Thermodynamic description of the Fe-C-Cr-Mn-Ni-O system

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Abstract

The Fe-C-Cr-Mn-Ni-O system is of fundamental importance when describing the influence of oxygen on high alloyed steels. Both solid and liquid phases are of great interest: The solid phases regarding oxidation processes like the formation of oxide layers, inner oxidation, sintering processes and high temperature corrosion. The liquid phase is of interest concerning the interaction between steel and its slag in a metallurgical context. In this thesis the thermodynamic properties of this system is described using the Calphad technique. The main idea of the Calphad technique is to describe the Gibbs energy of all phases in the system as a function of temperature, pressure and composition using appropriate thermodynamic models. When thermodynamic descriptions of all phases taking part in the system are modelled and described in a database, the equilibrium state could be calculated with a software that minimizes the total Gibbs energy.

Models within the compound energy formalism are used for all solution phases, among them the ionic two-sublattice liquid model, to describe both the metallic and oxide melts. All simple spinels (Cr$_3$O$_4$, FeCr$_2$O$_4$, Fe$_3$O$_4$, FeMn$_2$O$_4$, Mn$_3$O$_4$, MnCr$_2$O$_4$, NiCr$_2$O$_4$, NiFe$_2$O$_4$, NiMn$_2$O$_4$) within this system are described using a four-sublattice model. In this thesis several binary and ternary systems have been assessed or partly reassessed. The Fe-C-Cr-Mn-Ni-O database achieved can be used with an appropriate thermodynamic software to calculate thermodynamic properties, equilibrium states and phase diagrams. In general, the agreement between calculated and experimental values is good.

Keywords: thermodynamic modelling, thermodynamic assessment, Calphad, phase diagram, spinel, compound energy formalism, ionic two-sublattice liquid model.
List of publications

The work presented in this thesis was carried out at the division of Computational Thermodynamics, Department of Material Science and Engineering, School of Industrial Engineering and Management, KTH (Royal Institute of Technology), Stockholm, Sweden. The thesis consists of an introduction to the thesis topic and the following attached papers:

I  Parameters in the compound energy formalism for ionic systems  
   M. Hillert, L. Kjellqvist, H. Mao, M. Selleby and B. Sundman  

II Thermodynamic modelling of the Cr-Fe-Ni-O system  
   L. Kjellqvist, M. Selleby and B. Sundman  
   Calphad 32 (2008) 577-592

III Adding C to the thermodynamic description of the Cr-Fe-Ni-O system  
   L. Kjellqvist and M. Selleby  
   Calphad 33 (2009) 393-397

IV Thermodynamic assessment of the Fe-Mn-O system  
   L. Kjellqvist and M. Selleby  
   Submitted to Journal of Phase Equilibria and Diffusion

V  Thermodynamic assessment of the Cr-Mn-O system  
   L. Kjellqvist and M. Selleby  
   Submitted to Journal of Alloys and Compounds

VI Thermodynamic assessment of the Mn-Ni-O system  
   L. Kjellqvist and M. Selleby  
   Submitted to International Journal of Materials Research
Other reports produced during the doctoral studies at KTH, but not included in the thesis:

  I  Java interface for Thermo-Calc
     L. Kjellqvist
  II Users’ guide - Interface for steel/slag/gas equilibria calculations
     L. Kjellqvist
  III Thermodynamic assessments of the Al$_2$O$_3$-TiO$_2$, CaO-TiO$_2$, FeO-TiO$_2$, Fe$_2$O$_3$-TiO$_2$, MgO-TiO$_2$ and MnO-TiO$_2$ systems.
     L. Kjellqvist, M. Selleby and B. Sundman
  IV Simulation of decarburization of a high alloyed liquid steel using a reactor model within Thermo-Calc
     L. Kjellqvist and B. Sundman

- Thermodynamic assessment of the Al-Ti-O system, L. Kjellqvist and B. Sundman, manuscript, 2009.
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Chapter 1

Introduction

Experimental work is a time-consuming and costly task. Computer calculations are useful in the development of new materials as well as for controlling and improving metallurgical processes. Mathematical modelling of thermodynamic properties is used to understand or predict reality.

The equilibrium state of a material is determined by its thermodynamic properties. The correlation between thermodynamics and phase equilibria was established in the 19th century by Gibbs [1], and approximately 100 years later, Kaufman and Bernstein [2] summarized the general features of the calculation of phase diagrams, thus laying the foundation for the Calphad [3] method. Enormous progress has been made in the calculation of phase diagrams during the past 40 years. This progress will continue as model descriptions are improved and computational technology advances.

Thermo-Calc [4] is a software for thermodynamic calculations of phase equilibria in multicomponent systems and is used for all calculations throughout this thesis. It is based on thermodynamic data assessed with the Calphad technique and minimization of Gibbs energy.

