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# THERMODYNAMICS OF MATERIALS: FROM *AB INITIO* TO PHENOMENOLOGY

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## ABSTRACT

Quantum mechanical-based (or *ab initio*) methods are used to predict the stability properties of materials although their application is limited to relatively simple systems in terms of structures and number of alloy components. However thermodynamics of complex multi-component alloys requires a more versatile approach afforded within the CALPHAD formalism. Despite its success, the lack of experimental data very often prevents the design of robust thermodynamic databases. After a brief survey of *ab initio* methodologies and CALPHAD, it will be shown how *ab initio* electronic structure methods can supplement in two ways CALPHAD for subsequent applications. The first one is rather immediate and concerns the direct input of *ab initio* energetics in CALPHAD databases. The other way, more involved, is the assessment of *ab initio* thermodynamics “à la CALPHAD”. It will be shown how these results can be used within CALPHAD to predict the equilibrium properties of multi-component alloys. Finally, comments will be made on challenges and future prospects.

## INTRODUCTION

The study of alloy properties and the various attempts to reach the ultimate goal of *alloys-by-design* have concentrated in recent years heavily on gaining a detailed knowledge of the electronic structure of materials and its effects on microscopic and macroscopic behaviors [1-3]. Modern theory of alloys is almost exclusively based on the mapping of the Hamiltonian describing the system at the electronic level to that associated with the Ising model [2,3]. Despite its success limitations in the number of alloy components and the structural complexity impose severe constraints on the applicability of *ab initio* methodologies to alloys of technological interest.

On the other hand, since the early 70's the so-called CALPHAD (CALculation of PhAse Diagram) approach has been very successful in describing the thermodynamics of complex alloy systems [4,5]. A standardized framework has been established to facilitate communication among scientists, and a number of assumptions have been made to simplify the calculations particularly about the legitimacy of defining the Gibbs energy of any element or alloy in any structure (the so-called “lattice stability” assumption). However its success depends on the reliability of its thermodynamic database. Hence it becomes clear that by taking advantage of the power of each methodology *ab initio* can efficiently supplement CALPHAD especially in the absence of reliable experimental data. The interface can be considered at two distinct levels. First, the immediate usage of output information on alloy energetics from *ab initio* can be used within CALPHAD. This is particularly useful in case data are required on hypothetical structures for pure elements or on metastable or “unstable” phases in the case of multi-component alloys. Second, *ab initio* results of alloy energetics and of phase diagrams can appropriately supplement thermodynamic databases in terms of Gibbs energies as functions of temperature and alloy composition that are used within the phenomenological CALPHAD approach for predicting the stability properties of complex materials.

Following a brief overview of the first-principles and phenomenological methodologies, examples of interfacing will be presented with applications to multi-component alloys.

## FROM ELECTRONIC HAMILTONIAN TO ISING MODEL

The two questions about alloy stability at zero temperature (ground-state properties) and phase stability at finite temperature can presently be addressed through a combination of electronic structure calculations and a statistical mechanics treatment of the Ising model [2,3]. Let us then briefly mention the two main pathways that facilitate this mapping.

To extract many-body interactions for alloys out of electronic structure calculations, it is worth mentioning the methods that are based on the electronic structure of random alloys, such as the Generalized Perturbation Method (GPM) [2], and those that rely on the calculation of the electronic structure of specific ordered configurations of alloys, such as the so-called Connolly-Williams Method (CWM) [6].

So far, all methods in the first category have been developed within the Coherent-Potential Approximation (CPA) [2] for the study of the electronic structure of substitutionally disordered alloys. It is proved that the formation energy of an alloy  $A_{1-c}B_c$  in a given configuration C at the specific composition  $c = c^C$  is expressed as

$$\Delta E_{Formation}^C = E_{Total}^C - (1 - c^C)E_{Total}^A - c^C E_{Total}^B = \Delta E_{Mix}(c^C) + \Delta E_{Ord}^C \quad (1)$$

where the mixing energy is given by

$$\Delta E_{Mix}(c^C) = E_{Total}^{CPA}(c^C) - (1 - c^C)E_{Total}^A - c^C E_{Total}^B \quad (2)$$

and the ordering energy associated with the configuration C of the alloy, to lowest order in perturbation, is written as

$$\Delta E_{Ord}^C \approx \frac{1}{2} \sum_{nm \neq n} (p_n^C - c^C)(p_m^C - c^C) V_{nm}(c^C) \quad (3)$$

where  $p_n^C$  is, at zero temperature, an occupation number equal to 0 or 1 depending on the occupation of site n by a B or A species. The total energy of the disordered state of the alloy  $E_{Total}^{CPA}$  is calculated within the CPA, and is concentration dependent. The expansion is derived with reference to the CPA medium, and the effective pair interactions (EPI),  $V_{nm} = V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB}$ , are also concentration dependent.

