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A NOTE ON MODELS FOR PHASES WITH ORDER/DISORDER TRANSITIONS IN THERMODYNAMIC SOFTWARE AND DATABASES

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Abstract

The Calphad method is an important tool to assist the development of new alloys. There are several different thermodynamic software and databases available for such calculations. In some of these alloys there are is an important order/disorder transition, like in superalloys (Ni-based) or Al-Ti alloys. This paper describes the modeling of such systems and a new software that has improved the implementation of the modeling of this transition which can extend the composition range of the application of the model.

Keywords**:** *Calphad method; CEF model; Gibbs energy; Open Calphad software; Long range ordering.*

1. Introduction

The use of the Calphad method is described extensivly in many pares and in the book by Saunders and Miodownik [1]. In the Calphad method each phase is described with a model for the Gibbs energy as a function of T, P and the phase constitution. With appropriate software and assessed databases the user can calculate phase equilibria, phase diagram and to simulate phase transformations.

The Calphad method has been implemented in several commercial software and databases [2-5]. More recently a free software has been developed with improved modeling and software techniques. This will be briefly described in section 3.

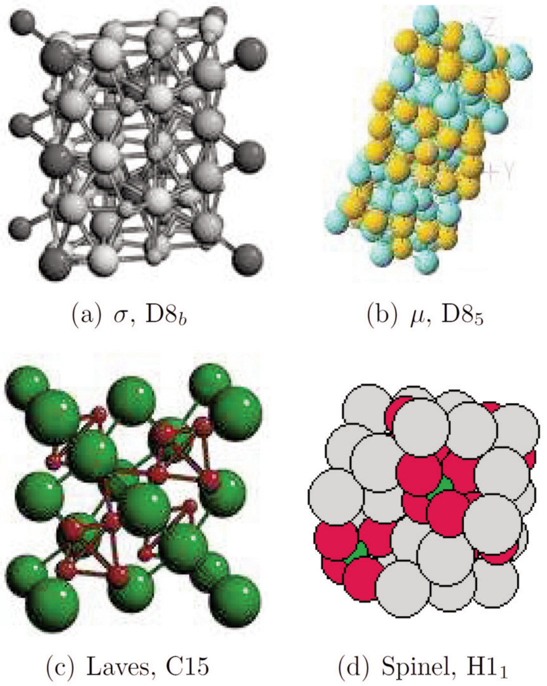
2. The CEF model

The Compound Energy Formalism (CEF) is used in the Calphad method as a framework for several models for different kinds of phases. A phase can have several crystallographically different sublattices and as constituents in these one can have atoms, ions or molecules and also vacancies representing an empty lattice site. On each sublattice the constituents are assumed to mix randomly. A substitutional solution phase a with a single lattice site and without vacancies has a Gibbs energy, G_m^α per mole component described by:

$$G_m^\alpha = \sum_i x_i \, {}^\circ G_i^\alpha + RT \sum_i x_i \ln(x_i) + {}^E G_m^\alpha + {}^{phys} G_m^\alpha \qquad (1)$$

$$\sum_i x_i = 1 \qquad (2)$$

where x_i is the mole fraction of constituent i, ${}^\circ G_i^\alpha$ is the Gibbs energy for constituent i relative to a defined reference state. The second term is the configurational


(a) σ, D8_b (b) μ, D8_5

(c) Laves, C15 (d) Spinel, H1_1

Figure 1. *Four complex crystalline structures*

Dedicated to the memory of Professor Dragana Živković

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entropy where R is the gas constant and T the absolute temperature. ${}^{E}G_m^{\alpha}$ is the excess Gibbs energy including interactions between the constituents and ${}^{phys}G_m^{\alpha}$ can be used to describe particular physical contributions for example from magnetic transitions. This and other kinds of models are described in detail in the book by Lukas et al [9].

2.1 Phases with long range ordering

When a crystalline phase has several different kinds of lattice sites, for example an intermetallic like the σ, *μ* or Laves phases this can be described by specifying several sublattices with different sets of constituents. Several of these sublattices may have vacant sites and rather than model the Gibbs energy per mole components it is convenient to model the Gibbs energy per mole lattice sites i.e. per mole of formula units. This is denoted by a subscript M, G_M, rather than $_m$ as in G_m in eq. 1. A generalization of eq. 1 using CEF is:

$$G_M = \sum_i \prod_I (y)\,{}^{o}G_I + RT \sum_s a_s \sum_i y_{is} \ln(y_{is}) + \\ + {}^{E}G_M + {}^{phys}G_M \tag{3}$$

$$\sum_i y_{is} = 1 \tag{4}$$

where *I* represent a “compound” or “endmember” of the phase specifying one constituent i in each sublattice s. $\prod_I (y)$ is the product of the constituent fractions, y_{is} specified by *I*, and this can be considered as the “probability” of having this compound in the phase.

