Developing the third generation of Calphad databases: what can ab-initio contribute?

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To Siamak.
Out beyond ideas of wrongdoing and rightdoing there is a field; I’ll meet you there.

- Rumi
Abstract

Developing the third generation of Calphad databases with more physical basis valid within a wider temperature range is the aim of the present work. Atomistic scale (ab-initio) methods, particularly techniques based on DFT theory, are used for modelling different phenomena, so as to gauge the capacity for use in Calphad modelling.

Several systems are investigated in this work for studying different phenomena, such as magnetism and vibration of atoms. In the case of pure elements (unaries), thermodynamic properties of Mn, Al and C are optimized in the whole temperature range by the help of new models. In addition, DFT results and specific characteristics of these elements are also used to develop models for describing magnetic properties and atomic vibrations.

With regards to coupling between DFT and Calphad, the EMTO technique is used for determining the magnetic ground state of the metastable hcp phase in Fe and Mn, and the TU-TILD technique is used for modelling solid phases above the melting point. TU-TILD is also used for calculating thermodynamic properties of bcc Mn at finite temperatures.

The same phenomena are investigated in higher-order systems, i.e. the binaries Fe-Mn and Mn-C. Thermodynamic properties and phase diagrams of these systems are assessed against experimental data. Moreover, the revised magnetic model is used for modelling magnetic properties in these systems.

It is shown through this investigation that although the DFT methods are powerful tools for model development and for resolving discrepancies between different experimental datasets, they should not be overly-trusted. Caution must be taken when using DFT results, since the approximations and assumptions for computational implementations may cause some errors in the results. Moreover, implementing them into Calphad software as a connected methodology is not currently accessible due to the computational limitations.

It is concluded that coupling between the DFT and Calphad approaches can currently be achieved by using DFT results as an input in Calphad modelling. This will help to improve them until they can be integrated into the Calphad approach by the progress of computational possibilities.

One of the advantages of developing the third generation Calphad databases is the possibility of using the 0 K DFT results in Calphad modelling, since the new databases are valid down to 0 K. This has not been possible in the past, and such potential opens a new door to bring more physics into the Calphad approach.
Sammanfattning

Att utveckla den tredje generationen Calphad-databaser med mer fysisk grundgående inom ett större temperaturområde r syftet med detta arbete. Atomistiska (ab-initio) metoder, speciellt tekniker baserade på DFT-teorin, används för att modellera olika fenomen, frå att uppskatta potentialen frå dess användning inom Calphad-modellering.

Flera system undersöks i detta arbete för att studera olika fenomen, som magnetism och vibrationer av atomer. Nr det gäller rena element (unaries) optimeras de termodynamiska egenskaperna hos Mn, Al och C i hela temperaturområdet med hjälp av nya modeller. Dessutom används DFT-resultat och specifika egenskaper hos dessa element frå att utveckla modeller frå att beskriva magnetiska egenskaper och atomvibrationer.

Nr det gäller kopplingen mellan DFT och Calphad används EMTO-tekniken frå att bestamma det magnetiska grundtillståndet frå den metastabila hep-fasen i Fe och Mn, och TU-TILD-tekniken används frå modellering av fasta faser ver snittpunkt. TU-TILD används också frå berkning av de termodynamiska egenskaper hos bcc-Mn vid temperaturer ver noll kelvin.

Samma fenomen undersöks i system av högre ordningen, dvs binärerna Fe-Mn och Mn-C. Termodynamiska egenskaper och dessa systemas fasdiagram utvärderas mot experimentella data. Dessutom används den reviderade magnetiska modellen frå modellering av de magnetiska egenskaperna.

Det framgår av denna undersökning att ven om DFT-metoderna r kraftfulla verktyg frå modellutveckling och frå att frst vilka experimentella dataset som r bst, br inte alltför stor tillit tillskrivas dem. Srskild frskiktighet mste beaktas vid användning av DFT-resultat, eftersom approximationerna och antaganden kan ge fel resultat. Dessutom r det fr nrvarande inte mjligt att implementera dem direkt i Calphad-programvaran p grund av begränsningar i berkningskapacitet.

Slutsatsen r att kopplingen mellan DFT och Calphad-metoderna fr nrvarande bst kan uppnas genom att använda DFT-resultat som indata i Calphad-modellering. Detta kommer att bidra till att fritvåra dem tills de kan integreras i Calphad-programvaran nr berkningskapaciteten har blivit tillräckligt kraftfull.

En av frdelarna med att utveckla tredje generationens Calphad-databaser r mjligheten att använda 0 K DFT-resultat direkt i Calphad-modellering, eftersom de nya databaserna r giltiga till 0 K. Detta har inte varit mjligt tidigare och ppnar en ny drr frå att f in mer fysik i Calphad-metoden.
List of appended papers


Contribution Statement: Sedigheh Bigdeli performed the thermodynamic modelling and prepared the manuscript.


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Other contributions


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Nomenclature

FCC – Face Centered Cubic
BCC – Body Centered Cubic
HCP – Hexagonal Close-Packed
CEF – Compound Energy Formalism
R-K – Redlich-Kister
DFT – Density Functional Theory
MD – Molecular Dynamics
AIMD – Ab-Initio based Molecular Dynamics
EMTO – Exact Muffin Tin Orbital

UP-TILD – Upsampled Thermodynamic Integration using Langevin Dynamics
TU-TILD – Two-stage Upsampled Thermodynamic Integration using Langevin Dynamics
TOR-TILD – Two-Optimized References Thermodynamic Integration using Langevin Dynamics
Chapter 1

Introduction

1.1 Modelling thermodynamic properties of materials

Application of thermodynamic properties of materials to predict the stable phases in a system has been in use for decades [1]. The concept is to set the conditions in the system in such a way that the degrees of freedom according to Gibbs phase rule are equal to zero. Then the set of stable phases at equilibrium is the one with the lowest overall Gibbs energy.

This simple method has been very useful to calculate and predict phase diagrams of materials, as the basis of materials science. The method is used in the Calphad software such as Thermo-clac. Calphad stands for Calculations of Phase Diagrams and denotes the method used to evaluate thermodynamic properties from experimental information.

Over the years, an enormous number of systems have been evaluated using the Calphad method. However, the starting point for this approach is to properly model the Gibbs energy of pure elements (unaries) and other terms will accordingly be added to find a good agreement with the experimental data for higher-order systems. A schematic is shown in Fig. 1.1 of the Gibbs energy for the imaginary $\alpha$ phase in a hypothetical binary system A-B [2].

As seen in Fig. 1.1, the line of reference for modelling the Gibbs energy in the binary system is totally dependent on the descriptions of the unaries. Thus, the more accurate the unary descriptions are, the easier it is to model the higher-order systems. The unary descriptions should be optimized by fitting model parameters to the experimental data. In the 1990s [3], it was agreed that for the unaries globally accepted descriptions should be developed and used. In addition to stable allotropes of each unary, the unstable and metastable phases of an element should be included, as these phases might be stable in other elements and when mixing in the alloys of higher-order systems, they become stable. Therefore, to be able to use the Calphad approach, there should be a description for such phases that the Gibbs energy minimization can be per-
formed for equilibrium calculations. The metastable or unstable unary phases are called end-members in Calphad terminology.

As will be discussed in detail in the next chapter, there have been two generations of the Calphad databases for the unaries. Although these descriptions have been very practical for modeling different systems, they have some limitations. Since most of the phase transformations occur at high temperatures, when developing previous generations, the main focus was to properly model this temperature region. As a result, these databases are mostly valid down to 600 K and unreliable at room temperature. This limitation makes it difficult to use them for modeling phase transformations that occur at low temperature, such as martensitic and bainitic transformations and carbide formation.

As computational approaches for materials design are advanced, thermodynamic descriptions valid at low temperatures become more necessary. Having descriptions available in that temperature range as an input in different techniques, e.g. phase field modeling, diffusion simulations etc., make it important to pay more attention to low temperatures. Moreover, even at high temperatures, due to some artifacts in some systems, producing proper results is difficult. Although it has become routine to calculate the thermodynamic properties of materials at 0 K using the Density Functional Theory (DFT), such useful results could not
be used as input in thermodynamic modelling, since Calphad descriptions have existed only down to room temperature until now. This has been a great loss, especially for the mechanically unstable phases and hypothetical end-members for which there is no experimental data.

As part of an international effort, people have started to dig into different possibilities to develop new models and databases that do not contain the aforementioned problems, both for unaries and higher-order systems. There have been frequent international workshops in Schloss Ringberg, Germany [4–7] for discussing these issues.

Some of the outcomes of these workshops will be discussed in the next chapters. It can be shortly mentioned that in these workshops, it was agreed that remodelling of unaries in a more accurate and physically-based way can resolve some of the problems. In connection to this suggestion, the development of the third generation of Calphad databases was started, in which the main focus has been to apply the ideas suggested in the Ringberg workshops, with the current computational capabilities.

1.2 Third generation of Calphad databases: a short introduction

In the most recent Ringberg workshop [7], using DFT calculations was discussed and tried extensively in different contexts, i.e. crystalline phases, lambda transitions, etc. Since DFT calculations deal with the atomistic scale and correlate properties of the materials to their atomic structure, as is the case in nature, they are considered to be very accurate. However, in many cases the results of such calculations cannot be validated against reality since there is no possibility to perform such experiments. Most of the DFT techniques are limited to 0 K, which is not experimentally accessible. However, since the thermodynamic descriptions in the third generation Calphad databases are valid down to 0 K, they open a new door to use 0 K DFT results.

Despite this limitation, some approximations have succeeded to reproduce experimental data at finite temperatures, for example the quasi-harmonic approach, using empirical inter-atomic potentials and some practical approaches such as the Debye model. In the case of Calphad modelling, when it comes to modelling of the end-members and metastable allotropes of the unaries, having some value, even at 0 K, can be more useful than just approximations or empirical relations.

For these reasons, in the article from the crystalline group [7], using DFT data, especially the phonon frequencies of the atoms, was strongly recommended and shown to be very accurate in some case studies.