The results of this thesis are presented in the appended papers. The intention of this introductory part is to give a short overview of the topic, and is organised as follows: Chapter 2 describes the Calphad technique, in Chapter 3 a survey of some of the different models used in this thesis is found and in Chapter 4 the developed database is discussed. Finally, a summary of the appended papers and a discussion are presented in Chapter 5.
Chapter 1. Introduction

1.1 Overview of this work

In this thesis a thermodynamic database for the Fe-Cr-Mn-Ni-O system has been developed, composed of critically assessed binary and ternary systems. These systems have been taken either from literature or assessed by the present author. Previous assessments of the metallic subsystems have all been accepted in this work. Most of the oxide systems have been assessed earlier by other authors [5–11] and some of them are accepted in this work, some with small modifications, while others are reassessed. Some authors did not use the same thermodynamic models as in this thesis, and even though the same models were used, inconsistencies, especially regarding the spinel phase, resulted in necessary reassessments.

The Fe-Cr-Ni-O system has been reviewed and necessary parts reassessed, with special focus on the modelling of the spinel phase. Earlier attempts have been made to thermodynamically describe the spinel phase in Fe-Cr-Ni-O [5], but ending up with a nonconsistet description. The liquid and spinel phases in Mn-O have been reassessed and assessments of the C-Fe-O, C-Ni-O, Cr-Mn-O, Fe-Mn-O and Mn-Ni-O systems have been performed within this thesis.

1.2 Applications of the alloys

The Fe-Cr-Mn-Ni-O system is of fundamental importance when describing the influence of oxygen on stainless steels. The solid phases are of interest regarding oxidation processes like the formation of oxide layers on stainless steels, inner oxidation, sintering processes and high temperature corrosion and the liquid phase for the interaction between steel and its slag in a metallurgical context.

Magnetite (Fe$_3$O$_4$) is the most magnetic naturally occurring mineral on Earth, and was used as the earliest form of magnetic compasses. Oxide spinels are used as industrial refractory materials because of their cheapness, cubic structure (i.e. uniform thermal expansion) and high melting temperature. More high tech applications of the oxides within this system, in particular those of spinel type, are solid oxide fuel cells (SOFCs), semiconductors and resistors among other things.

SOFCs have been extensively studied as an environmentally friendly power generation system with high efficiency and fuel flexibility. The main difficulties to solve before the commercial introduction of SOFCs are the cost and durability, particularly related to the long-term stability of materials, such as the interconnect. The interconnect provides physical separation between air and fuel in the SOFC and electronically connect the anode of one cell with the cathode of the adjacent cell. Interconnects must be good electronic conductors and stable in both oxidizing (cathode-side) and reducing (anode-side) environments. Ceramic as well as
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Metallic materials are being considered as construction materials for such interconnects. LaCrO$_3$-based perovskites are the most common materials used today, but metals have gained more and more attention as possible replacement because they offer a number of advantages over ceramic materials. Metals are easier, cheaper and less brittle. Moreover, they have better machinability and higher electrical and thermal conductivities than most ceramics. The main drawback of metallic interconnects are their reactivity with the anode and cathode at the high operating temperatures. The resulting high temperature corrosion leads to dimensional changes and formation of oxide scales on the surface, which most likely have a low conductivity. Based on the requirements, Cr-based alloys and high-Cr ferritic steels seem to be the most promising metallic materials. Their ability to form protective oxide scales which possess sufficiently slow growth rates to keep the oxidation below an acceptable level are an important property of these alloys. Recent studies have shown that the main oxides forming on ferritic stainless steels are Cr$_2$O$_3$ and MnCr$_2$O$_4$ spinel [12–14]. A database for the Fe-Cr-Mn-Ni-O system could thus be of invaluable help to understand the oxidation behaviour of the interconnects.

Oxides involving two 3d-transition metals (e.g. Mn and Ni) have been well studied due to their outstanding semiconducting properties [15, 16]. Transition metal manganites $M_x$Mn$_{3-x}$O$_4$, $0 < x < 1$ (M=Ni, Cu, Co etc.) are also technologically important for use in thermally sensitive resistors. The electron transfer in NiMn$_2$O$_4$ can be treated as conduction between different electron states which is thermally activated and displays a negative temperature coefficient (NTC) behaviour where, the resistance decreases logarithmically with increasing temperature. This makes the compound well suited for temperature sensing applications.
Chapter 2

The Calphad technique

Phase diagrams are visual representations of the state of a system as a function of temperature, pressure and concentrations of the constituent components. The CALPHAD (CALculation of PHAse Diagrams) technique is used to describe the thermodynamics of materials. The energetic state of a closed system in equilibrium at fixed temperature, pressure and composition is described by its Gibbs energy. The main idea of the Calphad technique is to describe the Gibbs energy of all phases in the system, using appropriate thermodynamic models.

