } G(\text{BCC-4SL}, \text{B:B:B:B}; 0) &= {}^\circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \end{aligned}$$

The functions for the ordered and disordered phases must be carefully considered if both are to be described exactly using first-principles calculations. If the interaction parameters of the disordered phase are not obtained directly from first-principles, they can be extracted using the approximations derived by Abe and Shimono [8].

The total energies of the ordered phases  $G_m^{\text{bcc}}(y_i^{(s)})$  at the composition and sublattice occupations represented by the end-members of the four-sublattice model are

$$\begin{bmatrix} G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{A2}; x_{\text{A}} = 1) \\ G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{D03}; x_{\text{A}} = \frac{3}{4}) \\ G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{B2}; x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{B32}; x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{D03}; x_{\text{A}} = \frac{1}{4}) \\ G_m^{\text{bcc}}(y_{\text{A}}^{(s)} := \text{A2}; x_{\text{A}} = 0) \end{bmatrix} = \begin{bmatrix} G_m^{\text{bcc:dis}}(x_{\text{A}} = 1) \\ G_m^{\text{bcc:dis}}(x_{\text{A}} = \frac{3}{4}) \\ G_m^{\text{bcc:dis}}(x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_{\text{A}} = \frac{1}{4}) \\ G_m^{\text{bcc:dis}}(x_{\text{A}} = 0) \end{bmatrix} + \begin{bmatrix} G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{A2}; x_{\text{A}} = 1) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{D03}; x_{\text{A}} = \frac{3}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{B2}; x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{B32}; x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{D03}; x_{\text{A}} = \frac{1}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} := \text{A2}; x_{\text{A}} = 0) \end{bmatrix} - \begin{bmatrix} G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = 1) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = \frac{3}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = \frac{1}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_{\text{A}}^{(s)} = x_{\text{A}} = 0) \end{bmatrix} \quad (61)$$

where the notation  $(y_{\text{A}}^{(s)} := \text{D03}; x_{\text{A}} = \frac{3}{4})$  indicates that the sublattice population fulfils the condition of the D03 phase as given in Table 2, while the overall composition is  $x_{\text{A}} = \frac{3}{4}$ .

The energy of the disordered phase at each necessary composition is given by

$$\begin{aligned}
\begin{bmatrix} G_m^{\text{bcc:dis}}(x_A = 1) \\ G_m^{\text{bcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{bcc:dis}}(x_A = 0) \end{bmatrix} &= \begin{bmatrix} \circ G_{A_1-A_4}^{\text{bcc:ord}(4\text{SL})} + \frac{1}{4} \circ G_{A_1-B_4}^{\text{bcc:ord}(4\text{SL})} + RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) + \left( \frac{3}{4} \right) \left( \frac{1}{4} \right) \sum_{\nu} \left( \frac{3}{4} - \frac{1}{4} \right)^{\nu} \cdot \nu L_{A,B}^{\text{bcc:dis}} \\ \frac{1}{2} \circ G_{A_1-A_4}^{\text{bcc:ord}(4\text{SL})} + \frac{1}{2} \circ G_{A_1-B_4}^{\text{bcc:ord}(4\text{SL})} + RT \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ \frac{1}{2} \circ G_{A_1-A_4}^{\text{bcc:ord}(4\text{SL})} + \frac{1}{2} \circ G_{A_1-B_4}^{\text{bcc:ord}(4\text{SL})} + RT \left( \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) \\ \frac{1}{4} \circ G_{A_1-A_4}^{\text{bcc:ord}(4\text{SL})} + \frac{3}{4} \circ G_{A_1-B_4}^{\text{bcc:ord}(4\text{SL})} + RT \left( \frac{1}{4} \ln \frac{1}{4} + \frac{3}{4} \ln \frac{1}{4} \right) + \left( \frac{1}{4} \right) \left( \frac{3}{4} \right) \sum_{\nu} \left( \frac{1}{4} - \frac{3}{4} \right)^{\nu} \cdot \nu L_{A,B}^{\text{bcc:dis}} \\ \circ G_{A_1-B_4}^{\text{bcc:ord}(4\text{SL})} \end{bmatrix} \quad (62)
\end{aligned}$$

and the contribution due to ordering from each structure in the fully ordered case  $G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)}; x_A)$  defines the parameters of the four-sublattice model  $\circ G^{\text{bcc:ord}(4\text{SL})}$ .