${}^{o}G_I$ is the Gibbs energy of formation of endmember *I* from the reference states of the components. In the configurational entropy a_s is the number of sites on sublattice *s*. The mole fraction of a component *i* can be calculated from the constituent fractions as:

$$x_i = \frac{\sum_s \alpha_s \sum_j b_{ij} y_{is}}{\sum_k \sum_s \alpha_s \sum_j b_{kj} y_{js}} \tag{5}$$

where b_{ij} is the stoichiometric factor of component *i* in constituent *j*.

This model has been used successfully to describe many different kinds of phases with long range ordering (LRO) like interstitial solution [6], intermetallics [7] and phases with order/disorder transitions [8]. But frequently the models have simplified the real crystallography because the number of endmembers increases rapidly with the number of constituents on the sublattices. For example the σ phase has 5 crystallographic lattice sites but it is often described with just 3 to simplify the calculations and the database development.

Even with few sublattices there are often not enough data to determine values for all endmembers as the phases are stable only in a limited composition and temperature range. The use of DFT calculations to determine endmember energies can simplify the modeling as shown by Fries and Sundman [10].

Additionally many endmember energies calculated by DFT for the given structure have imaginary phonon frequencies which mean that they are not mechanically stable. If the unrelaxed value is taken it will be more positive than could be expected for the endmember and if the structure is relaxed the crystallography will change and no longer represent the correct structure. However, if the endmember is far fram any stable composition of the phase that may not be very important but a more a more severe problems is that the number of endmembers for a phase with 5 components and where all elements are considered on all sublattices require 3125 DFT calculations. This is quite a lot but as will be explained in the next section there are ways to simplify this.

2.2 Partitioning of the Gibbs energy of LRO phases

Many of the complex crystalline lattices can be considered as a distorted substitutional lattice and this can be used to simplify the description of phases with several sublattices.

This fact suggests that one can partition the Gibbs energy expression in two parts

$$G_M = G_M^{subst*}(x_i) + G_M^{ord}(y_{js}) \tag{6}$$

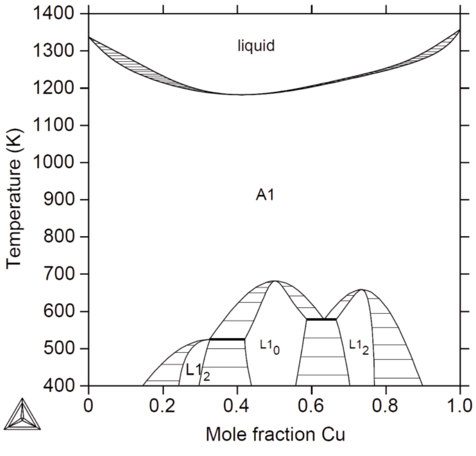
$$x_i = \sum_s \alpha_s y_{is} \tag{7}$$

where y_{is} is the sublattice constitution, assuming that the constituents are same as the components, and $G_M^{subst*}(x_i)$ describes a “baseline” of the Gibbs energy for the phase using a substitutional model like eq. 1, but without the configurational entropy.

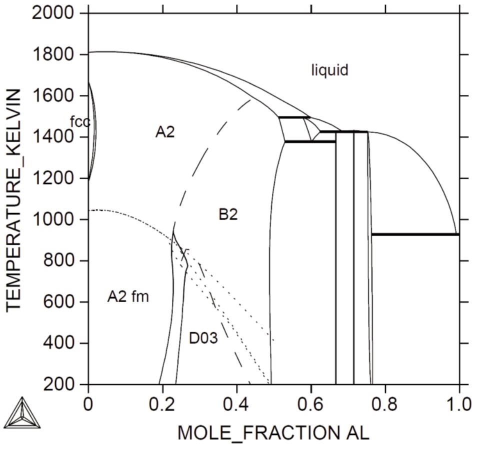
$G_M^{ord}(y_{js})$ describes the configurational entropy and includes only those endmember energies that has a lower Gibbs energy than the baseline, i.e. for which the phase is or could be expected to be stable. All endmembers that have energies above the baseline, in particular those representing structures that are mechanically unstable, can be ignored. This means there are only a few endmember parameters needed in G_M^{ord} part representing compositions close to where the phase is stable or where DFT calculations predict the phase may be stable. This simplification will reduce the number of endmembers that must be determined by DFT calculations significantly.