The main question in this work is to find the possibilities and limitations of different methods suggested in Ringberg workshops, for different case studies. It is attempted to take advantage of different methods in order to come up with the best possible solutions for difficulties in modelling different phenomen-
ena, e.g. magnetism, liquid-glass transitions, etc. The main goal is to bring as much physics as possible into the Calphad descriptions and create databases valid in larger temperature ranges within the limitations of current tools. Such databases can be used in the mean time, until better computational methods and techniques make it possible to model thermodynamic properties of the materials from the atomic-scale starting point, as is the ambition of the Calphad community.
Chapter 2

CALPHAD modelling

2.1 Modelling unaries in the first and second generations of Calphad databases

The Calphad method has been used for over 30 years for modelling and predicting thermodynamic properties of materials and calculating phase diagrams. In the first and second generation of Calphad databases [1], pure elements (unaries) were modelled using the experimental data for their thermodynamic properties. In [8], as the initial step for developing the first generation of unary databases, the concept of "lattice stability" was introduced, defined as the energy difference between different allotropes of an element. In addition, physically based models were used to calculate the lattice stability of different allotropes of Ti and Zr. The models used in [8] were actually simple parameters suggested by Weiss and Tauer [9–11] for separating contributions to the heat capacity of elements into different terms. Their approach was quite straightforward for these elements and the binary system, since they both exist as hcp and bcc allotropes with no magnetic ordering. So, the experimental data for the heat capacity at different temperatures, enthalpy and entropy at room temperature were used to determine different contributions to the energy. They formulated the "free energy" of a solid phase \( \alpha \), which is non-magnetic, as equation 2.1 (A is an imaginary element):

\[
F_{A}^{\alpha} = H_{A}^{\alpha}(\tau_{0}) + F\left(\frac{\theta_{A}^{\alpha}}{T}\right) - \left(\frac{10^{-4}R}{2}\right)[\left(\frac{3}{2}T - \theta_{A}^{\alpha}\right)^{2} + \frac{3}{4}T^{2}] - \frac{\gamma_{A}^{\alpha}T^{2}}{2} \quad (2.1)
\]

where \( F \) is the free energy, \( T \) is temperature and \( R \) is the gas constant. In this equation, the non-magnetic specific heat is represented by the summation of a single Debye function \( \theta \), an electronic contribution \( \gamma \) and a correction for \( C_{p} - C_{v} \). If the \( \alpha \) phase exhibits magnetic ordering, an energy term \( F_{A}^{\alpha}(\mu) \) will be added to equation (2.1). The liquid model in [8] was based on the experimental enthalpy difference between solids and liquids at the melting point, and the fact
that these two phases are in equilibrium at this temperature. 
Stable allotropes of Fe, as a more complicated case study including magnetic 
contributions, were modelled by Kaufman [12] using this formalism. In a later 
work, Ismail et al. [13] extrapolated heat capacity data for the hcp Fe-Ru alloys 
and derived the parameters in equation 2.1 for metastable hcp-Fe. Applying 
these models, Kaufman [14] investigated different cases for modelling the lattice 
stability of refractory metals, their binaries and ternaries. This was a pioneering 
work in developing the Calphad databases using thermodynamic models imple-
mented in computer programs. While such models had a simple but strong 
physical basis, there were difficulties in modelling dynamically unstable phases 
since they were impossible to investigate experimentally. The DFT methods 
were not yet extensively used for calculating thermodynamic properties of ma-
terials, mainly due to the computational limitations, although the DFT theory 
was already developed by Hohenberg and Kohn [15]. 

These difficulties led to the development of a new generation of unary databases 
in early 90s, detailed in [3], through applying phenomenological models. This 
approach took advantage of a very simple yet very strong and effective math-
ematical tool for fitting thermodynamic properties of the elements. Dinsdale’s 
data compilations, known as SGTE (short for Scientific Group Thermodata Eu-

erope [1]) descriptions [3] brought the polynomials into the Calphad world and 
showed their flexibility for modelling very complicated behavior of elements, 
i.e., Equation 2.2 for modelling Gibbs energy ($G$):

\[
G = a + bT + cT \ln(T) + \Sigma dT^n \tag{2.2}
\]

In difficult cases, e.g., no experimental data, pragmatic solutions were suggested 
and tried: lattice stabilities of such phases were assumed to differ with respect 
to the stable ones, as an $A + BT$ contributing term to the energy (where $A$ and $B$ 
are constants). The approach used by SGTE [3] has been the basis for Calphad 
assessment of higher-order systems and globally accepted.

2.2 Third generation of Calphad databases

The SGTE compilations of the elements created a fundamental basis for the 
Calphad assessments, to develop multicomponent databases. However, they 
suffer from some limitations and problems. Lack of physical meaning behind 
the polynomials has been a weakness and a subject of criticism by the physics 
community and can cause a series of other problems when modelling different 
phena in elements or higher-order systems. Among the problems, the most 
obvious is when for some elements, e.g. Al, an artificial kink is observed in the 
heat capacity curve of the fcc phase at the melting point, which is experimentally 
and physically wrong. In addition, when reaching to the higher-order systems, 
another artifact is observed at the melting point of pure elements, when plotting 
heat capacity of the alloys versus temperature at a specific composition. Another
issue is the discrepancy, found recently by Xiong et al. [16], between the SGTE and experimental values, for magnetic properties of Cr. This issue will be addressed in section 2.2.3.

These problems, which were clear but unavoidable when developing the SGTE databases, have been encountered by the community when dealing with complicated phase transformations in different systems. Moreover, as mentioned in the introduction, some phase transformations cannot be modelled using these databases, since they are only valid down to 298 K (room temperature). Thus, the Calphad community started to look into these descriptions once more, with the help of physicists to come up with new descriptions where these problems were solved. Their main goal was to separate different physical phenomenon contributing to the free energy. In this way, they could compare these contributions with experimentally measured or calculated properties. However, one has to be realistic when dealing with such problems, since the computational tools impose restrictions on model implementations.

2.2.1 Modelling of the crystalline phases

In the 1995 Ringberg workshop [4], the crystalline phases group [17], sought a return to the original ideas from Kaufman [8] to bring more physical meaning to Calphad modelling. They suggested using heat capacity data as the main property to fit, since it has the most curvature. The other thermodynamic properties can be manipulated with a high confidence, consequently, if the fit to the heat capacity is well achieved. They returned to Equation 2.1 presented in [8], and rewrote it as Equation 2.3:

\[ C_p = C_{\text{Debye/Einstein}} + \gamma T + bT^2 \]  

(2.3)

In this equation, the \(\gamma\) and \(b\) parameters contain the electronic and anharmonic vibration contributions to the heat capacity. In principle, other power series of temperature can be added to this expression to fit experimental data, if needed. The free energy which is derived from Equation 2.3 will have a similar form as Equation 2.1. In these two equations, the harmonic vibration of the atoms is modelled by either the Einstein or Debye model and the anharmonic and electronic contributions are parameters, evaluated by fitting to the experimental data. In both cases, the magnetic ordering contribution, if it exists, will be added, according to Inden’s model [18, 19], which will be discussed in more detail in section 2.2.3. The model suggested by Chase et al. [17] was shown to work properly for case studies of Ag, Cu, Ti and Sn.

Similar to SGTE, in 1995 Ringberg the case studies were investigated down to room temperature [17]. However, it is emphasized in that work that \(S_{298.15K}\) (entropy at 298 K) must be accurately fitted. This fitting will provide the necessary curvature for possible fitting to the thermodynamic data at the temperatures in vicinity and lower than 298.15 K.

In the 1995 Ringberg workshop [17], the case studies were mainly assessed up to the melting point. But it was suggested that in the absence of information,
to extrapolate the solid descriptions above the melting point, the heat capacity
of the solid phase should reach that of the liquid at $T > T_m$. It should be
mentioned that the idea of extrapolating Gibbs energy of solid and liquid to
the instability temperature ranges was originally suggested by SGTE [3]. In the
1995 Ringberg workshop it was also suggested to avoid an artificial kink at $T_m$,
the mathematical expressions should be extrapolated in a way that first and
second derivatives of the heat capacity have the same values at $T_m$.

These suggestions were tried and shown to work nicely, for the first time in 2001,
by Chen and Sundman [20], for the case study Fe. Their suggested Gibbs energy
descriptions are presented in Equations 2.4 and 2.5. Chen and Sundman [20]
applied all the suggestions by Chase et al. [17] and managed to provide a con-
tinuous smooth curve for all thermodynamic properties of the stable phases of
pure Fe. For $T > T_m$, they used a mathematical expression which can satisfy all
the criteria discussed above. In addition, they modified the polynomials used
in the magnetic contribution, which will be discussed later.

\[
G = E_0 + \frac{3}{2} R \theta_E + 3RT \ln [1 - \exp(\frac{\theta_E}{T})] - \frac{a}{2} T^2 - \frac{b}{20} T^5 + G_{mag}, \quad 0 < T < T_m
\]

\[
G = E_0 + \frac{3}{2} R \theta_E + 3RT \ln [1 - \exp(\frac{\theta_E}{T})] + H' + S'T + a'T(1 - \ln T) - \frac{b'}{30} T^{-50} - \frac{c'}{132} T^{-11} + G_{mag}. \quad T_m < T < 6000.
\]

In Equation 2.4, $\theta_E$ is the Einstein temperature of the solid phase, entering into
the Einstein model to represent the harmonic lattice vibration. $a$ and $b$ are the
electronic and anharmonic corrections, respectively and $E_0$ denotes the energy
at 0 K. These parameters are optimized through fitting to the experimental data
for the heat capacity and enthalpy and entropy at room temperature.

$a'$, $b'$ and $c'$ in Equation 2.5 are calculated based on the constraint that these
two equations should yield the same value for the heat capacity and its first
derivative at $T_m$. It is also assumed that Equation 2.5 gives a heat capacity
value for the solid equal to that of the liquid in a temperature much beyond the
melting point, e.g., 3000 K. $H'$ and $S'$ are the enthalpy and entropy of melting
of the solid phase, respectively.

The models applied by Chen and Sundman [20] are rather simple model, but it is
very practical and can reproduce the thermodynamic properties of one of the
most important and most complicated elements, i.e. Fe, very accurately.

In connection to the unaries, at the 2013 Ringberg workshop, the crystalline
group [7] discussed the advantages and limitations of different methods and tech-
niques. As computing power has increased enormously in the last two decades,
it is believed that DFT methods based on quantum theory, can start to play a
very important role in thermodynamic modelling. While this is to some extent true, there is still a long way to go, for it being able to model material behavior starting merely from the atomistic scale. However, some time- and cost-efficient techniques can be used to calculate thermodynamic properties of materials. Using clever sampling algorithms, these techniques allow for the reduction of the calculation time while retaining the accuracy. These will be discussed in more detail in Chapter 3.

What can be mentioned as the main outcome of Ringberg 2013 in this chapter, is the emphasis on using the phonon frequencies of atomic vibrations as an input into the Calphad software, to be the starting point for calculating other properties. From a physical point of view, the more information about the phonons, the more accurate results which can be achieved. However, in many cases, calculating phonon frequencies, their interactions and phonon-electron interactions is not at all straight forward. As explained in [7], the phonon frequencies are affected by the temperature and thermal expansion of the lattice in a very complicated way; as for a solid with \( N \) atoms, there are \( 3N \) degrees of freedom for phonon frequencies. It has been shown that up to the so-called Einstein/Debye temperature, the vibration frequencies can be approximated as harmonic, but above \( \theta_E/\theta_D \), the anharmonicity starts to matter. This contribution is not simple to calculate.