All available experimental information, both phase diagram data and thermochemical data, are collected and evaluated, and then used in an optimisation procedure to fit the model parameters. The determination of the coefficients is frequently called assessment or optimisation of a system. Phase diagram data could be measurements on phase equilibria like solidus and liquidus lines, phase boundaries, solid solubility etc. Thermochemical data are for example enthalpies, entropies, heat capacities or activities. Results from first-principle calculations can also be used as experiments, and are becoming more and more important in thermodynamic modelling. Enthalpies of formation of stable compounds are routinely predicted by first-principles calculations. To get as good description as possible of the properties, it is necessary to use all experimental information simultaneously, both phase equilibria and thermochemical data. Each phase is usually modelled within the entire temperature and composition range, and not only in the range where it is stable. Some parameters will refer to metastable, or sometimes unstable, structures. As a consequence of this, a thermodynamic database provides the possibility to do calculations also of metastable states, where experimental information is hard to find.

To perform an assessment, computerised methods are necessary. A computer program called PARROT, included in the Thermo-Calc software, has been developed
to fit the model parameters to the experimental data, by a least mean square method that minimizes the quadratic errors. When thermodynamic descriptions of all phases taking part in the system are obtained, the equilibrium state could be calculated by minimizing the total Gibbs energy. Generally, in a thermodynamic database, all binary and ternary systems are assessed from experimental data. Using these data, reliable extrapolations into higher order systems could be calculated with good accuracy. Sometimes, also quaternary systems are assessed. It has frequently been shown that reliable phase equilibria can be calculated for multicomponent systems, using assessed databases, see for example Frisk and Selleby [17]. Models and databases, developed within the Calphad technique, help to improve the understanding of various industrial and technological processes.
Chapter 3

Thermodynamic modelling

In Calphad assessments the Gibbs energy is used as the modelled thermodynamic property. The choice of Gibbs energy as the minimizing function is due to the fact that Gibbs energy is a function of temperature and pressure, properties that are convenient to control in experiments. From the Gibbs energy, other thermodynamic quantities, e.g. entropy or enthalpy, can easily be derived.

The temperature dependence of Gibbs energy for a pure element can be described using an empirical formula and is expressed as $G - H^{SER}$, where $SER$ denotes the reference state of the element, the stable state at 298.15 K and 1 atm. Normally the pressure dependence in the system is ignored, i.e. the expression is only valid for atmospheric pressure.

\[
G - H^{SER} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + \ldots \tag{3.1}
\]

The Gibbs energy of a phase should be described for the whole composition range. The phase is described for the pure elements, even if no such phase is stable for the pure elements, and how the atoms of the pure elements mix. The total Gibbs energy of a phase is expressed by:

\[
G_m = \text{sr}f G_m + \text{phys} G_m - T \cdot \text{conf} S_m + \text{E} G_m \tag{3.2}
\]

The superscript “sr" stands for “surface of reference” and represents the Gibbs energy of the components of the phase relative to its reference state. The quantity $\text{phys} G_m$ represents the contribution to the Gibbs energy due to physical effects like the magnetic transition. $\text{conf} S_m$ is the configurational entropy of the phase and is based on the number of possible arrangements of the constituents in the phase. $\text{E} G_m$ is the so-called excess Gibbs energy and describes the remaining part of the Gibbs energy, that is not included in the other terms. It represents the deviation
from the ideal behaviour. The excess term for a multicomponent system could contain binary, ternary and even higher order interactions.

The surface of reference \( srf G_m \) for the Gibbs energy of a phase is expressed by:

\[
srf G_m = \sum_{i=1}^{n} y_i^o G_i \tag{3.3}
\]

where \( ^o G_i \) is the Gibbs energy of the component \( i \). In this case the constituent fractions, \( y_i \), and not the mole fractions, \( x_i \), are used because there can be more constituents than components and the mole fractions are only defined for the components. Random mixing of the atoms are assumed, so the configurational entropy \( conf S_m \) is expressed by:

\[
conf S_m = -R \sum_{i=1}^{n} y_i \ln(y_i) \tag{3.4}
\]

The magnetic contribution to Gibbs energy is given by the model proposed by Inden [18] and adopted by Hillert and Jarl [19]:

\[
magn G_m = RT \ln(\beta + 1) f(\tau) \tag{3.5}
\]

where \( \tau = T/T_C \). \( T_C \) is the critical temperature for magnetic transition and \( \beta \) is the Bohr magneton number. \( T_C \) and \( \beta \) are model parameters that may be determined through an optimisation procedure. The composition dependence of \( T_C \) and \( \beta \) in binary and higher order systems is described in the same way as for Gibbs energy in a database.

A variety of models have been proposed for phases that deviate from the ideal behaviour to describe the excess Gibbs energy. Models of this kind may be non-physical, but can be justified by their ability to reproduce experimental data.