$$\begin{aligned}
\begin{bmatrix} G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := A2; x_A = 1) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := D0_3; x_A = \frac{3}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := B2; x_A = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := B32; x_A = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := D0_3; x_A = \frac{1}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} := A2; x_A = 0) \end{bmatrix} &= \begin{bmatrix} \circ G_{A_2-A_4}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{D0_3-A_3B}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{B_2-A_2B_2}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{B32-A_2B_2}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{D0_3-AB_3}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{A_2-B_4}^{\text{bcc:ord}(4\text{SL})} \end{bmatrix} \quad (63)
\end{aligned}$$

and

$$\begin{aligned}
& \left[ \begin{array}{l} G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 1) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{3}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{2}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = \frac{1}{4}) \\ G_m^{\text{bcc:ord}(4\text{SL})}(y_A^{(s)} = x_A = 0) \end{array} \right] = \left[ \begin{array}{l} \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} \\ \left( \frac{3}{4} \right)^4 \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{3}{4} \right)^3 \left( \frac{1}{4} \right) \circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} + 2 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^2 \circ G_{\text{B2-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ + 4 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^2 \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{3}{4} \right) \left( \frac{1}{4} \right)^3 \circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ + \left( \frac{1}{4} \right)^4 \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \\ + RT \left( \frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \\ + \left[ 4 \left( \frac{3}{4} \right)^4 \left( \frac{1}{4} \right)^2 + 8 \left( \frac{3}{4} \right)^3 \left( \frac{1}{4} \right)^3 + 4 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^4 \right] L_{\text{A,B:}*:\text{A,B}:*}^{\text{bcc:ord}(4\text{SL})} \\ + \left[ 2 \left( \frac{3}{4} \right)^4 \left( \frac{1}{4} \right)^2 + 4 \left( \frac{3}{4} \right)^3 \left( \frac{1}{4} \right)^3 + 2 \left( \frac{3}{4} \right)^2 \left( \frac{1}{4} \right)^4 \right] L_{\text{A,B:A,B}:**}^{\text{bcc:ord}(4\text{SL})} \\ \left( \frac{1}{2} \right)^4 \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} + 2 \left( \frac{1}{2} \right)^4 \circ G_{\text{B2-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ + \left( \frac{1}{2} \right)^4 \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \\ + RT \left( \ln \frac{1}{2} \right) \\ + 16 \left( \frac{1}{2} \right)^6 L_{\text{A,B:}*:\text{A,B}:*}^{\text{bcc:ord}(4\text{SL})} \\ + 8 \left( \frac{1}{2} \right)^6 L_{\text{A,B:A,B}:**}^{\text{bcc:ord}(4\text{SL})} \\ \left( \frac{1}{2} \right)^4 \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} + 2 \left( \frac{1}{2} \right)^4 \circ G_{\text{B2-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{2} \right)^4 \circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ + \left( \frac{1}{2} \right)^4 \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \\ + RT \left( \ln \frac{1}{2} \right) \\ + 16 \left( \frac{1}{2} \right)^6 L_{\text{A,B:}*:\text{A,B}:*}^{\text{bcc:ord}(4\text{SL})} \\ + 8 \left( \frac{1}{2} \right)^6 L_{\text{A,B:A,B}:**}^{\text{bcc:ord}(4\text{SL})} \\ \left( \frac{1}{4} \right)^4 \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right) \circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} + 2 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^2 \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ + 4 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^2 \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} + 4 \left( \frac{1}{4} \right) \left( \frac{3}{4} \right)^3 \circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ + \left( \frac{3}{4} \right)^4 \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \\ + RT \left( \frac{1}{4} \ln \frac{1}{4} + \frac{3}{4} \ln \frac{3}{4} \right) \\ + \left[ 4 \left( \frac{1}{4} \right)^4 \left( \frac{3}{4} \right)^2 + 8 \left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right)^3 + 8 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^4 \right] L_{\text{A,B:}*:\text{A,B}:*}^{\text{bcc:ord}(4\text{SL})} \\ + \left[ 2 \left( \frac{1}{4} \right)^4 \left( \frac{3}{4} \right)^2 + 4 \left( \frac{1}{4} \right)^3 \left( \frac{3}{4} \right)^3 + 4 \left( \frac{1}{4} \right)^2 \left( \frac{3}{4} \right)^4 \right] L_{\text{A,B:A,B}:**}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \end{array} \right] \quad (64)
\end{aligned}$$