On the other hand, even if these quantities could be calculated, the use of them in the Calphad software is a serious challenge. The basis of the Calphad method is the fact that, by using proper models, when the Gibbs energy of a material is known, all other properties can be derived/evaluated; conversely the DFT calculation results are in the format of single points, e.g. free energy at discrete volume-temperatures. The Gibbs energy minimization is not possible for a discrete grid of data points though, these data, if validated by the experiment, can be used as an input in the Calphad parameterization in the best-case scenario. As much as this can be very valuable in the cases no experiment can be performed, e.g., metastable end-members, extra caution should be taken to avoid using inconsistent data. This situation can lead to more harm than good, e.g. artifacts in the higher-order systems. Moreover, even DFT cannot calculate phonon frequencies at finite temperature for every type of material, such as dynamically unstable phases. It should be kept in mind that, although one of the main goals of the third generation of Calphad databases is to describe low temperature properties, in principle no phase transformation occurs at 0 K.

It can be concluded that DFT can produce different types of data, e.g. phonon frequencies, energy, etc., as data points, stored in some table format. Use of data tables is not new for thermodynamic properties, JANAF tables\(^2\) are examples of such data in the past. However, they were abandoned due to the limitations they may cause in modelling some physical phenomenon, like ferromagnetism [19]. In this case, if ferromagnetism is not modelled with a function that allows composition dependence of magnetic properties, like the Curie temperature and Bohr magneton number, there will be complications in modelling

\(^2\)[http://kinetics.nist.gov/janaf/]
alloys. As a result, in the present work it was attempted to stick to the models suggested by Kaufman and Chase et al. \[8,17\] (Equation 2.3) for developing new unaries using the Calphad approach.

For the harmonic vibration of the atoms, the Einstein model is used in this work, as it was shown to be suitable for pure Fe \[20\]. It is true that this model compresses all phonon frequencies of the atoms to a single one but, up to intermediate temperatures, it can produce a good approximation of this contribution \[7\]. Above this temperature region, the power series of temperature used in Equations 2.1 and 2.3 can be considered the best correction for the anharmonicity and \(C_v - C_p\), if the model needs to represent such deviations \[7\]. Besides, the problems in the SGTE unaries are avoided in these descriptions. Finally, the magnetism can be nicely represented by the magnetic model suggested by Inden and Hillert and Jarl \[18,19\] from 0 K up to the melting point. As shown in the paper I, such models work fine for the case study of Mn. Mn can be considered the most complicated transition metal, with 5 allotropes and different magnetic behavior in each of them. The SGTE description of Mn is based on the assessment by Fernández Guillermet and Huang \[21\], from which the heat capacity of all solid phases is shown in Fig. 2.1a. The same is calculated in the present work, shown in Fig. 2.1b, and both are compared to the experimental data recommended by Desai \[22\]. The latter figure shows a more smooth and continues variation of \(C_p\) with temperature, from 0 K up to 3000 K, compared to SGTE.

![Graphs of heat capacity for Mn](image)

Figure 2.1: Heat capacity of solid phases for pure Mn, from SGTE and present work, compared to the experimental data recommended by Desai \[22\].

However, in some cases the Einstein or Debye temperatures do not predict correct results for harmonic behavior up to the \(\theta_E/\theta_D\). Graphite is the best example of such a case, since this allotrope of carbon is anisotropic. Carbon atoms vibrate with different frequencies in the \(z\) direction than in the \(xy\) plane. The heat capacity of graphite shows a specific curvature at low temperatures.
due to this phenomenon. Anisotropy in graphite comes from the weak inter-plane Van der Waals forces in the \( z \) direction and strong covalent bonds in the \( xy \) plane. This gives extraordinary properties to this allotrope. However, from a modelling point of view, the specific trend of heat capacity cannot be fitted by a single Einstein or Debye temperature. This was the main reason that in an earlier attempt by Naraghi et al. [23] to model carbon down to 0 K for an assessment of binary Fe-C, the Chen and Sundman’s model [20] could not be applied. Naraghi et al. [23] instead extrapolated the SGTE description from 298 K to 0 K, by a formulation based on the Chen and Sundman’s model [20], which was suggested by Vřešťálo et al. [24] to modify the current unaries (SGTE [3]). Nevertheless, although this description gives a perfect fit to the experimental data down to 0 K (Fig. 2.2b), as mentioned in [7], such descriptions do not have any physical meaning and should be avoided in developing third generation of Calphad databases.

To keep consistent to Chase et al. [17], in the present work different solutions were attempted. The first solution which came to mind was using a temperature dependent Einstein temperature. Einstein and Debye temperatures are in principle fitting parameters to a property of the materials which shows variation with temperature. Thus, if different temperature regions or different properties are selected for fitting, different Einstein temperatures will be achieved [7]. This can be interpreted as if the Einstein model is compressing the whole phonon spectrum to a single frequency. So, no wonder that different properties, e.g. thermal expansion, heat capacity, entropy, etc., reflect different information about the phonon spectrum. It can be summerised that, by having different Einstein temperatures and parametrizing them using a temperature-dependent expression, one may be able to conserve more information about the spectrum of the harmonic contribution [25].

This solution seems empirical and useful, but in practice this cannot be used in the Calphad type of software; since these software work based on the derivatives to calculate the thermodynamic properties. Using any type of expression rather than the standard Einstein model for the harmonic contribution to the heat capacity will result in Gibbs energy descriptions different from those in Equations 2.4 and 2.5 and cannot be used. Besides, the numerical problems due to the logarithmic nature of the Einstein model (dealing with negative logarithm in specific temperatures) causes more difficulties and limitations for this idea.

The best solution for expressing the specific thermodynamic behavior of graphite within the current limitations was found to be different Einstein temperatures, to separate different vibration branches. The details of this work are presented in article III, from which the graphite description is shown in Fig. 2.2a. The low temperature region is shown in higher magnification in Fig. 2.2b, using 5 Einstein temperatures (purple solid line) and 2 Einstein temperatures (black solid line) obtained in the present work, compared to the experimental data and 2D and 3D Debye model, suggested by Krumhansl and Brooks [26] (dotted lines).

It can be seen that by using 2 \( \theta_E \), the agreement with experimental data is not acceptable below 100 K, while by using 5 \( \theta_E \) for describing the unique DOS of
Figure 2.2: Heat capacity of graphite from present work with $5\theta_E$ (solid purple line), compared to applying Debye model (dotted lines), $2\theta_E$ (solid black line) and experimental data.

graphite, a perfect fit can be achieved.

At the end of this section, it is worth mentioning that the major question regarding the model by Chen and Sundman [20] is that why the Einstein model is used instead of the Debye? It is generally believed that since the Debye model is replacing the single spectrum (from the Einstein model) by a statistic distribution over temperature, better agreement to the experimental heat capacity can be obtained by applying it. Although this argument is correct for the intermediate temperatures, at low temperatures, either model is adequate. This is shown in Fig. 2.3 for case study $\alpha$-Mn, calculated by an open-source Calphad program, called pycalphad [27]. Fig. 2.3 shows small differences between these two models, for this element at $T < 100$ K. This similarity, and the fact that the Einstein model is more convenient for software implementation and numerical solutions than the Debye, made this model the most proper choice for developing the new generation of Calphad databases at present.

2.2.2 Modelling liquid/super-heated solid

In developing the first and second generations of Calphad databases, the liquid phase was modelled by optimizing fitting parameters of a simple polynomial, to the enthalpy of fusion and heat capacity data. In principle, the heat capacity of the solid phase was extrapolated above the melting point, using the well-known Meyer-Kelley polynomial, presented in equation 2.6 [28]:

$$c_p = a + bT + cT^{-2} + dT^2$$  \hspace{1cm} (2.6)

However, when modelling the liquid, one should bear in mind a phenomenon
called the Kauzmann paradox \[28\]. The Kauzmann paradox is about supercooling the liquid, or superheating the solid, to a very low temperature, or a very high temperature respectively. In case of solid, if the crystallisation is avoided, a paradox would occur in which the entropy of the undercooled liquid becomes smaller than that of the stable crystalline state, at a temperature called "Kauzmann" temperature \(T_K\). In reality, a glass transition occurs at temperatures above the Kauzmann temperature and there is no paradox, since the glass has almost the same entropy as the solid crystalline phase.

The same goes for superheating the crystal towards high temperatures when at "inverse Kauzmann" temperature, the entropy of the crystal becomes larger than that of the stable liquid phase. The amorphous phase, however, has an entropy equal to the entropy of liquid at this temperature.

To avoid these problems, it was suggested in SGTE \[3\] to model the \(C_L^p\) and \(C_S^p\) in such a way that their difference goes to 0 at \(0.5T_m\) and \(1.5T_m\). They also tried to assure that the Gibbs energy curve of the liquid intersects the one for solid only once (at \(T_m\)). It was attempted to keep the heat capacity of liquid constant above the melting point, which was believed to be the true physical picture.

The SGTE extrapolation causes several problems, among which the artificial break points (kinks) in entropy and heat capacity at the melting point of the pure elements are the most serious. These break points remain as artifacts in the higher-order systems, as well. The other problem is that the entropy and heat capacity below the melting point, calculated from the extrapolated thermodynamic functions describing liquid, do not have meaningful values. Thus,

Figure 2.3: Comparison between Debye and Einstein model, for the case study \(\alpha\)-Mn, calculated by the pycalphad program \[27\].
these functions are not a good basis for the description of glassy or amorphous alloys [29].

To overcome these problems and developing models with physical meaning, the two-state model was suggested by Ågren [30]. Ågren [30] suggested that liquid and amorphous (glassy phase) can be treated as one phase in the whole temperature range. In this model, the liquid-amorphous phase is assumed as a mixture of the two types of atoms: defected and non-defected ones. Here, the defected atoms are those being introduced into the glassy structure on heating, having translational degrees of freedom and the possibility to introduce defects such as vacancies in the material. The Gibbs energy of this mixture can then be formulated similar to any other solution phase, as Equation 2.7:

$$\Delta G = G - G^\circ = x(\Delta H_d - RT) + RT \ln(x \ln x + (1 - x) \ln(1 - x))$$  \hspace{1cm} (2.7)$$

where $x$ is the fraction of defected atoms and $G^\circ$ is the Gibbs energy of defect-free system. The equilibrium number of defects can be found from minimizing equation 2.7, i.e. $\frac{\partial \Delta G}{\partial x} = 0$, as equation 2.8:

$$x = \frac{e^{-\Delta H_d/RT}}{1 + e^{-\Delta H_d/RT}}$$  \hspace{1cm} (2.8)$$

where $\Delta H_d$ denotes the enthalpy of formation of one mole of defects in the glassy state. The transition from liquid state to glass occurs when a certain amount of defected atoms is reached (15% of the atoms), i.e. in a certain configurational entropy and enthalpy. If equation 2.8 is normalized to $\Delta H_d$, the glass transition from equation 2.7 can be obtained as $\frac{RT}{\Delta H_d} = 0.37$. A popular rule of thumb, on the other hand, offers that the glass transition occurs at $T_g \approx 0.7 \Delta H_d$. It can be concluded that the melting temperature, i.e. $3T_g$, occurs if the difference in enthalpy between the perfectly glassy state and crystalline state is $0.7\Delta H_d$ at 0 K.