Implicitly, for methods belonging to this category, the electronic structure theory should rely most advantageously on the Green function formalism, and therefore methods such as the KKR and the TB-LMTO [1] are most suitable.

For the methods of the second category, it is assumed (ansatz) that the formation energy of an alloy  $A_{1-c}B_c$  in a given configuration C can be written as

$$\Delta E_{Formation}^C = V_0 + \sum_{\alpha} \sigma_1^C \sigma_2^C \cdots \sigma_{\alpha}^C V_{\alpha} \quad (4)$$

where the “spin” variable  $\sigma_n^C$  is related to the occupation number  $p_n^C$  by  $\sigma_n^C = 2p_n^C - 1$ .

Hence after selection of the maximum cluster(s)  $\alpha$  and a set of ordered configurations  $\{C_i\}$  of the alloy, the many-body interactions  $V_{\alpha}$  are determined by solving a set of linear equations once the formation energies of the alloy in each configuration  $C_i$  has been determined with an electronic structure code. Methods in this category are usually wave-based (such as Pseudo-potential, APW, ASW, LASTO, LMTO) although in principle Green functions methods can also be used. Here, the advantages are: ease of implementation, possible handling of complex structures, and accuracy afforded by full-potential methods. On the negative side, the selection *a priori* of the most pertinent set of clusters  $\{\alpha\}$  and ordered configurations  $\{C_i\}$  that are used to set up the system of linear equations (from which the interactions are determined) is ill defined. Note that the interactions are concentration independent except via volume effect, and usually the rate of convergence of the expansion given by Eq. (4) is rather low. Finally, because methods in this category are merely fitting procedures, the physics behind the interactions is rather obscure to

say the least.

In summary, although the differences between the two categories seem rather subtle, they both lead to a completely different way of handling the statistical mechanic part of the problem. In the first category, it is formally shown that the ordering-energy contribution to the total energy can be expanded in terms of pair and multi-site interactions, and the energy of the chemically random state of the alloy is separately calculated with the electronic structure method that can handle chemical disorder. On the other hand, in the second category, the total energy of the alloy is expanded in terms of multi-site interactions, and the energy of the disordered state is also expressed with the same interactions that describe chemical order according to

$$\Delta E_{\text{Mix}}(c) = \Delta E_{\text{Formation}}^{\text{Dis}}(c) = V_0 + \sum_{\alpha} (2c - 1)^{\alpha} V_{\alpha} \quad (5)$$

## CALPHAD THERMODYNAMICS

The modeling of the Gibbs energy of individual phases, and the coupling of phase diagram and thermo-chemistry together make CALPHAD a powerful technique in computational thermodynamics of multi-component materials [4,5]. For pure elements and stoichiometric compounds, the most commonly used model is the one suggested by the Scientific Group Thermodata Europe (SGTE) [7] with the data for all the pure elements of the periodic table compiled by Dinsdale [8].

For multi-component solution phases, the Gibbs energy has the following expression [5]

$$G = G^{\circ} + G_{\text{mix}}^{\text{ideal}} + G_{\text{mix}}^{\text{xs}} \quad (6)$$

where  $G^{\circ}$  is the contribution from the mechanical mixing of the pure components,  $G_{\text{mix}}^{\text{ideal}}$  is the ideal mixing contribution, and  $G_{\text{mix}}^{\text{xs}}$  is the excess Gibbs energy of mixing due to non-ideal interactions which is, for solution phases that exhibit chemical order, usually expressed within a sub-lattice model [5].

Thermodynamic modeling begins with the evaluation of the thermodynamic descriptions of unary and binary systems. By combining the thermodynamic descriptions of constitutive binary systems and ternary experimental data, a thermodynamic description of ternary systems is developed, and so forth for higher-order component alloys.

As said in the introduction *ab initio* output, such as structural energies, heats of formation, heats of transformation, elastic and magnetic properties, can be used in a CALPHAD description of alloy properties. This is the most immediate application of *ab initio* to CALPHAD. Furthermore, when the link between *ab initio* electronic structure calculations and statistical mechanics has been achieved, the information on thermodynamic functions as function of alloy composition and temperature, and on phase diagram results is available. This can be included in a theoretical assessment “à la CALPHAD” of the thermo-chemistry of alloys (the same way an assessment is carried out within CALPHAD solely based on experimental data). This input from *ab initio* adds to the capabilities of CALPHAD to predict the thermodynamic properties of complex multi-component alloys.