2.3 Phases with order/disorder transitions

A particular case of LRO occur in some phases with a simple lattice like FCC, BCC and HCP. These phases are usually modeled with a substitutional model like eq. 1 but in some alloys these phases can have an ordering transition where some constituents prefer a certain set of sites. An example is the Au-Cu system where one can, at low temperature, have several ordered structures based on the FCC lattice shown in the phase diagram in Fig.2(a) from an assessment by Sundman et al. [11]. The corresponding superlattices are shown in Fig. 3.



(a) Au-Cu



(b) Fe-Al

Figure 2. *Calculated phase diagrams for Au-Cu and Fe-Al*

For physical reasons the ordered forms of FCC should be modeled with a single Gibbs energy function which requires at least a 4 sublattice tetrahedron model in order to have a symmetrical description. As the transformations from the A1 to the ordered structures are first order it is in principle possible to describe each ordered form as a separate phase but when dealing with ordering of the BCC phase there are frequently second order transitions between the different superlattices, as shown in phase diagram for the Fe-Al system in Fig. 2(b) from an assessment by Sundman et al [13]. In such cases it is mandatory to have a single Gibbs energy expression like eq. 3 for these phases.

The ordered forms of BCC in Al-Fe are shown in Fig. 4 together with the Heusler structure which can appear in ternary system. These can be modeled with a 4 sublattice model according to eq. 3 with a notation as:

$$(\mathrm{Al,Fe,Va})_{0.25}(\mathrm{Al,Fe,Va})_{0.25}(\mathrm{Al,Fe,Va})_{0.25}(\mathrm{Al,Fe,Va})_{0.25}$$

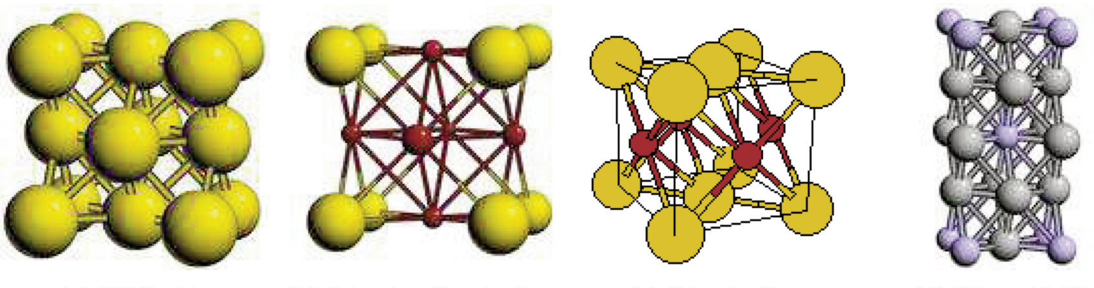
where Al and Fe can enter all sublattices. In order to be compatible with the modeling of the B2 phase in the Al-Ni system the vacancy, denoted “Va” is also included on all sublattices because the B2 phase in the Al-Ni system is stable at higher concentration that 50% Al due to the replacement of Ni atoms by vacancies.

There are 81 endmembers in the model for the ordered BCC in the Al-Fe system but many of them describe the same state, they are permutations and this will be further discussed in section 2.5. Written explicitly for a 4 sublattice model eq. 3 becomes:

$$\begin{aligned} G_M = {} & \sum_i \sum_j \sum_k \sum_l y_{i,1} y_{j,2} y_{k,3} y_{l,4}\, {}^{\circ}G_{ijkl} + \\ & + RT \sum_s a_s \sum_i y_{is} \ln(y_{is}) + {}^{E}G_M + {}^{phys}G_M \end{aligned} \tag{8}$$

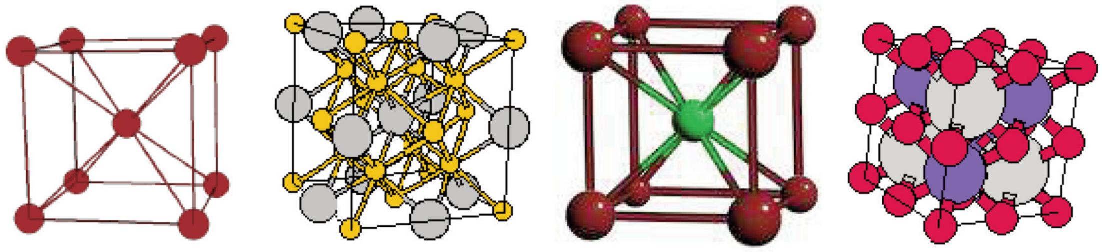
For the expressions for ${}^{E}G_M$ and ${}^{\mathrm{phys}}G_M$ please refer to the book by Lukas et al. [9].