The defected atoms properties, e.g. $H_d, S_d$ etc., can be physically interpreted as terms which describe the vibrational and translational degrees of freedom of the atoms. In $T > T_m$ atoms have more translational degrees of freedom, i.e. more liquid-like behavior, while below $T_m$, they have more vibrational degrees of freedom, i.e. solid-like (amorphous) behavior.

This model was tried at the 1995 Ringberg workshop [28] for modelling liquid phases, avoiding SGTE type of artifacts in the whole temperature range, from 0 K up to far above the melting point. They introduced the Debye/Einstein parameters to the model, to describe the harmonic vibration of atoms, while the anharmonicity can be treated by a polynomial, fitted to the available experimental thermodynamic data. The formulation was nicely presented by Chen and Sundman [20], as Equation 2.9:

$$G^{liq-am} = G^{am} - RT \ln[1 + exp\left(\frac{-\Delta G_d}{RT}\right)]$$  \hspace{1cm} (2.9)$$
where \( \Delta G_d = \delta G^{\text{liq}} - \delta G^{\text{am}} \) and \( \delta G^{\text{am}} \) and \( \delta G^{\text{liq}} \) are Gibbs energy of the system where all the atoms are in the amorphous-like state and liquid-like state, respectively [20].

In this equation \( \Delta G_d \) is the Gibbs energy for formation of one mole of defects in the glassy state., \( \delta G^{\text{am}} \) is modelled as explained above, e.g. using the Einstein model and some fitting parameters, shown in equation (2.10):

\[
\delta G^{\text{am}} = G_h^m \left( \frac{\theta_E}{T} \right) + A + BT^2 + \ldots
\]  

(2.10)

The \( \theta_E^{\text{sys}} \) can be selected as initial value for the optimizing parameter \( \theta_E \) and evaluated together with other coefficients, i.e. \( A \) and \( B \), by fitting to the experimental data. The \( \Delta G_d \) term has an expression like equation (2.11):

\[
\Delta G_d = C + DT + ET \ln T + \ldots
\]  

(2.11)

The \( C \) and \( D \) terms in this equation can be understood in the same way as described for the glass transition, in [30]. It is assumed that at the melting point we have: \( RT_m \approx \Delta H_d \), from which at \( T_m \), we have \( \Delta G_d = -0.7 \Delta H_d \). It should be kept in mind that these conclusions are valid only if there are no other factors contributing to the Gibbs energy difference between glassy state and crystalline at 0 K except the defects, and the formation of one mole of defects gives an extra entropy increase of \( R \) to the liquid at \( T_m \). Consequently, the \( C \) parameter in Equation (2.11) can be estimated equal to the enthalpy of fusion and \( D \) equal to \(-R\) (known as the "communal entropy"). The \( E \) parameter is optimized together with other fitting parameters in modelling amorphous phases, i.e. \( \delta G^{\text{am}} \) in Equation (2.9) using the experimental data for heat capacity of liquid and amorphous phases.

This model was shown to work perfectly well for many case studies, including Fe [20]. The magnetic contribution can be added to this equation using the same formulation, described in [2.2.3] if the amorphous phase shows magnetic properties. Also, there might be cases where by using \(-R\) for parameter \( D \), the experimental data cannot be fitted properly. In such cases, it is recommended to use the entropy of melting instead [29].

It is worth mentioning that the validity of the assumption by SGTE to keep \( C_p^L \) constant at \( T > T_m \), has been difficult to examine in the absence of experimental or calculated data for liquid in that temperature region. For many elements there is not much reliable data for the liquid phase at temperatures above or below the melting point.

It is shown in [29], for the case studies of Au and Ga, for which there are experimental data for \( C_p^{\text{liq-amorph}} \) below the melting point, that this quantity actually increases by decreasing temperature. Becker et al. [29] showed that this behavior can be accurately modelled by the help of the two-state model. Regarding such behavior, Grimvall [31] analyzed the temperature dependence of the heat capacity of several low-melting metallic liquids. He concluded that
there is a gradual decrease in $C_v$ by increasing the temperature, from the Dulong Petit value of $3R$ towards $2R$ at $T > T_m$. It was also pointed out by Becker et al. [29], from MD simulations, both the classical interatomic-potential basis and DFT ones, that the enthalpy of liquids is roughly linear above the melting temperature.  

Heat capacity of unary Al, modelled using the two-state model in paper IV, is shown in Fig. 2.4 (black solid line), compared with the SGTE description (red dashed line) and experimental data from Desai [32] in blue. As can be seen, by the help of the two-state model the artificial kink from SGTE is gone. Moreover, the description agrees with the extrapolated $C_p$ values above the melting point (error bars show the uncertainty of the extrapolated data from Desai [32]). In addition, $C_p$ decreases with increasing temperature above $T_m$, as predicted by Grimvall [31], and shows a temperature dependent behavior, as shown by MD simulations [29].

Figure 2.4: Heat capacity of liquid Al using the two-state model (black solid line), compared with SGTE (red dashed line) and experimental data from Desai [32] in blue. Error bars show the uncertainty of the experimental data.
The liquid group in Ringberg 2013 [29] also presented a detailed review of different techniques and models. It was concluded that the two-state model is consistent with the understanding of glassy behavior derived from experiment and molecular simulation. Although it cannot capture the full complexity of an energy landscape approach, the simplicity of the model without neglecting the characteristic features of the liquid makes it a promising approach to model liquids and amorphous phases in the Calphad approach [29].

In that work, [29], a detailed description of MD methods for calculating thermodynamic properties of liquids is presented and compared with the two-state model in Calphad, which will be explained briefly in 3.2.

2.2.3 Modelling magnetism

In the first generation of Calphad databases, [8,33], the magnetic contributions were neglected, due to the complexity of this phenomenon. In the SGTE [3] databases, on the other hand, this important contribution was included, using the Inden-Hillert-Jarl model (called "IHJ" model in short) which will be explained in detail in this section [18,19]. But first, it should be mentioned that an improper treatment of magnetism was one of the main reasons for stronger attempts in developing the third generation of Calphad databases [34]. The discrepancy, found by Xiong et al. [16], between experimental and assessed data for magnetic properties of pure Cr, seemed to cause serious problems for proper use of these thermodynamic descriptions as an input in phase field modelling of spinodal decomposition.

The reason of data selection for magnetic properties by SGTE [3] is not clearly explained. However, it is expected that reducing such error will improve the predictability of thermodynamic descriptions, significantly [7].

A magnetic model for treating unaries was suggested by Tauer and Weiss [35]. They suggested empirical formulations, shown in equations 2.12 and 2.13, for the magnetic enthalpy and entropy, by comparing these quantities for some elements and compounds, where $T_c$ is the critical temperature, i.e. Curie or Néel temperature, and $2s$ is the number of unpaired electrons [35]:

$$H^{mag} = RT_c$$  \hspace{1cm} (2.12)

$$S^{mag} = \ln(2s + 1)$$  \hspace{1cm} (2.13)

The basis for these formulations was subtracting the lattice vibrations from the experimental properties, using a Debye model and then calculating the terms $\frac{H}{RT_c}$ and $\frac{S^{mag}}{R\ln(2s+1)}$. They found almost the same values for these quantities for all the elements and compounds they studied, and concluded that these might possibly be proper formulations for all materials. This approach has been the basis for Calphad modelling, in which the most important task is the proper deconvolution of non-magnetic heat capacity. Thus, the results totally depend on deconvolution method, especially since there is no experimental method for measuring the magnetic heat capacity, but only different magnetic properties.
Their model was later completed by Inden \cite{18}, by adding a truncated series of temperature to the heat capacity, which was obtained by fitting a mathematical expression to $c_p$ data for different elements, with the same structure. In this way, Inden \cite{18} made this formulation structure-dependent, shown in equations 2.14 and 2.15:

$$C_{p}^{\text{mag}} = KR \ln \frac{1 + \tau^{-5}}{1 - \tau^{-5}}, \tau = \frac{T_c}{T}$$ (2.14)

$$S_{p}^{\text{mag}} = \ln \beta + 1$$ (2.15)

where, $K$ is the structure-dependent constant. The logarithmic treatment by Inden \cite{18} was later replaced by polynomials by Hillert and Jarl \cite{19} since the integration of such expressions, to obtain the Gibbs energy, would result in a very complicated expression which is in principle polynomial-based. Thus, it can be simpler to replace it by the polynomials before integration. Equations 2.16 and 2.17 show the magnetic contribution to the heat capacity, based on the model by Hillert and Jarl \cite{19}:

$$C_{p}^{\text{FM}} = KR(\tau^3 + \frac{\tau^9}{3} + \frac{\tau^{15}}{5}), \tau < 1$$ (2.16)

$$C_{p}^{\text{PM}} = KR(\tau^{-5} + \frac{\tau^{-15}}{3} + \frac{\tau^{-25}}{5}), \tau > 1$$ (2.17)

This formulation has been the basis for modelling magnetism in Calphad since then, except that the powers of the temperature polynomial was modified by Chen and Sundman \cite{20}, to have a better fit to the magnetic properties of bcc-Fe, as Equations 2.18 and 2.19:

$$C_{p}^{\text{FM}} = KR(\tau^m + \frac{\tau^{3m}}{3} + \frac{\tau^{5m}}{5} + \frac{\tau^{7m}}{7}), \tau < 1$$ (2.18)

$$C_{p}^{\text{FM}} = KR(\tau^{-n} + \frac{\tau^{-3n}}{3} + \frac{\tau^{-5n}}{5} + \frac{\tau^{-7n}}{7}), \tau < 1$$ (2.19)

In these equations, $m = 3$ and $n = 5$. This treatment can reproduce the lambda shape of the magnetic heat capacity of bcc-Fe better, and has been applied in the present work, for new unaries.

It is worth mentioning that in the Ringberg workshops, there has been a group, focusing on the magnetic transitions, called the ”Lambda transition” group. In the work of this group in 1995 \cite{36}, different approaches were discussed and it was concluded that the polynomial treatment offers enough flexibility for modelling magnetism, especially if the powers of temperatures are allowed to vary during optimization. It was also recommended that Inden’s model is also implemented in the Calphad software as an alternative, for the cases where Hillert’s model is not sufficient, e.g., unary Gd.

One important issue discussed in Ringberg 1995, \cite{36}, is the meaning of the $\beta$ parameter, in Equation 2.15. This value refers to the magnetic moment of the
atoms, which is a measurable quantity. However, in some cases, such as Cr and MnO, if the experimental value is used, it will result in a strong singularity at the critical temperature, thus a sharp lambda peak in $C_p$. The Calphad community, alternatively uses a "thermodynamic" $\beta$, which in principle, is a fitting parameter to the magnetic entropy and heat capacity, and has a smaller value than the large experimental one in such cases.