## APPLICATIONS

The results of the *ab initio* calculations presented in this section were carried out on the basis of the charge self-consistent fully relativistic version of the TB-LMTO-CPA method within the atomic-sphere approximation and the local-density approximation (LDA) of density functional theory [9]. The effects of statistical fluctuations away from the CPA average medium have been accounted for by the GPM. *Ab initio* alloy phase diagrams were computed with a generalized mean-field statistical treatment, namely the cluster variation method (CVM) [2,10]. Finally the CALPHAD calculations were carried out with the Thermo-Calc application software [11].

### AB INITIO FORMATION ENERGIES INPUT TO CALPHAD

In CALPHAD databases no energetic information was available for the ordered Ni<sub>2</sub>Cr phase (C11<sub>b</sub> or oP6) that is observed experimentally. Furthermore, to describe the quaternary Ni-Cr-Mo-W system, data on the formation energy of the hypothetical ordered Ni<sub>2</sub>Mo and Ni<sub>2</sub>W phases were required. Hence, *ab initio* calculations were performed for these three compounds and the results are shown in Fig. 1. It is worth noting that Ni<sub>2</sub>Mo is barely stable whereas Ni<sub>2</sub>W is unstable.

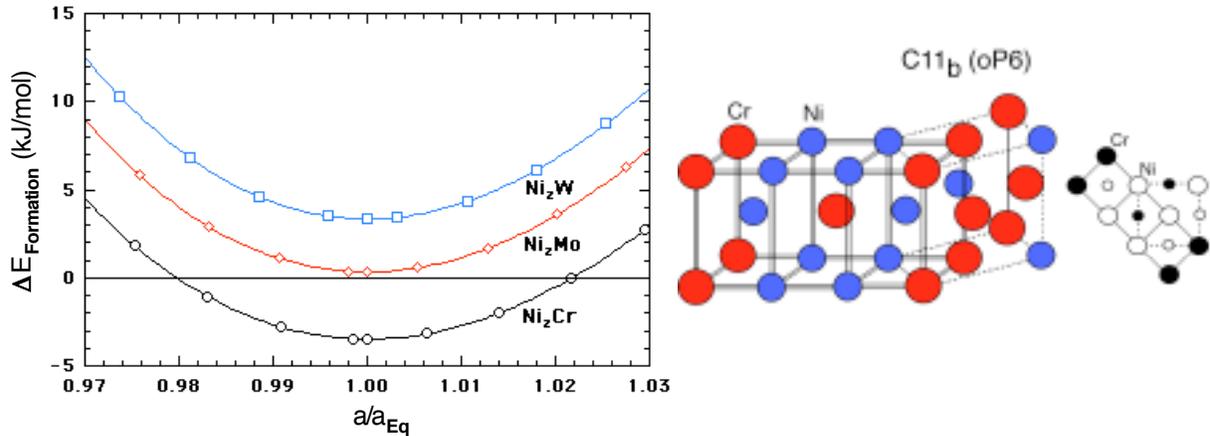


Figure 1. Total energy (in kJ/mol) versus normalized lattice parameter (*i.e.*,  $a/a_{Eq}$ , where  $a$  is the lattice parameter and  $a_{Eq}$  is the equilibrium lattice parameter) for Ni<sub>2</sub>Cr, Ni<sub>2</sub>Mo, and Ni<sub>2</sub>W of Ni<sub>2</sub>Cr-type (C11<sub>b</sub> or oP6 shown on the right). The zero of energy is taken as the concentration weighted average of the total energies of fcc Ni and bcc Cr (Mo, W).

For the quaternary Ni-Cr-Mo-W system the ordered phase was treated within a two-sub-lattice model with Cr, Mo, and W on one sub-lattice, and Mo, Ni, W on the other sub-lattice. The compound phase parameters of the three binary subsystems determined from *ab initio* have been included in the CALPHAD treatment of phase stability.

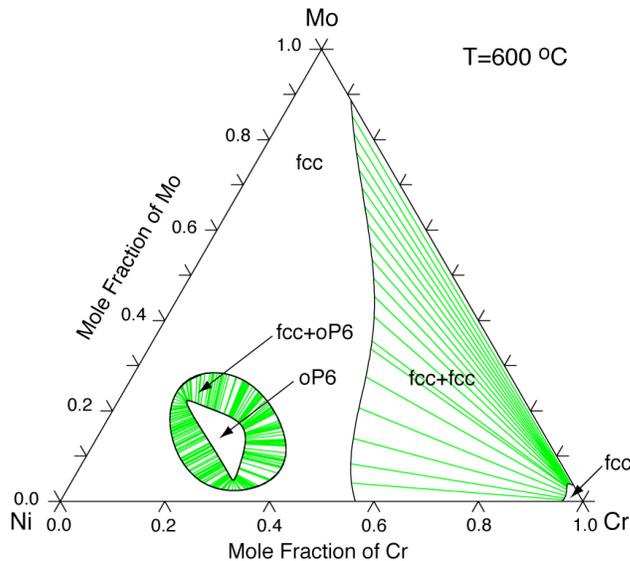


Figure 2. Calculated isothermal section of the Ni-Cr-Mo phase diagram at 600 °C. Only the fcc matrix and the oP6-ordered phase are considered for this set of calculations.