with  $L_{\text{A,B:}*:\text{A,B}:*}^{\text{bcc:ord}(4\text{SL})}$  and  $L_{\text{A,B:A,B}:**}^{\text{bcc:ord}(4\text{SL})}$  also being functions of the Gibbs energies via a reciprocal interaction parameter framework from the Bragg-Williams-Gorsky model in Section 2.2. The configurational entropy terms cancel, leaving only terms that are functions of the  $\circ G_{i;j:k:l}^{\text{bcc:ord}(4\text{SL})}$  parameters, therefore this can be expressed as

$$\begin{aligned}
& \left[ \begin{array}{l} G_m^{\text{bcc}}(y_A^{(s)} := \text{A2}; x_A = 1) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{D03}; x_A = \frac{3}{4}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{B2}; x_A = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{B32}; x_A = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{D03}; x_A = \frac{1}{4}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{A2}; x_A = 0) \end{array} \right] - \left[ \begin{array}{l} G_m^{\text{bcc:dis}}(x_A = 1) \\ G_m^{\text{bcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{bcc:dis}}(x_A = 0) \end{array} \right] = \underline{\underline{\mathbf{M}^{\text{bcc}}}} \left[ \begin{array}{l} \circ G_{\text{A2-A4}}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{D03-A3B}}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{B2-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{B32-A2B2}}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{D03-AB3}}^{\text{bcc:ord}(4\text{SL})} \\ \circ G_{\text{A2-B4}}^{\text{bcc:ord}(4\text{SL})} \end{array} \right] \quad (65)
\end{aligned}$$

where  $\underline{\underline{\mathbf{M}^{\text{bcc}}}}$  represents the matrix that may be obtained by rearranging above, connecting the total energies of the ordered end-member phases and disordered phases at various compositions (which may be calculated from first-principles) and the parameters in the four-sublattice order-disorder model, and is dependent on the interaction parameters of the four-sublattice model.

Therefore, if the total energies of the ordered and disordered phase are known from first-principles or assessment, the parameters for the model may be obtained by inverting matrix  $\underline{\underline{\mathbf{M}^{\text{bcc}}}}$  as

$$\begin{bmatrix} G_{\text{A2-A}_4}^{\text{bcc:ord}(4\text{SL})} \\ G_{\text{D0}_3\text{-A}_3\text{B}}^{\text{bcc:ord}(4\text{SL})} \\ G_{\text{B2-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} \\ G_{\text{B32-A}_2\text{B}_2}^{\text{bcc:ord}(4\text{SL})} \\ G_{\text{D0}_3\text{-AB}_3}^{\text{bcc:ord}(4\text{SL})} \\ G_{\text{A2-B}_4}^{\text{bcc:ord}(4\text{SL})} \end{bmatrix} = (\underline{\underline{\mathbf{M}^{\text{bcc}}}})^{-1} \left( \begin{bmatrix} G_m^{\text{bcc}}(y_A^{(s)} := \text{A2}; x_A = 1) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{D0}_3; x_A = \frac{3}{4}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{B2}; x_A = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{B32}; x_A = \frac{1}{2}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{D0}_3; x_A = \frac{1}{4}) \\ G_m^{\text{bcc}}(y_A^{(s)} := \text{A2}; x_A = 0) \end{bmatrix} - \begin{bmatrix} G_m^{\text{bcc:dis}}(x_A = 1) \\ G_m^{\text{bcc:dis}}(x_A = \frac{3}{4}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{2}) \\ G_m^{\text{bcc:dis}}(x_A = \frac{1}{4}) \\ G_m^{\text{bcc:dis}}(x_A = 0) \end{bmatrix} \right) \quad (66)$$