The explanation above, describes the reason of the discrepancy between SGTE [3] and experiment for magnetic properties of some elements [16]. While using this thermodynamic $\beta$ can prevent strong singularities in magnetic heat capacity, it seems this can decrease the predictability of higher-order databases. One solution suggested by Xiong et al. [34], was to use the individual magnetic moments of atoms in the Calphad software, instead of the average one. This has a more physical meaning, since in other cases rather than ferromagnetic materials, different atoms have in reality different magnetic moments. As mentioned in [36], the magnetic entropy can be calculated using Equation 2.20:

$$\Delta S_{mag} = R \sum x_i \ln(\beta_i + 1) \cong R \ln(\langle \beta \rangle + 1)$$ (2.20)

where, $\langle \beta \rangle = \sum x_i \beta_i$. $\beta_i$ and $x_i$ in this equation are the mole fractions and magnetic moments of atoms kind $i$, respectively. Such formulation can be used for alloys containing elements of different atoms, or one element, containing the same atoms with different spins. This will allow modelling of more complicated magnetic configurations than the simple ferromagnetic and anti-ferromagnetic materials, e.g. none-collinear configurations, as discussed in the Lambda transition group’s publication, in Ringberg 2013 by Körmann et al. [37]. More details of the publication from the Lambda transition group, in Ringberg 2013 [37] is presented in Chapter 3, since they have mainly focused on DFT methods. It only can be mentioned in this section that Körmann et al. [37] recommended to use magnetization ($M$) instead of magnetic moment to model magnetic contribution to the heat capacity. This quantity is much easier to measure and one can calculate the thermodynamic potential for a ferromagnet ($\phi$), using the Ginzburg expression (Equation 2.21):

$$\phi = \phi_0 + \frac{1}{2} AM^2 + \frac{1}{4} BM^4 + \frac{1}{6} CM^6 + \ldots$$ (2.21)

where the coefficients $A, B, C, \ldots$ are parameters depending on temperature or external pressure. If $M_0$ is the ground state magnetization, the magnetic heat capacity can be calculated as equation 2.22:

$$C_{mag} = -\frac{\tau}{T_C} [\phi_0(\tau) + \frac{M_0}{2} A''(\tau) \sigma^2 + \frac{M_0}{2} A(\tau) \frac{\partial^2 \sigma}{\partial \tau^2}]$$ (2.22)

where $\sigma = M/M_0$.

At the end of this section, it can be concluded that although the Calphad approach is simple, it can reproduce the lambda shape of the magnetic transitions.
accurately, and can be used until there is a possibility of using more advanced techniques which can serve this purpose equally well.

**Two-state magnetism in Fe**

For modelling magnetism in fcc-Fe, Chen and Sundman [20] used the two-state model, suggested for the first time by Weiss [38], to model the 'Invar' effect observed for this allotrope (the decrease of volume with increasing temperature). The "Weiss model" suggests that fcc-Fe has a Néel temperature equal to 67 K and a Curie temperature equal to 1800 K. As a result, this phase has a low-moment-low-volume antiferromagnetic ground state and a high-moment-high volume ferromagnetic state. In the finite temperature range a mixture of two types of spins co-exist, i.e., low and high spins. This model gives a reasonable estimation of the magnetic properties of fcc Fe. However, the existence of the stable ferromagnetic state in fcc-Fe has never been proven, neither by first principles calculations nor by experiments. In the finite temperature range, fcc-Fe has the paramagnetic state, which is a mixture of antiferromagnetic electron spins and an unknown, complicated electron spin. This combination was simplified in the "Weiss model" to estimate the overall magnetic effect by assuming the existence of the ferromagnetic state. Equation [2.23] presents the contribution of this phenomenon to the Gibbs energy:

\[ G^{2st} = -RT \ln(1 + \frac{g_2}{g_1} \exp(-\frac{\Delta E_{2st}}{T})) \] (2.23)

where \(-\Delta E_{2st}\) is the energy gap between the two states and the term \(\frac{g_2}{g_1}\) denotes the degeneracy ratio of the two states. If the mixture of AFM and FM spins is assumed for fcc-Fe, \(-\Delta E_{2st}\) can be fitted with experimental data and \(\frac{g_2}{g_1}\) has a value larger than 1. The same situation is assumed for Fe-Ni alloys in a composition range that shows the Invar effect.

The only limitation of this model is the numerical problem, when implementing in the Calphad software for higher-order systems. At present, the parameters of this model can be entered in the Thermo-Calc software, using a parameter named "GD" in the program, as equation [2.24]

\[ GD = A + BT \] (2.24)

This means:

\[ GD = \Delta E_{2st} - RT \ln \frac{g_2}{g_1} \] (2.25)

which yields:

\[ G^{2st} = -RT \ln(1 + \exp(-\frac{\Delta E_{2st} - RT \ln \frac{g_2}{g_1}}{T})) \] (2.26)

However, using this parameter for binaries is not straightforward. The possibility of expanding this model using the GD parameter in Thermo-Calc software, was tried for the Fe-Mn binary. The main difficulty in this case is that there is
no such two-state contribution to the pure fcc-Mn. Therefore, the parameters should be set in such a way that $G^{2st}$ is equal to zero for pure Mn. This can be done by setting $-\Delta E_{2st}$ equal to an extremely large value which means the energy difference between the two states is too large for fcc-Mn, so it is not possible for them to co-exist. Meanwhile the degeneracy ratio, $g_2/g_1$, should be set to a value $\approx 1$, that implements the co-existence of antiferromagnetic and paramagnetic states.

For implementing $G_D = A + BT$ in Thermo-Calc, the $A$ variable should be set to an extremely large value and $B \approx 0, (g_2/g_1 \approx 1)$ to have no contribution to pure fcc-Mn. The difficulty with this solution is that the $A$ value cannot be chosen randomly, since it should be possible to fit experimental data of $-\Delta E_{2st}$ in other systems, e. g. Fe-Ni. The only possible solution for the time being, is to define the $G_D$ for fcc-Fe in the old way of writing functions in Thermo-Calc, instead of using the $G_D$ parameter in this software. Other aspects of proper treatment of magnetism in higher-order systems will be discussed in Chapter 4.
Chapter 3

Using DFT methods for Calphad modelling

The main attempt in developing unary databases since the beginning has been to use the quantum theory, in particular the DFT method, as a tool or an input for Calphad modelling. This intention could not come to reality in the first and second generation of Calphad databases, due to the limitations of computers in the past. Since the 1990s, when computational tools improved enormously, more of this theory could be applied for different systems.

Although the ab-initio methods are based on the fundamental theories of quantum physics, there are two types of parameters, due to approximations for computational implementations, that can affect the accuracy of the results: controllable parameters, which can be converged and reliable error estimate can be provided for, and non-controllable parameters, which originates from the approximations and assumptions made within DFT implementations. Examples of controllable parameters are the quality of the basis set and the sampling density of k-points, the size of the supercell, etc. The accuracy of the calculation results is strongly dependent on the convergence of controllable parameters [39]. Non-controllable parameters, on the other hand, come from the basis of DFT theory itself, different types of the exchange-correlation (XC) functional take advantage of specific approximations, which determine their accuracy. However, there is no best or worst XC, since each XC might work the best for different systems. For example, among the two most frequently used XC functionals, i.e. local-density approximation (LDA) and the generalized-gradient approximation (GGA), GGA gives more accurate results for bulk properties of metals, while LDA can provide more accurate values for vacancy formation energies [39].

In this chapter, application of DFT techniques for calculating different contributions in the heat capacity is described. It is also shown how these techniques can be very useful for developing empirical models for Calphad assessments, with a more physical basis.
3.1 Modelling magnetism

DFT can be a very useful tool for calculating different magnetic properties, even in cases where no experiments can be performed [37]. Such methods have the advantage that the degree of freedom can be switched one-by-one, thus each thermodynamic contribution can be calculated separately. However, they might not be additive, due to strong interactions between different contributions. Spin polarized DFT is available to compute accurate magnetic ground state properties. For calculating magnetic excitations additional approaches are required. The "Lambda transition" group in Ringberg 2013, Körmann et al. [37] suggested two model Hamiltonians. Since the model quantum-mechanical Hamiltonian shows that the origin of the magnetism is associated with the interaction between electrons, one can use model Hamiltonians, i.e., Anderson and Heisenberg Hamiltonians, describing this interactions, as suggested in [37]. Details of these two methods are explained in [37]; further discussion is not in the scope of this thesis. What can be mentioned here is that for solving them, one may use some approximations, for example Weiss mean-field (MF) or Green’s functions as implemented in random-phase approximation (RPA). However, for practical implementation into Calphad software, a mathematically closed analytical expression for these Hamiltonians is required, which is not generally possible. The best thing one can do using such methods, is using the calculated properties as an input in Calphad assessment, i.e. instead or together with experimentally measured data, named as a "virtual matter experiment" in [37].

As already mentioned, although DFT methods are based on very strong physics, they have some limitations regarding magnetism calculations. In this sense, their accuracy is the main issue, since the different treatments of exchange correlation functionals is a completely uncontrollable approximation. Also, even ab-initio based approaches contain some empirical assumptions which cause some uncertainty [37]. So, one should be very careful when selecting or using a set of DFT data.

In the present work, DFT techniques were used for calculating the thermodynamic properties of magnetic materials and the results were used as an input or ”virtual matter experiment” in the Calphad modelling. The two main techniques used in this work are exact muffin tin orbital (EMTO) and ab-initio molecular dynamics (AIMD) methods, explained in the following section. In the AIMD calculations, the VASP-PAW [40,41] code was used for the initial MD runs for obtaining inter-atomic potentials.

3.1.1 EMTO method

The EMTO formalism was developed by Andersen et al. [43], in 1994, as the third generation of MTO methods. The main idea was to avoid the full potential complexity, but to achieve the same accuracy in the electronic structure and total energy calculations. The initial EMTO code was developed by Vitos et al. [44,45] and later developed by Kollar et al. [46] and Vitos et al. [47,48].
In combination with the locally self-consistent Green’s function technique, EMTO provides accurate description of the energetics of random alloys with atomic short range order. It allows one to consider multicomponent alloys in the paramagnetic state with longitudinal spin fluctuations and can be used for non-collinear and spin-spiral magnetic calculations. EMTO also provides access to the effective chemical interactions, which can be used in the atomistic modelling of alloys. It can be used for calculations of the magnetic exchange interaction parameters, which allows investigation of magnetic properties of alloys. This code provides relatively accurate total energies for close-packed systems. However, since the energetics are not accurate enough, it cannot perform atomic relaxations and, consequently, it does not have the possibility to do molecular dynamics simulations. The accuracy is greatly reduced for open and complex structures.