### 3.1 Compound energy formalism

A general formalism widely used in Calphad assessments of binary and higher order systems, is the compound energy formalism [20] (CEF). CEF was constructed in order to describe models of the thermodynamic properties of phases with two or more sublattices, which show a variation in composition, i.e. \( (A,B)_i(C,D)_j \). The concept constituent array is introduced, which specifies one or more constituent on each sublattice and is denoted \( I \). The constituent arrays can be of different orders and the zeroth order has one constituent on each sublattice. The Gibbs energy for a phase is described as:

\[
G_m = \sum_{I_0} P_{I_0}(Y)^o G_{I_0} + RT \sum_{s=1}^{n} a_s \sum_{i=1}^{n_s} y_i^s \ln(y_i^s) + \text{phys} G_m + \text{mag} G_m + E G_m \tag{3.6}
\]
where $I_0$ is a constituent array of zeroth order and $P_{I_0}(Y)$ is the corresponding product of the site fractions specified by $I_0$. $^oG_{I_0}$ represents the Gibbs energy of the compound $I_0$. The factor $a_s$ is the number of sites on sublattice $s$, $y_i^s$ denotes the site-fraction of component $i$ on sublattice $s$ and $E_{G_m}$ is the excess Gibbs energy:

$$E_{G_m} = \sum_{I_1} P_{I_1}(Y)L_{I_1} + \sum_{I_2} P_{I_2}(Y)L_{I_2} + \ldots$$

(3.7)

where $I_1$ is a constituent array of first order and $L_{I_1}$ is the interaction parameters defined by $I_1$. A constituent array of first order has two constituents in one sublattice but only one in the remaining sublattices. A constituent array of second order could have either three interacting constituents on one sublattice, or two interacting constituents on two different sublattices. The second case is a so-called reciprocal parameter. Higher order terms may also be added.

### 3.2 The ionic two-sublattice liquid model

Within the framework of the CEF, the ionic two-sublattice liquid model [21, 22] was developed to be used when there is a tendency for ionisation in the liquid, e.g. liquid oxides and sulphides. The same model can be used both for metallic and oxide melts. At low levels of oxygen, the model becomes equivalent to a substitutional solution model between metallic atoms. Two sublattices are assumed, one containing charged cations and one containing charged anions, neutrals and vacancies:

$$(C_i^{\nu_i})_P(A_j^{\nu_j},Va^{-Q},B_k^0)_Q$$

where $C$ represents cations, $A$ anions, $Va$ vacancies and $B$ neutrals. The indices $i, j$ and $k$ denotes specific constituents. Charged vacancies are introduced on the second sublattice to keep electroneutrality when the composition approaches metallic liquid. The site numbers, $P$ and $Q$, on the sublattices vary so that electroneutrality is maintained:

$$P = \sum_j y_{A_j}(-\nu_j) + Qy_{Va}$$

(3.8)

$$Q = \sum_i y_{C_i}\nu_i$$

(3.9)
The Gibbs energy of the liquid phase is expressed by:

\[ G_m = \sum_i \sum_j y_{C_i} y_{A_j} G_{C_i:A_j} + Q y_{V_a} \sum_i y_{C_i} G_{C_i} + Q \sum_k y_{B_k} G_{B_k} + \]

\[ RTP \sum_i y_{C_i} \ln(y_{C_i}) + RTQ \sum j y_{A_j} \ln(y_{A_j}) + RTQ y_{V_a} \ln(y_{V_a}) + \]

\[ RTQ \sum k y_{B_k} \ln(y_{B_k}) + E G_m \]  

(3.10)

The binary interaction parameters are given by:

\[ E G_m = \sum_{i_1} \sum_{i_2} \sum_j y_{C_{i_1}} y_{C_{i_2}} y_{A_j} L_{C_{i_1}.C_{i_2}:A_j} + Q y_{V_a} \sum_{i_1} \sum_{i_2} y_{C_{i_1}} y_{C_{i_2}} L_{C_{i_1}.C_{i_2}:V_a} + \]

\[ \sum_{i} \sum_{j_1} \sum_{j_2} y_{C_i} y_{A_{j_1}} y_{A_{j_2}} L_{C_i:A_{j_1}:A_{j_2}} + y_{V_a} \sum_{i} \sum_j y_{C_i} y_{A_j} L_{C_i:A_j,V_a} + \]

\[ \sum_{i} \sum_j y_{C_i} y_{A_j} y_{B_k} L_{C_i:A_j,B_k} + Q y_{V_a} \sum_{i} \sum_k y_{C_i} y_{B_k} L_{C_i:B_k,V_a} + \]

\[ \sum_{k_1} \sum_{k_2} y_{B_{k_1}} y_{B_{k_2}} L_{B_{k_1}.B_{k_2}} \]  

(3.11)

A colon is used to separate species on different sublattices and a comma is used to separate species on the same sublattice. Ternary parameters are also frequently used. A selection of commonly used parameters is:

\[ E G_m = Q y_{V_a}^3 \sum_{i_1} \sum_{i_2} \sum_{i_3} y_{C_{i_1}} y_{C_{i_2}} y_{C_{i_3}} L_{C_{i_1}.C_{i_2}.C_{i_3}:V_a} + \]

\[ y_{V_a} \sum_{i_1} \sum_{i_2} \sum_j y_{C_{i_1}} y_{C_{i_2}} y_{A_j} L_{C_{i_1}.C_{i_2}:A_j,V_a} \]  