Model compatibility is an important feature when assessing experimental and theoretical data to describe the Gibbs energy of the phases in binary and ternary system. The same models must be used for the same phases in different systems in order to combine



(a) FCC, A1 (b) L1$_2$, Au$_3$Cu, AuCu$_3$ (c) L1$_0$, AuCu (d) D0$_{22}$, Al$_3$Ti

Figure 3. *The disordered FCC and three ordered superlattices*



(a) BCC, A2 (b) D0$_3$, Fe$_3$Al (c) B2, AlFe (d) L2$_1$, Heusler

Figure 4. *The disordered BCC and three ordered superlattices*

them in a thermodynamic database. Another essential contribution to obtain compatibility is the SGTE unary database [12] which provides Gibbs energy functions for the pure elements, $^{o}G_i$ in many different phases, including lattice stabilities for such phases for which the pure element is never stable.

2.4 Partitioning of the Gibbs energy for order/disorder

The FCC, BCC and HCP phases are common in many alloy systems and in order to combine assessments where the these phases have no ordering transformation with system where the phases are described with sublattices for ordering we can make use of a similar kind of partitioning as described in section 2.2. But in this case the "baseline" describes a real phase and the ordering part describe an extra contribution due to the ordering:

$$G_M = G_M^{\mathrm{dis}}(x_i) + \Delta G_M^{\mathrm{ord}}(y_{js}) \tag{9}$$

$$\Delta G_M^{\mathrm{ord}} = G_M^{\mathrm{ord}}(y_{js}) - G_M^{\mathrm{ord}}(y_{js} = x_i) \tag{10}$$

where $G_M^{\mathrm{dis}}(x_i)$ describes the disordered Gibbs energy with a substitutional model like eq. 1 and $\Delta G_M^{\mathrm{ord}}(y_{js})$ describes the contribution due to LRO using eq. 3. In this case the configurational entropy is included in all G_M calculations. This should be zero when the phase is disordered and the simplest way to achieve this is to calculate the Gibbs energy for the CEF model twice, once with the original constituent fractions, y_{is}, and once with these replaced by the mole fractions using $x_i = \sum_s \alpha_s y_{is}$ and take the difference.

2.5 Model parameter permutations

A final problem when dealing with ordering in FCC, BCC and HCP is that many endmember parameters represent the same state. For example in Au-Cu system using a 4 sublattice model for the FCC phase with all superlattices the L1$_2$ ordered AuCu$_3$ phase is described by 4 different endmembers that must be equal:

$$^{o}G^{\mathrm{ord}}_{\mathrm{Au:Cu:Cu:Cu}} = {}^{o}G^{\mathrm{ord}}_{\mathrm{Cu:Au:Cu:Cu}} = {}^{o}G^{\mathrm{ord}}_{\mathrm{Cu:Cu:Au:Cu}} = {}^{o}G^{\mathrm{ord}}_{\mathrm{Cu:Cu:Cu:Au}} \tag{11}$$

An ordered model for the FCC phase with 4 constituents modeled with 4 sublattices has 256 endmembers but only 35 unique values. This is a complication for the administration of databases as it is very easy to forget a permutation which will make the phase always ordered and give wrong thermodynamic properties even in the disordered state. But it is possible to implement these permutations in the software and thus the databases need only to provide values for the unique endmembers.

3. The Open Calphad software

Since 2013 there a group of dedicated scientists has been engaged in the development of a new free thermodynamic software called Open Calphad [14] (OC). The OC software use modern techniques to store model parameters together with the best algorithms [15] to minimize the Gibbs energy in order to calculate the equilibrium for a flexible set of conditions. There is also an application software interface which makes it possible to integrate OC in simulation software [16].

The OC software has implemented the partitioning of the Gibbs energy in a new way which reduces the calculation times. Recently the OC software has also implemented the permutation of parameters in ordered FCC, BCC and HCP phases using a new technique that reduces the calculation times even more. It is important for interested scientists to have access to a free software in order to develop new models or improved versions of existing models.

The OC software is free with a GNU license and can be downloaded from the Opencalphad website [17] or the development version from the github website [18].

4. Summary

The method to model the Gibbs energy of phases with LRO is briefly described tigether with some details of handling this in the software and databases. In the current databases many simplifications in the modeling has been made for the database management as well as to speed up the calculations. For example the σ phase is often described with just 3 sublattices and in particular the ordering in FCC, BCC and HCP phases are described with a 2 sublattice model.

In the case of the $L1_2$ phase described with 2 sublattices this leads to a very unsymmetric model and many ternary and higher order parameters must be added to compensate for this. With a 4 sublattice model this is simplified but a 4 sublattice model leads to a considerable increase the time to calculate an equilibrium. This is due to the fact that the calculation time is roughly proportional to the square of the number of constituents and with 4 sublattices the number of constituents are doubled. But with new software it is possible to find ways to speed up the calculations and make it possible to use models that are closer to reality also in practical calculations.

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