EMTO codes are considerably time- and computationally-efficient, and can be used to calculate the 0 K energy values for very complicated structures easily. This is a significant advantage for the Calphad-based users who do not want to spend a long time to learn the difficulties and complications of the other DFT techniques. Although the code is not user friendly, by the help of code developers one can manage to gain results that are sufficient for Calphad modelling. When the 0 K results, which are very valuable when dealing with metastable phases using Calphad approach, are obtained, one even can get the finite temperature properties, e.g. $C_v$ and bulk modulus, by fitting the 0 K data to the Debye-Gruneisen model.

In addition to providing data for metastable phases, DFT methods can be a great tool to find the support for reliable data selection in case experimental data from different measurements show discrepancy. This is shown in paper II, where the EMTO method is used for calculating the magnetic ground state of metastable hcp alloys and unaries in Fe-Mn system at 0 K. The problem in this case was the completely different composition-dependence of critical temperature in hcp Fe-Mn alloys from different measurements, as shown in Fig. 3.1. Such discrepancy not only causes difficulty during assessment of binaries; it also makes it impossible to decide the magnetic ground state of the metastable unaries. Since hcp Fe and Mn are not stable at ambient pressure and temperature, measuring their magnetic properties accurately is not possible. From such scattered data in the binary, it is impossible to extrapolate a value for $\beta\mu$ to the pure corners confidently.

It is shown in paper II that the disordered local moment (DLM) state and different types of antiferromagnetism (AFM) can be calculated for disordered hcp alloys of this system using EMTO, to find a strong support for the magnetic ground state of unaries. The two different AFM configurations are shown in Fig. 3.2. These results predict that in hcp-Fe, AFM-II is the ground state, while hcp-Mn is paramagnetic in different volumes. The results for the alloys of such combination agree well with the experimental data by Hinomura et al. [49], Fig. 3.3, proving these data can be trusted in binary optimization.
Figure 3.1: Discrepancy between different data-sets for the critical temperature versus composition in hcp Fe-Mn alloys.

Figure 3.2: The anti-ferromagnetic structures denoted by AFM\textsubscript{I} (a) and AFM\textsubscript{II} (b) for a hcp described by an orthorhombic cell. Layers located at $z = 0$ are in blue and layers with $z = \frac{c}{2}$ are in yellow. In the AFM\textsubscript{I} structure the anti-ferromagnetic layers are perpendicular to the $z$ direction while in AFM\textsubscript{II} the layers are perpendicular to the $x$ direction.

### 3.1.2 UP-TILD and TU-TILD methods

UP-TILD method, (short for Upsampled Thermodynamic Integration using Langevin Dynamics), was developed by Grabowski et al. [50] for calculating thermodynamic properties of Al at finite temperature. This method takes advantages of a clever sampling technique, to perform time efficient ab-initio molec-
Figure 3.3: Variation of magnetic moment versus composition in hcp Fe-Mn alloys, calculated by EMTO.

Having such an energy surface, one can derive all other thermodynamic properties which can be directly used as an input into Calphad optimization. The UP-TILD method was extended to the TU-TILD, Two-stage Upsampled Thermodynamic Integration using Langevin Dynamics, by Duff et al. [51], for decreasing the computational time and resources even further.

The basis of these two methods is a perturbative upsampling. In both cases, the energy surface is calculated for a system with low convergence parameters, i.e., low number of k-points, cutoff energy, etc. The low parameters (low-para) save computational time and resources. In the next step, snapshots of low-para calculations are calculated with high parameters (high-para). These snapshots make it possible to define a path for coupling these two results. The only criteria here is that the energy differences between these two sets of calculations should be almost constant. The results of these calculations for unary Al [50], are shown in Fig. 3.4.

To calculate the full energy surface, one needs to capture different aspect of physical phenomenon, i.e. electronic, harmonic, anharmonic and magnetic. However, calculating the anharmonicity is a very difficult task. The low-para energies actually contain the fully anharmonic vibrations and should be calculated relative to a reference. This reference should be simple to calculate and validate, for example the quasi-harmonic approach. A coupling constant is then used for integrating the system across this reference and fully anharmonic state. Across the path, the system can be considered as a mixture of fully anharmonic and
fully harmonic in different steps of the path, i.e. different $\lambda$ values. 

Within the UP-TILD method, the DFT system is coupled via thermodynamic integration to a quasiharmonic reference. In strongly anharmonic systems, such a coupling is very inefficient. Within TU-TILD an intermediate system is introduced by fitting an optimized interatomic potential (using the MEAMfit code [52]) to a set of DFT MD simulations. This potential allows for a very efficient coupling to DFT via thermodynamic integration on the one hand, and to the quasiharmonic reference on the other hand (see Fig. 3.5).

The UP-TILD and TU-TILD methods have successfully been used for calculating thermodynamic properties of several elements [50, 51, 53–55]. In the present work, the bcc phase of unary Mn was investigated using this method, as the first paramagnetic case study. Since bcc is a high-temperature allotrope of Mn, there are some experimental data for the heat capacity of this phase. These experimental data and simplicity of the bcc crystallographic structure make it possible to validate this method efficiently. After assuring the accuracy of the method for this case, one can use the technique for more complicated cases, or use it for the dynamically unstable phases confidently.

The details and results of these calculations are presented in Paper VI. The special quasirandom structures (SQS) supercell was used for paramagnetic configuration of atoms in this work and several improvements were put forward to increase the accuracy and agreement with the experimental data.
One of the main challenges in this work was to create a smooth energy landscape for deriving thermodynamic properties. Since heat capacity is correlated to the second derivative of the Gibbs energy, it is very sensitive to the energy changes and even small oscillations in the energy can cause large difficulties in the derivations. This is shown in Fig. 3.6.

This figure shows energy versus volume, at 1000 K, calculated from different approaches. The red curve represents the energies from the quasi-harmonic approach for which the imaginary frequencies are eliminated to aid comparison. As can be seen, this curve show the largest oscillations of all. However, the results from the standard TU-TILD (gray curves) do not vary completely smoothly versus temperature, either.

Paramagnetism can be suspected to be responsible for this problem, especially at volumes larger than the equilibrium volume (2.79 Å), where spins of the atoms have more freedom. Since the oscillation of the free energy is due to the various spin configurations that are accessible at T=0 K, changing the reference state to another temperature, e.g. room temperature, can solve the problem. The black curve, which is calculated with reference to 298.15 K, proves this to be true. This concept can be understood through the schematic of the energy landscape in Fig. 3.7.

Fig. 3.7 shows that, since there are no well-defined T=0 K properties, this temperature cannot be used as the reference state, because this leads to jagged free energies. Deriving thermodynamic properties from such an energy surface is impossible. Using instead room temperature to define a reference state, smooth free energies are obtained and thermodynamic properties can be derived. The results of present calculations for heat capacity and entropy of a SQS bcc supercell of 54 Mn atoms are shown in Fig. 3.8. In case of entropy, the agreement

\begin{equation}
F_\text{harm} + \Delta F_\text{TU-TILD} + \Delta F_\text{DFT,low} + \Delta F_\text{DFT,high}
\end{equation}
2.7 2.75 2.8 2.85 2.9
Lattice constant (Å)
-450
-400
-350
-300
-250
Free energy (meV/atom)
qh without imaginary
qh+ah from TU-TILD with 0 K ref.
qh+ah from reference-free TU-TILD

Figure 3.6: Free energy at different temperatures as a function of volume for a SQS supercell of Mn atoms at 1000 K, obtained from different approaches (explained in text).

Figure 3.7: Schematic of how a change of reference state improves the energy landscape for thermodynamic integration.

is perfect with Calphad description. There is a small discrepancy between the present work and experimental data [22] in case of the heat capacity, which is assumed to be caused by magnetism. The present work shows how by changing the reference state, even the thermodynamic properties of a complicated paramagnetic structure for a dynamically

29
unstable phase can be calculated at finite temperatures, using the TU-TILD method. This can create a benchmark for the future in using DFT results as an input into the Calphad modelling for a wide variety of materials.

Another challenge in calculating thermodynamic properties of bcc-Mn was the omega transition. It has been observed that bcc Ti shows a tendency to transform to the omega structure \[^{[56]}\]. The crystallographic structure of \(\omega\)-Ti is shown in Fig. 3.9 from \[^{[57]}\].

The initial AIMD calculations results for bcc-Mn were carefully investigated to study the possible \(\omega\) transition in this allotrope. Schematics of the omega transition are shown in Fig. 3.10 from \[^{[56]}\]. The two inner atoms move in opposite [111] directions, whereas the outer atoms on the corners remain in the bcc positions.

The movement of the atoms was analyzed using an order parameter, which determines whether the atomic positions are shifted from the bcc positions (\(\Delta \approx 0\) shows no shift) after reaching the equilibrium. The results for different temper-
Figure 3.10: Schematics of omega transition in a bcc cell from [56], due to slight movement of atoms in the [111] direction.

atures and volumes are shown in Fig. 3.11. These values are results of MD runs for a $3 \times 3 \times 3$ SQS supercell of Mn atoms.

Figure 3.11: Order parameter of a equilibrated SQS supercell of 54 Mn atoms for different temperatures and volumes, showing weather the atoms are shifted from bcc positions ($\Delta \approx 0$ shows no shift) after reaching equilibrium.
As can be seen, for this supercell the omega transition occurs in 1000 ± 200 K in all volumes. Investigating the impact of the supercell size on the transformation temperature by calculating the order parameter from MD runs for a 64 atomic supercell show a decrease in transformation temperature of about 600 K. This can be understood by an analysis of the commensurability between bcc and ω as performed in [56]. Based on this analysis the transformation temperature for a size-converged supercell can be estimated around 700 K, but definitely below 1200 K. Thus, the maximum possible transformation temperature for the 54 atomic supercell is 1200 K.

Such investigations provide an understanding of the atomic scale behavior of materials and explains why in specific conditions, the atomistic results have to be carefully analyzed, since they are actually calculations of another phase (here, omega instead of bcc). Also, these results can be used for Calphad modelling of end-members that are stable or metastable phases in the higher-order systems, e.g. in alloys containing Ti.

3.2 Modelling solid and liquid phases

As mentioned in chapter 2 in the liquid group at Ringberg 2013 [29], different atomistic scale methods were reviewed, i.e., so-called quantum-mechanical/first principles/ab-initio and classical/empirical approaches, for calculating thermodynamic properties of liquids in temperature regions far from the melting point. Such techniques, if able to calculate thermodynamic properties of the liquid state, are very useful, especially in the cases where there is little or no experimental data. In addition, they can give us an insight into physical phenomena and mechanisms. These methods are generally based on calculating energies and forces between atoms and integrating different contributions to get the thermodynamic properties of the systems [29].