(3.12)

where \( L_{C_{i_1}.C_{i_2}.C_{i_3}:V_a} \) represents interaction between three metallic elements, for example in Cr-Fe-Ni: \( L_{Cr,Fe,Ni} \). The charge is not relevant in this case, since no anion is present. In order for the parameter to be equivalent to the corresponding parameter in a substitutional solution model, it must be multiplied with \( y_{V_a}^3 \). \( L_{C_{i_1}.C_{i_2}:A_j,V_a} \) is a so-called reciprocal parameter, which represents for instance the interaction between two oxides and metals, for example in FeO-MnO-Fe-Mn: \( L_{Fe^{2+}.Mn^{2+}:O^{-2},V_a} \).

In the Fe-Cr-Mn-Ni-O system, considering \( Cr^{+3}, Fe^{+2}, Mn^{+2}, Ni^{+2}, O^{-2}, FeO_{1.5}, MnO_{1.5}, C \) and vacancies, the liquid phase is described as:

\((Cr^{+3},Fe^{+2},Mn^{+2},Ni^{+2})_P(O^{-2},Va^{-Q},C,FeO_{1.5},MnO_{1.5})Q\)

The liquid phase in the Fe-O system was first modelled [23] with \((Fe^{+2},Fe^{+3})_P(O^{-2},Va^{-Q})_Q\), but later [24] \(Fe^{+3}\) was replaced by a neutral species,
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FeO\textsubscript{1.5}. This change was imposed by an equivalent change for Al-containing systems where Al\textsuperscript{+3} was replaced by AlO\textsubscript{1.5} in order to better control the unwanted reciprocal miscibility gaps that occurred in e.g. Al\textsubscript{2}O\textsubscript{3}-CaO-SiO\textsubscript{2}. However, even though a new model for liquid Al\textsubscript{2}O\textsubscript{3} (without AlO\textsubscript{1.5}) has been developed [25], the FeO\textsubscript{1.5} species has been kept. Also the liquid phase in the Mn-O system was originally modelled [26] using Mn\textsuperscript{+2} and Mn\textsuperscript{+3}, but Mn\textsuperscript{+3} is in this thesis replaced by the neutral MnO\textsubscript{1.5} species [27] to conform with the model in the Fe-O system.

A number of models have been proposed for the liquid phase besides the ionic two-sublattice liquid model, for example the associate solution model [28], the modified quasi-chemical model [29,30] and the cellular model [31,32].

3.3 The spinel phase

Most of the spinels in this study (Fe\textsubscript{3}O\textsubscript{4}, FeCr\textsubscript{2}O\textsubscript{4}, MnCr\textsubscript{2}O\textsubscript{4}, Cr\textsubscript{3}O\textsubscript{4} among others) have the cubic crystal structure. However, many spinel type oxides are known to show phase transition due to the cooperative Jahn-Teller effect [33–38], caused by a lattice distortion. Among the spinels in this study, NiCr\textsubscript{2}O\textsubscript{4} and Mn\textsubscript{3}O\textsubscript{4} have a tetragonal distortion originating from the Jahn-Teller effect. Mn\textsubscript{3}O\textsubscript{4} is a tetragonal spinel (α-Mn\textsubscript{3}O\textsubscript{4}) at low temperatures and transforms to a cubic spinel (β-Mn\textsubscript{3}O\textsubscript{4}) at approximately 1440 K. α-Mn\textsubscript{3}O\textsubscript{4} normally dissolves only small amounts of other elements, while β-Mn\textsubscript{3}O\textsubscript{4} extend up to cubic Fe\textsubscript{3}O\textsubscript{4}, Cr\textsubscript{3}O\textsubscript{4} etc. NiCr\textsubscript{2}O\textsubscript{4} have a transition temperature and becomes tetragonal below 300 K. This transformation is not modelled in this work due to the relatively low temperature at which it takes place.

Both the tetragonal and cubic spinels are modelled in similar ways. Below, the modelling concerns the cubic spinel, which is called just spinel from now on, but most parts of the discussion hold for both phases.

In the spinel structure, the O\textsuperscript{2−} ions form a cubic closed packed (fcc) lattice, with one eight of the tetrahedral and one half of the octahedral interstices filled by cations. This means that we have two types of cubic cells inside a large fcc lattice filling all eight octants, see Figure 3.1.