where the  $G_m^{\text{bcc}}$  represent the calculable molar Gibbs energy of the end-member ordered phases with particular composition and sublattice configuration,  $G_m^{\text{bcc:dis}}$  represent the molar energy of the disordered phase at a particular composition, and  $\underline{\underline{\mathbf{M}^{\text{bcc}}}}$  depends on the four-sublattice 1nn and 2nn interaction parameters of the ordering energies. The notation  $(y_A^{(s)} := \text{D0}_3; x_A = \frac{3}{4})$  indicates that the sublattice population fulfils the condition of the  $\text{D0}_3$  phase as given in Table 2, while the overall composition is  $x_A = \frac{3}{4}$ .

However, in separating the known ordering and disordered contributions to the Gibbs energy within the four substitutional sublattice order-disorder model, with the approximations for the first and second nearest neighbour interaction energies provided by Abe and Shimono [8] (equations (19) and (20)), it is not possible to exactly specify both the energy of the ordered phases and disordered phase because the four-sublattice interaction parameters cannot be expressed as linear combinations of the Gibbs energies. The approximation from Abe and Shimono is intended to describe the interaction parameters of the ordered phase when a symmetrical approximation for the disordered phase is used. However, in the order-disorder partitioning model, the interactions of the phases described by four sublattices have energy and interaction energy contributions from both the disordered part and the ordering energy part. Therefore the total reciprocal interaction energy (which may be considered an approximation to the energy contribution due to short range ordering [2]) has a finite value if the disordered phase is non-ideal, even if the ordering energy contribution to the reciprocal interaction parameters is zero. Lindahl *et al.* [9] found that it was effective to introduce interactions between the ordered phases implicitly by use of an asymmetric disordered phase description, where the interaction parameters of the ordering energy beyond the contributions from the disordered phase assume ideality. As the disordered phase is described from first-principles calculations in this work, it is assumed that the non-ideal interactions are described well by the contributions from the disordered phase at all temperatures, and no additional four-sublattice interaction parameters are needed, allowing the inverted matrix approach to be used. This assumption is similarly used to include the 2nn interactions in the fcc model demonstrated by Kusoffsky *et al.* [1].

With this assumption that all four-sublattice interaction parameters for the order-disorder partitioning model can be set as zero, the matrix  $\underline{\underline{\mathbf{M}^{\text{bcc}}}}$  is given by

$$\underline{\underline{\mathbf{M}^{\text{bcc}}}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ -\left(\frac{3}{4}\right)^4 & 1 - 4\left(\frac{3}{4}\right)^3\left(\frac{1}{4}\right) & -2\left(\frac{3}{4}\right)^2\left(\frac{1}{4}\right)^2 & -4\left(\frac{3}{4}\right)^2\left(\frac{1}{4}\right)^2 & -4\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)^3 & -\left(\frac{1}{4}\right)^4 \\ -\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & 1 - 2\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & -\left(\frac{1}{2}\right)^4 \\ -\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & -2\left(\frac{1}{2}\right)^4 & 1 - 4\left(\frac{1}{2}\right)^4 & -4\left(\frac{1}{2}\right)^4 & -\left(\frac{1}{2}\right)^4 \\ -\left(\frac{1}{4}\right)^4 & -4\left(\frac{1}{4}\right)^3\left(\frac{3}{4}\right) & -2\left(\frac{1}{4}\right)^2\left(\frac{3}{4}\right)^2 & -4\left(\frac{1}{4}\right)^2\left(\frac{3}{4}\right)^2 & 1 - 4\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)^3 & -\left(\frac{3}{4}\right)^4 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (67)$$

If other approximations for the reciprocal interaction parameters were used, where the reciprocal interaction parameters could be written as a linear sum of the ordering energies of the end members, they could be incorporated into the model as in the fcc case.

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