However, compared to the Calphad approach, the cost and speed of such calculation is enormously huge [29]. The expense of the atomic-scale methods makes them limited, in the best case, to systems containing less than a thousand atoms, and thus difficult to apply for the bulk properties of materials [29].

A relatively faster but less physically-based approach is the semi-empirical tight-binding method (TBM), which takes advantage of the inter-atomic interactions (also called force fields). In this method, a functional form is parametrized to the experimental or first-principles data. From this, functions are defined that describe the energies and forces between interacting atoms. Rather simple or complex functions can be used for this purpose, which also determines the expense of the calculations. The type of used potential has a very strong impact on the accuracy of the results [29].

The selected potential will be used for the further steps of the calculations. The common types of methods used for calculating thermodynamic properties of liquid phase are the MD or Monte Carlo (MC) methods. The details of these methods will not be explained here. It is only worth mentioning that if the forces in MD runs are determined using DFT methods, the simulation method
is called "ab-initio MD" or AIMD. If the interatomic potentials are used, it is
called "classical MD" or just MD.
MD simulations results can suffer from a dependence on the inter-atomic poten-
tial. To compare MD with experimental data for enthalpies and heat capacities
one needs to add the electronic, as well as the magnetic contributions in spin-
polarized systems [29].
Choice of reference state when reporting energies is however, the main issue
when using results of MD simulations in Calphad modelling. As they are often
reported in absolute units (such as eV/atom), not relative to another reference
state such as a fcc crystal at 300 K. This difference in the reference states
makes it very difficult to compare the thermodynamic quantities from different
approaches. AIMD methods, on the other hand, are very powerful tool to pro-
duce liquid data. This approach combines speed of the classical MD with the
accuracy of the quantum-mechanical calculation, for equilibrated liquid [29].
Becker et al. [29] tried the classical MD simulations, using different types of
fitted inter-atomic potentials for calculating the liquid properties of unaries Ni
and Au. For selecting the potentials, one should keep in mind that there is no
"best choice" for all problems or to recommend; the selections should be made
based on how well different potentials can reproduce the materials properties
relevant for the problem in the focus [29].
It is shown in [29] that the potential Au-G05 for Au and Ni-M12 for Ni, (both
derived from fitting to the AIMD simulation results), show a good agreement
with the experimental results and the two-state model. It can be concluded
that the two-state model accurately describes the changing degrees of freedom
of the atoms in the liquid with variation of temperature, which proves a strong
physical basis of this model.
As suggested in [29], MD methods can be used to adjust the parameters of the
two-state model in Calphad approach, when experimental data are missing or
conflicting. In that case, if these methods can successfully reproduce the liquid
properties, they can also provide data for metastable or arbitrary phases, e.g.
supercooled liquid or superheated solid. Becker et al. [29] also suggested more
testing of the two-state model for different systems, to assure its potential for
modelling liquids which show short range order.
The idea of using MD simulations for modelling the superheated solid was tried
in the present work for Al, as shown in paper IV, to predict and model the super-
heated crystalline fcc above the melting point. The method used in this work,
called TOR-TILD [58] (short for Two-Optimized References Thermodynamic
Integration using Langevin Dynamics), is an AIMD based method, in which
the inter-atomic potentials are carefully fitted to AIMD results and selected, to
ensure the best choice is made. The details are explained in the following.

3.2.1 Modelling superheated solid and undercooled liquid
using TOR-TILD method
One of the main challenges in using Chen and Sundman’s model [20], is how
to extrapolate the descriptions for the solids above the melting point, known
as superheated solid. Since physics is a major concern here, the main question is what physics can tell us about the behavior of crystalline phases above the melting point. From an experimental point of view, the answer is simple: there is no solid above the melting point. However, the strength of Calphad approach is its predictability for materials properties and stable phases, in different conditions. In the other words, each phase should have a description in the whole temperature/pressure/volume space, to make it possible to minimize the free energy of the system for finding the stable phases in equilibrium. Thus, even above the melting point of an element, where there is no solid, there should be a thermodynamic description and here is where the theoretical physics can come to help for giving us a picture in this region, while simple assumption of the solid’s heat capacity reaching that of the liquid, as suggested in [17], may sound fictional.

Modelling the superheated solid was also investigated in Ringberg 2013 [7], where it was argued that a temperature can be assumed for each solid above the melting point where the solid phase is no longer stable, called $T_{\text{inst}}$. If the phonon frequencies are calculated up to this temperature, they will start to get imaginary (negative values), above it. This means that above this temperature, the entropy of solid is larger than that of liquid, which is physically wrong. Here again, the DFT results could not be used directly in Calphad modelling even if there was a way to use phonons in Calphad software. However, this temperature gives us an idea about the region where the solid does not exist anymore and thus, can be used as the break point for high temperature description of the crystalline phase.

The TOR-TILD technique [58] is an improvement of the TU-TILD method, in which a DFT-optimized EAM potential is used. The potential is fit to a wide range of DFT molecular dynamics simulations, by the help of the MEAM-fit code [52], to simulate the superheated conditions. These potentials, which showed a highly efficient reference for free energy calculations of the solid phase, as in paper VI and [51], also show that the TU-TILD method is applicable to the liquid phase [58]. In paper IV, this method was used for modelling the fcc-Al above the melting point.

The heat capacity of fcc-Al phase was previously calculated very accurately at finite temperatures, using DFT method [55, 59]. In the paper IV, data from these works were extrapolated to the temperatures well above the melting point of pure Al (934 K). Fig. 3.12 shows results for different contributions to the heat capacity, compared to SGTE (light blue curve), showing a drastic increase at $T > T_m$.

The drastic increase above the melting point is also observed for the thermal expansion (Fig. 3 in paper IV), suggesting the "explosion" of the solid at higher temperatures.

Using the method developed in [58], the enthalpy of superheated solid was calculated for this element. The results show that at 1200 K, the superheated solid collapses to the liquid. Thus, it can be concluded that the extrapolated DFT data shown in Fig. 3.12 may be used for Calphad modelling only up to 1200 K. However, one challenge is how to model thermodynamic properties above $T_{\text{inst}}$. 


meaning the solid becomes unstable.

It is shown in paper IV, that a description can be suggested for fcc-Al (and liquid, accordingly) by the help of the enthalpy of superheated solid, in which the heat capacity of solid is not forced to reach the value of the liquid (Fig. 3.13). Besides, the solid phase does not become stable again above the melting point, as is the concern in [7]. This work shows how DFT can help in model development in the Calphad approach, as well as providing input for this modelling.

Another important issue which should be addressed in the third generation of Calphad databases, is how to model defects, especially vacancies [39]. Vacancies play an important role in modelling diffusion of the interstitial atoms and volume expansion. It is shown by experimental measurements [60][61] and DFT calculations [50][55] that vacancy contributions are significant at high temperatures, especially close to the melting point.

In [55], it is also shown that applying a linear Arrhenius function to model the energy formation of vacancies, enormously overestimates this contribution at lower temperatures for Al (Fig. 3.14).

Although the linear Arrhenius model agrees well to the experimental and DFT
Figure 3.13: Heat capacity of different phases of pure Al: I and II) fcc phase modelled based on DFT data for the superheated solid and liquid phase based on that, III and IV) fcc phase based on model by Chen and Sundman [20] and liquid phase based on that. Experimental data in red, from Desai [22], and $C_p$ data from DFT [55] in black.

Data at high temperatures (highlighted with shaded area in Fig. 3.14), using it as a contribution into the Gibbs energy of formation might cause a very sharp artifact at $T > T_m$, in higher-order systems. As shown in paper IV, one possible solution would be to subtract this contribution from the experimental heat capacity and optimize the fitting parameters to these data. In this way, the obtained description would be the non-vacancy part and that contribution can be added in a later stage properly. Results for case study Al (from paper IV) are shown in Fig. 3.13 where two descriptions are presented, curve I for data including vacancies and curve II, excluding them.

In the case of Al, the above solution was possible by the help of DFT data for the vacancy contribution to the heat capacity [50,55]. This method, however, is
Figure 3.14: Vacancy contribution to the heat capacity of Al, calculated by Glensk et al. [55], compared to the linear Arrhenius model and experimental data [60,61].

not straightforward or possible for all the other elements, for which such calculations do not exist. The main obstacle in calculating the vacancy contribution using ab-initio is that the harmonic or quasi-harmonic approximation for the finite temperature calculations is probably inadequate in many cases. Thus, the DFT results can be validated versus experimental data for the vacancy concentrations, since they can actually be measured experimentally only at high temperatures [39]. In such cases, some empirical relation [62] can be used. One challenge that needs to be addressed is how to include this contribution afterwards, in a consistent way for all of the elements with same crystallographic structure. This can be considered as the future work.

When dealing with the higher-order systems in Calphad assessments, the vacancies are defined as an end-member, whose properties are independent of the multi-component phases.
Chapter 4

Higher-order systems

4.1 Magnetism in higher-order systems

It was already pointed out in chapter 2 that magnetic transitions in elements are modelled in Calphad approach using the "IHJ" model [19]. The formalism of this model is presented in section 2.2.3 for unaries and end-members. The composition dependence for these properties in higher-order systems is added in the form of Redlich-Kister polynomials as interaction parameters fitted to the experimental data, shown in equation 4.1, [19]:

\[
\ln(\beta + 1) = x_A \ln(\beta_A + 1) + x_B \ln(\beta_B + 1) + x_Ax_B[b_0 + b_1(x_A - x_B) + b_2(x_A - x_B)^2 + ...]
\]

(4.1)

where \(b_0, b_1, b_2, \ldots\) are the interaction parameters.

This simple model was shown to be very practical and reasonably accurate. However, as explained in paper V, for implementing it in the Calphad software, it was decided to use only one Redlich-Kister polynomial for both types of critical temperatures, i.e. Curie and Néel temperatures [63], for the sake of simplicity and computational necessity. The different critical temperatures were distinguished by using the Weiss factor as a coefficient to magnetic properties of antiferromagnetic phases; -1 for BCC and -3 for FCC.

This model was used for three decades, until Xiong et al. [34] noticed such treatment can cause artifacts in systems including end-members with different magnetic ground states. A schematic of different situations is shown in Fig. 4.1 from [34].

This schematic shows nicely how using one single polynomial function for fitting two different types of critical temperatures will add unrealistic contribution to the Gibbs energy. In both cases, either for alloys showing a different magnetic ground state, Fig. 4.1a, or the ones having no magnetism at all, middle-range composition in Fig. 4.1b, this contribution is not true. Another problem for both cases is inflexibility of the model to properly fit the experimental points.
Figure 4.1: Schematic of different artifacts caused by using one single polynomial for fitting magnetic properties, from [34]. Figures show an imaginary A-B system and data points, including end-members with different magnetic ground states.