The modelling of the spinel phase could be rather complicated, why we start by describing a stoichiometric spinel as a first approach. A simple spinel, AE\textsubscript{2}O\textsubscript{4}, where A is divalent and E is trivalent, is described using the formula:

\[(A^{+2},E^{+3})_1(A^{+2},E^{+3})_2(O^{-2})_4.\]

where the first sublattice represents the tetrahedral sites and the second sublattice represents octahedral sites. A normal spinel has the trivalent ions on the octahedral sites and the divalent ions on the tetrahedral sites. If the tetrahedral sites are
occupied with \( E \) ions, both \( A \) and \( E \) need to enter the octahedral sites in order to fulfill the condition of electroneutrality, and the spinel is referred to as inverse. The Gibbs energy of stoichiometric \( \text{AE}_2\text{O}_4 \) is given by:

\[
^0\!G_m = y_A^t y_A^t G_{AA} + y_A^t y_E^t G_{AE} + y_E^t y_A^t G_{EA} + y_E^t y_E^t G_{EE} - T S_m + E G_m
\]

(3.13)

where the superscripts \( t \) and \( o \) denote tetrahedral and octahedral sites, respectively. This is a reciprocal system with a neutral line between the \( ^0G_{AE} \) corner and the middle of the \( ^0G_{EA} - ^0G_{EE} \) side, see Figure 3.2. All points on the neutral line between the normal and inverse spinels represent the stoichiometric composition, but with different distributions of ions on the two sublattices. Only one point on the line represents the equilibrium composition at a given temperature, and this point is the only one available for experimental studies. At the best, one can hope to measure its position and the Gibbs energy for that condition.

The site fraction in Equation 3.13 could be replaced with a variable describing the disorder, \( \xi = y_E^t = 1 - y_A^t = 2 - 2y_E^t = 2y_A^t \). \( \xi = 0 \) yields the normal state \( (\text{A}^+)^2(\text{E}^{+3})_2(\text{O}^{-2})_4 \) and \( \xi = 1 \) yields the inverse state \( (\text{E}^{+3})_1(\text{A}^{+2}_{0.5};\text{E}^{+3}_{0.5})_2(\text{O}^{-2})_4 \). All interaction energies in Equation 3.13 should normally be neglected since there are already more compound energies than experimental information. Rearranging Equation 3.13, assuming the degree of inversion is low and expressing all site
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Figure 3.2: Compositional square for $\text{AE}_2\text{O}_4$. The possible neutral compositions are on the marked neutral line.

fractions in terms of $\xi$ yields:

\begin{align*}
G_m + TS_m(\xi) &= oG_{AE} + J_{AE}\xi + 0.5\Delta G_{AE:AE}\xi^2 \\
\Delta G_{AE:AE} &= oG_{AE} + oG_{EA} - oG_{AA} - oG_{EE} \\
J_{AE} &= oG_{EE} + 0.5oG_{AA} - 1.5oG_{AE}
\end{align*}

Gibbs energy of $\text{AE}_2\text{O}_4$ is given by the parameter $oG_{AE}$ and $J_{AE}$ is used to model the degree of inversion. Normally, these two parameters are the only two possible to evaluate from experimental studies. The two remaining parameters could be chosen rather arbitrary. A reasonable estimation is to assume that the reciprocal reaction should have $\Delta G_{AE:AE} = 0$. Using $\Delta G_{AE:AE} = 0$ implies that the energy for the exchange from an $A$ to an $E$ ion on the tetrahedral site is independent of whether the octahedral site is filled with $A$ or $E$ ions ($oG_{AA} - oG_{EA} = oG_{AE} - oG_{EE}$) etc. To be able to evaluate the fourth parameter, an arbitrary value could be given to any of the parameters $oG_{AA}$, $oG_{EA}$ or $oG_{EE}$ representing the reference for a charged compound. It is not practical to have more than one such reference for each phase. However, in the model for the spinel phase there is no common endmember for all systems as for example $oG_{V:a:O^{-2}}$ in the halite phase, which then is a natural choice as a reference for charge in that phase. In the spinel phase it has been agreed that the reference for charge is $oG_{Fe^{+2}:Fe^{+3};V:a:O^{-2}} = oG_{Fe^{+3};Fe^{+2};V:a:O^{-2}}$. If a system not including Fe is assessed, e.g. the Mn-O system, a new reference differing from $oG_{Fe^{+2}:Fe^{+3};V:a:O^{-2}} = oG_{Fe^{+3};Fe^{+2};V:a:O^{-2}}$ will inevitably be chosen. To make the $\text{Mn}_3\text{O}_4$ spinel compatible with the Fe-O reference, all $oG$ parameters with a net charge need to be adjusted with a value obtained from the Fe-Mn-O assessment.
When $\Delta G_{AE;AE} = 0$ is assumed Equation 3.16 can be written as:

$$J_{AE} = 0.5(\delta G_{EE} + \delta G_{EA}) - \delta G_{AE}$$

(3.17)

which is the energy difference between the inverse and normal spinel.