By limiting the analysis to the fcc matrix and the oP6 ordered phase (*i.e.*, all other stable phases have been ignored), isothermal sections of the Ni-Cr-Mo phase diagram were calculated. The isothermal section shown in Fig. 2 delineates a domain of stability of the oP6 phase in a diagram that would have only indicated a fcc-solid solution without *ab initio* input.

### **AB INITIO PHASE DIAGRAM INPUT TO CALPHAD**

The output *ab initio* thermodynamics can be converted to a CALPHAD format with an acceptable level of accuracy. The results of this conversion can then be combined with those of an existing CALPHAD thermodynamic database. The procedure is illustrated in the case of the Ta-W alloy system.

The Gibbs energies and molar enthalpies of formation of the bcc phase as well as the solid-state portion of the phase diagram obtained from CVM [10] with the energetics calculated from *ab initio* were obtained. The CVM results predict the existence of a domain of stability of B2 order for Ta-W [12]. This information was used in the CALPHAD fitting procedure performed with the PARROT module of Thermo-Calc [11].

The Gibbs energy differences between the CVM and CALPHAD results from 800 K to 3000 K are less than 2 %. As a consequence the CALPHAD phase diagram of Ta-W [13] displayed in Fig. 3 compares extremely well with the one from *ab initio*.

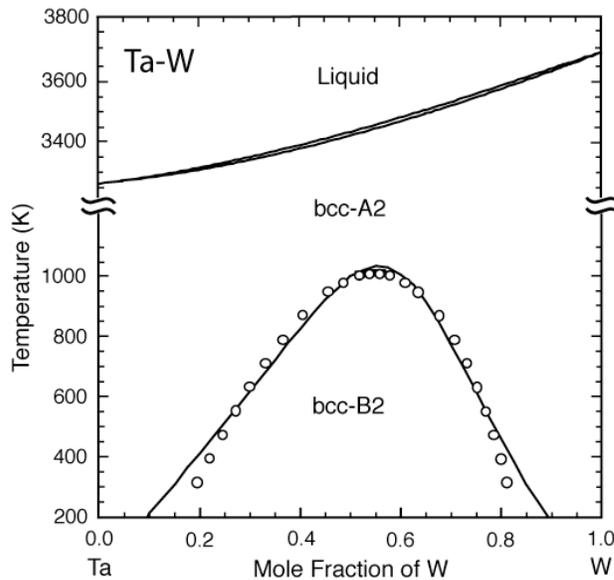


Figure 3. Ta-W phase diagram obtained from the application of Thermo-Calc to CALPHAD (solid line), and compared with the CVM results (open circles). Redrawn from Ref. [13].

This conversion provides a robust and yet simple scheme that is consistent with standard assessment of multi-component alloy phase diagrams. The CALPHAD assessment of *ab initio* data has been recently used to study Cr-Ta-W [13] with experimental input for Cr-W and Cr-Ta, and Mo-Ta-W [14] with additional *ab initio* input for Mo-Ta and Mo-W. In both examples it was shown that the adequacy of the *ab initio* results could advantageously supplement the CALPHAD database to predict alloy stability in higher-order component alloys.

### **CONCLUSIONS**

A wide variety of electronic structure codes are now available to obtain a wealth of results (not just energies!), and to provide an understanding at the atomistic level of the intricate relation between electronic structure properties and stability and chemical order in alloys. *Ab initio*

studies also rationalize trends that exist as functions of the number of valence electrons and the difference in the numbers of valence electrons. Any electronic structure code should be tested against a broad range of experimental data spanning from structural information to results from various spectroscopies that probe the electronic, elastic, magnetic (if any), *etc.*, properties so that a level of confidence can be established on the legitimacy of the various approximations (or constraints).

Energetics obtained from *ab initio* calculations can be readily input in thermo-chemical databases used in conjunction with CALPHAD, and be considered as educated starting guesses for further assessment of phase diagrams.

*Ab initio* phase diagram results can also be treated as experimental results and be assessed “à la CALPHAD” to enhance the predictive capabilities in an approach that is otherwise phenomenological in essence.

The two links that have been briefly discussed between *ab initio* and CALPHAD can also be used in a reverse mode to test, validate, and challenge the approximations built in any first-principles approach to alloy stability and order.

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