For these reasons, in the revised magnetic model [34], using two different Redlich-Kister polynomials were suggested and shown to reproduce the magnetic phase diagram of Fe-Cr binary more accurately. Xiong et al. [34] also showed how using this model can help in a more accurate modelling of spinodal decomposition in this system, and eventually phase field modelling of this phenomenon using the new thermodynamic description. Xiong et al. [34] also showed how imaginary contributions in a system can affect the higher-order systems, e.g. ternaries. This is a very important motivation for using this model in the third generation of Calphad databases.

The revised magnetic model was used in paper V, for the binary Fe-Mn. This is a good case study, since Fe and Mn have several allotropes showing totally different and complicated magnetic properties. Fig. 4.2 shows the magnetic
phase diagram for different phases in this system. This figure shows how by using the revised magnetic model, different critical temperatures can be modelled properly, instead of being neglected or treated by using empirical models in previous assessments of this system [64].

![Figure 4.2: Magnetic phase diagrams for different phases in the binary Fe-Mn system, using the revised magnetic model [34].](image)

### 4.2 Composition dependence of Einstein parameter

Using interaction parameters for different terms in the new models is mentioned briefly in paper V. This issue was discussed in the Ringberg workshop in 1997 [5] in the work by group 2 [65]. The main reason for this discussion was the treatment of composition dependence in magnetic contribution. As it was shown earlier, the normal formalism for the Gibbs energy in the Calphad approach, Equation 4.2, would cause complications for the magnetic systems.

\[
G_m = \sum_i x_i^2 G_i - T S_m^{ideal} + E G^m \tag{4.2}
\]

The magnetic contribution was thus separated from the description of the end-members and added to the solution instead, as a physical contribution, shown in Equation 4.3.

\[
G_m = \sum_i x_i (C G_i - G_i^{phys}) + G_m^{phys} - T S_m^{ideal} + E G^m \tag{4.3}
\]

In Ringberg 1995 [17, 28] it was suggested to treat other physical phenomena, for example the harmonic vibration of the atoms and glass-liquid transition, in a similar way. Since the Einstein model is used for modelling this contribution, the composition dependence of this parameter can be treated separately, instead of including it into the excess term.
According to Cacciamani et al. [66], the Einstein temperature for a solid solution can be defined as Equation 4.4 in which the masses of different atoms enter the Debye ($\theta_{D,S}$)/Einstein ($\theta_{E,S}$) term as a logarithmic averaged atomic mass, $M_{\log}^{-1/2}$:

$$\theta_{D,S} = 1.40\theta_{E,S} = K(x_1, x_2, ...) M_{\log}^{-1/2}$$

(4.4)

Here, $x_i$ is the atomic fraction of the element $i$, and the effective mass $M_{\log}$ is:

$$M_{\log} = M_1^{x_1}M_2^{x_2}...$$

(4.5)

and $K(x_1, x_2, ...)$ is a function which only depends on the electronic structure of the solid. However, generally there is not much known about the lattice vibration in solution phases. One way of treating this would be assuming a linear variation of $K$ between end-members. This should be done carefully in different systems, since this assumption might result in an error in the systems that the elements are so far away from each other in the periodic table.

It was pointed out in [65] that $\theta$ enters Equation 4.4 in the form of $\ln(\theta_T)$. If the linear variation of $K$ is assumed between end-members, then we will have:

$$\ln(\theta_T) = \sum_i x_i \ln(\theta_i)$$

(4.6)

This means that $G_m^{\text{phys}}$ is equal to $\sum_i x_i^0 G_i^{\text{phys}}$ and equation 4.3 is equivalent to equation 4.2. Accordingly, Ansara et al. [65] recommended not to treat the effect of harmonic vibrations separately and to use the classical Calphad approach instead. This means adding interaction parameters to the Einstein parameter should be included in the ordinary excess terms. They also emphasized that this treatment becomes less accurate below the Einstein temperature and the probably essential low temperature correction can be included in a temperature dependent $L$ parameter.

Based on this conclusion, it was decided in the present work not to use interaction parameters for $\theta$ when dealing with higher-order systems. However, one should bear in mind that when $\theta$ parameter is used as an implemented parameter in the software (TC for example) for the end-members, it will cause a contribution in the alloys automatically, since it has the form of equation 4.6 and changed linearly between end-members. The Einstein contribution to the Gibbs energy is shown in Fig. 4.3 for the hcp phase in the Mn-C binary system, using pycalphad open source software [27].
For the non-magnetic compounds (carbides, oxides, nitrides and fluorides), the same model as used by Chen and Sundman \cite{20} can be used for modelling different contributions to the Gibbs energy \cite{36}. However, such materials are nonmetallic and do not have an electronic contribution in their Gibbs energy. Also, the atomic vibrations in their lattice is more complicated and cannot be represented by a single Debye/Einstein temperature \cite{67}.

An alternative representation was suggested by Fontaine et al. \cite{36}, to use two Debye terms in the form of equation 4.7, for a binary compound $R_mX_n$:

\[
c_v = mf_D\left(\frac{\theta_R^D}{T}\right) + nf_D\left(\frac{\theta_X^D}{T}\right)
\]

(4.7)

where $f_D\left(\frac{\theta_R^D}{T}\right)$ is the Debye function and $\theta_R^D$ and $\theta_X^D$ are the Debye temperatures of elements R and X, respectively. The same approach can be applied to the magnetic salts \cite{67} and the metastable end-members, e.g. hcp or fcc in the Mn-C binary system.

When dealing with the stable compounds, e.g. carbides, oxides, etc., generally there are experimental data, for example heat capacity or enthalpy, that one can use for fitting to find $\theta_E$. As in Chen and Sundman \cite{20} for metals, the anharmonic vibration of atoms in the high temperature region can be modelled by fitting a polynomial of temperature to these data. One should only bear in

\[-75400\]
\[-75600\]
\[-75800\]
\[-76000\]
\[-76200\]
\[-76400\]
\[-76600\]
\[-76800\]
\[-77000\]

Figure 4.3: Linear variation of the Einstein contribution to the Gibbs energy versus composition, for the hcp phase $(Mn)_1(Va,C)_{0.5}$ in the Mn-C binary system, using pycalphad open source software \cite{27}.

4.3 Modelling compounds and the metastable end-members

For the non-magnetic compounds (carbides, oxides, nitrides and fluorides), the same model as used by Chen and Sundman \cite{20} can be used for modelling different contributions to the Gibbs energy \cite{36}. However, such materials are nonmetallic and do not have an electronic contribution in their Gibbs energy. Also, the atomic vibrations in their lattice is more complicated and cannot be represented by a single Debye/Einstein temperature \cite{67}.

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where $f_D\left(\frac{\theta_R^D}{T}\right)$ is the Debye function and $\theta_R^D$ and $\theta_X^D$ are the Debye temperatures of elements R and X, respectively. The same approach can be applied to the magnetic salts \cite{67} and the metastable end-members, e.g. hcp or fcc in the Mn-C binary system.

When dealing with the stable compounds, e.g. carbides, oxides, etc., generally there are experimental data, for example heat capacity or enthalpy, that one can use for fitting to find $\theta_E$. As in Chen and Sundman \cite{20} for metals, the anharmonic vibration of atoms in the high temperature region can be modelled by fitting a polynomial of temperature to these data. One should only bear in
mind that the $T$ term should be avoided in the Gibbs energy expression, since it would result in a non-zero entropy at 0 K and violate the third law of thermodynamics. This approach, however, is not equally straightforward in case of metastable end-members mentioned above. For example for the bcc phase in the Mn-C system, if the sublattice model $(Mn)_1(Va,C)_3$ is used, the end-members will be $Mn_1Va_1$ and $Mn_1C_3$. Since there is no experimental data for the end-member $Mn_1C_3$, it is not possible to determine $\theta_E$ or coefficients of the temperature polynomial for this phase. Some empirical approaches can be used in this case. For example analogy with similar compounds or using the Calphad software for optimizing their parameters relative to stable phases, or by the help of the elastic constant [68–70].

Li et al. [71] used an empirical approach, suggested by Hillert and Selleby [72] for modelling the end-members in the binaries Co-C and Cr-C. In this approach, a simple trick is used for avoiding the violation of the third law of thermodynamics, when using the Neumann Kopp rule (NKR). The NKR assumes a linear expression, i.e. $a + bT$, for estimating the temperature dependence of the heat capacity. The temperature dependent contribution in this expression results in a non-zero entropy at 0 K, which is in contradiction to the third law of thermodynamics. Hillert and Selleby [72] suggested a modified expression which guarantees that this contribution reaches zero at 0 K.

It should be pointed out that such solutions, mentioned above are just some simple tricks, which can be used in the meantime for developing databases that can be used for practical applications. It is hoped that in the close future, by help of improvement of computational possibilities, stronger methodologies and approaches replace these types of treatments.
Chapter 5

Concluding remarks

The main goal of this work is contributed to the development of a new generation of Calphad databases, that are valid down to 0 K and have more physical basis. For this purpose, the potentials and limitations of different techniques were investigated for several case studies and phenomena, e.g. magnetism, atomic vibrations, etc. It was mainly attempted to follow and try suggestions by Ringberg workshops, especially the last one in 2013, where applying DFT methods is strongly recommended for Calphad modelling.

Through this study, it was concluded that although atomistic scale techniques are founded on very strong physical basis, they also suffer from different types of errors and limitations. Some of these limitations are related to the nature of this theory, such as assumptions and approximations made in different approaches for treating complicated physical phenomena. These simplification are made to make the most precise estimation of the many-body Schrödinger equation, which is not possible to solve with current computational methods and techniques.

However, there are other sets of errors entering into the results of ab-initio calculations that are controllable, such as converging parameters and fitting or selecting inter-atomic potentials used in different types of calculations. It was attempted in this work to apply the best possible solutions and specify the most accuracy and resources to achieve the best results.

On the other hand, implementing DFT methods into Calphad software, as a connected model to the Calphad approach, is not straight forward at all, from numerical and computational point of view. The best one can do in the time being, is to use the results of DFT calculations as an input along with experimental data, for Calphad assessments. This task itself has some difficulties, since these results are mostly calculated at 0 K and deriving thermodynamic properties at finite temperature, which can be used directly into Calphad, is not time and cost efficient. However, since the third generation Calphad databases are valid down to 0 K, they open a new door to use 0 K DFT results. It should only be kept in mind that DFT results that are consistent to the existing experimental data should be selected. This is one of the advantages of developing
such databases. Despite all these limitations, it is also shown in the present work, that DFT techniques can be great help in finding support for data selection between different data sets that show discrepancy and developing models under conditions where no experiment can be performed. From this point of view, using them is strongly recommended, but due to limitations mentioned above, great caution must be considered not to overestimate their reliability.

It can thus be concluded that in the mean time, one can combine these two techniques in a very efficient way for developing thermodynamic databases which have more physical basis and can be reliable at low temperatures. In the future, by improving the computational possibilities, it may become possible to develop databases starting from atomic scale, which can be the "fourth generation of databases".
Bibliography