If we now treat a spinel with high degree of inversion, Equations 3.14 should be rearranged and expressed as:

$$G_m + TS_m(\xi) = 0.5(\delta G_{EE} + \delta G_{EA}) - (J_{AE} + \Delta G_{AE;AE})(1 - \xi) + 0.5\Delta G_{AE;AE}(1 - \xi)^2$$

(3.18)

Gibbs energy of $AE_2O_4$ is now given by $0.5(\delta G_{EE} + \delta G_{EA})$ and the parameter $\delta G_{AE}$ which were used to model the spinel with low degree of inversion is now involved only through $\Delta G_{AE;AE}$ and $J_{AE}$.

### 3.3.1 4-2 spinel

The condition of electroneutrality for a simple stoichiometric spinel, $AE_2O_4$, reads:

$$\nu_A + 2\nu_E + 4\nu_O = 0$$

(3.19)

where $\nu_A$ and $\nu_E$ are the charges on the $A$ and $E$ cations and $\nu_O$ that on the anions ($= -2$ for oxide spinels). The description in Section 3.3 holds for a so-called 2-3 spinel ($A = 2$, $E = 3$). Some spinels have $A = 4$, $E = 2$, defining a 4-2 spinel, among them $M_2TiO_4$ and $M_2GeO_4$ ($M$=Mg, Mn, Fe, Co, Ni, Zn) [39]. The $Mn_3O_4$ and $NiMn_2O_4$ spinels treated in this thesis are described with a formula using $Mn^{+4}$ in octahedral sites. To describe the spinel phase $Ni_{3-x}Mn_xO_4$ ($1.725 \leq x \leq 3$), more nickel than the formula $(Mn^{+2},Mn^{+3},Ni^{+2})_1(Mn^{+2},Mn^{+3},Ni^{+2})_2(O^{2-})_4$ allows is needed. No evidence for $Ni^{+3}$ or large amount of interstitial nickel is found, why a structure with $Mn^{+4}$ is the best assumption. $NiMn_2O_4$ is described using $(Mn^{+2}_xNi^{+2}_{1-x})(Mn^{+3}_2,Mn^{+4}_x,Ni^{+2}_{1-x})(O^{2-})_4$, where $\xi$ is the inversion parameter. Wickham [40] concluded that probably all oxides except the halite phase in the Mn-Ni-O system contain manganese in the +4 oxidation state.

### 3.3.2 Quaternary system

A solid solution of four simple spinels with common ions, $AE_2O_4$, $AF_2O_4$, $BE_2O_4$ and $BF_2O_4$, where $A$ and $B$ are divalent and $E$ and $F$ are trivalent, is described using the formula $(A^{+2},B^{+2},E^{+3},F^{+3})_1(A^{+2},B^{+2},E^{+3},F^{+3})_2(O^{2-})_4$. If all these spinels were normal spinels, the system could be described with $(A^{+2},B^{+2})_1(E^{+3},F^{+3})_2(O^{2-})_4$, all compound would be neutral and could be studied experimentally. Figure 3.3 shows a schematic representation of the relationship
between the four simple spinels. If the description of the four simple spinels were to be merged and used in the same database, the connection points ($^oG_{AA}$, $^oG_{BB}$, $^oG_{EE}$ and $^oG_{FF}$) must, of course, be the same in all descriptions. A solution with two spinels (AE$_2$O$_4$ and BE$_2$O$_4$), with one common endmember ($^oG_{EE}$) is considered first.

![Schematic figure with a spinel with four cations, showing the relationship between the four simple spinels. The dashed lines represent the neutral lines.](image)

If AE$_2$O$_4$ is assessed first and $^oG_{EE}$ is chosen as a reference for charges, the same reference is easily adopted when performing the BE$_2$O$_4$ assessment. If the two spinels were assessed independently of each other and different references were chosen, this could simply be fixed by adding or subtracting appropriate values to the compound energies based on the difference in $^oG_{EE}$. When adding a third spinel (e.g. AF$_2$O$_4$), $^oG_{AA}$, $^oG_{FF}$ and $^oG_{FA}$ will probably need to be adjusted to be compatible with the reference $^oG_{EE}$ chosen in the first spinel. Since AE$_2$O$_4$ and AF$_2$O$_4$ does not have $^oG_{EE}$ in common, different reference states is most likely used if $^oG_{EE}$ were chosen as a reference in AE$_2$O$_4$. Finally, when the fourth spinel (BF$_2$O$_4$) should be combined with the other three, both $^oG_{BB}$ and $^oG_{FF}$ need to be adjusted and this cannot be achieved only by a simple subtraction or addition to the different parameters.

Several alternatives are possible to solve the problem. The easiest, but perhaps not so attractive, way may be to add an interaction parameter to the last assessment. The other option, which may seem a little laborious, would be to reassess all systems
simultaneously to satisfy a condition, which is obtained from Equation 3.16:

\[ J_{AE} + 1.5^oG_{AE} - J_{AF} - 1.5^oG_{AF} + J_{BF} + 1.5^oG_{BF} - J_{BE} - 1.5^oG_{BE} = 0 \]  

(3.20)

Instead of assessing all eight parameters simultaneously, the system with the weakest information may be identified and examine if it would be possible to adjust only its two optimisation parameters, i.e:

\[ J_{BF} + 1.5^oG_{BF} = 0.5^oG_{BB} + ^oG_{FF} \]  

(3.21)

where \(^oG_{BB}\) and \(^oG_{FF}\) are fixed by the other systems.

In the Fe-Cr-Ni-O system, the Fe-O [23] and Cr-Ni-O [7] systems were assessed first. Those two systems have no common endmember and were assessed independently. A few years later when the Cr-Fe-O [6] and Fe-Ni-O [11] systems were assessed, \(^oG_{Fe^{+2};Fe^{+2}}\) and \(^oG_{Fe^{+3};Fe^{+3}}\) from Sundman’s Fe-O assessment [23] were used, but not \(^oG_{Ni^{+2};Ni^{+2}}\) and \(^oG_{Cr^{+3};Cr^{+3}}\) from Taylor and Dinsdale’s Cr-Mn-O assessment [7]. This resulted in that the Cr-Ni-O assessment became inconsistent with the other ones. In paper II [41] attached to this thesis, the problem was solved by introducing interaction parameters \((L_{Cr^{+3};Ni^{+2}};Cr^{+3})\) and \((L_{Cr^{+3};Ni^{+2}};Ni^{+2})\) in the Cr-Ni-O assessment. All parameter values in the Cr-Ni spinel besides \(^oG_{Ni^{+2};Cr^{+3}}\) were thus changed, but the calculated properties of NiCr\(_2\)O\(_4\) were unaffected.

Even if all assessments are performed one after another, using the appropriate reference state, there could still be problems when combining four assessments. Then, all systems except the last one are assessed using three optimising parameters, \(^oG\), \(J\) and \(\Delta G_{BF;BF}\). When the last system, e.g. BF\(_2\)O\(_4\), should be assessed both BB and FF are already fixed, and only two optimisation parameters can be used. If the information regarding the degree of inversion in this system is poor or lacking, \(\Delta G = 0\) could be assumed. Then only Gibbs energy of that spinel is evaluated and the degree of inversion will be calculated by \(J_{BF} = ^oG_{FF} + 0.5^oG_{BB} - 1.5^oG_{BF}\). This was the case in paper V, the assessment of the Cr-Mn-O system [42]. \(\Delta G = 0\) gave an almost perfectly normal spinel at all temperatures. Otherwise, if the degree of inversion is known and well described and \(\Delta G = 0\) does not give a satisfying result, the Gibbs energy of BF\(_2\)O\(_4\) and the degree of inversion \((J_{BF})\) could be assessed which would then lead to \(\Delta G \neq 0\).

### 3.3.3 Introduction of vacancies and interstitial cations

AE\(_2\)O\(_4\) could show more or less solid solubility on both sides of the stoichiometric composition. Vacant sites are formed in the octahedral sublattice to maintain electroneutrality when excess E ions are introduced to model the deviation
towards oxygen in equilibrium with $\text{E}_2\text{O}_3$. The extended spinel model is then $(\text{A}^{+2},\text{E}^{+3})_1(\text{A}^{+2},\text{E}^{+3},\text{Va})_2(\text{O}^{-2})_4$. A new neutral endpoint is found, a hypothetical metastable $\gamma$-$\text{E}_2\text{O}_3$ with spinel structure. Gibbs energy of this endpoint is

$$^\circ G_m = (5^\circ G_{EE} + ^\circ G_{EV} - 2RT(6\ln 6 - 5\ln 5))/6$$

where $^\circ G_{EV}$ is used to describe the deviation of $\text{AE}_2\text{O}_4$ towards excess oxygen.

To model $\text{AE}_2\text{O}_4$ with oxygen deficiency, A ions are assumed to enter interstitial sites according to the formula proposed by Sundman [23] when he assessed the Fe-O system. Thus, the final model for the spinel phase, taking both oxygen excess and deficiency into consideration, is $(\text{A}^{+2},\text{E}^{+3})_1(\text{A}^{+2},\text{E}^{+3},\text{Va})_2(\text{A}^{+2},\text{Va})_2(\text{O}^{-2})_4$. A new neutral endpoint is found, a hypothetical metastable $\gamma$-$\text{AO}$ with spinel structure. Gibbs energy of this endpoint is

$$^\circ G_m = (^\circ G_{AAV} + ^\circ G_{AAA} - 4RT\ln 2)/2$$

where $^\circ G_{AAA}$ is used to describe the deviation of $\text{AE}_2\text{O}_4$ towards oxygen deficiency. One more neutral endpoint is found, i.e. $(^\circ G_{EAA} + 3^\circ G_{EAV})/4$, but is of no interest here. The remaining six $^\circ G$ parameters ($^\circ G_{AVV}$, $^\circ G_{AVA}$, $^\circ G_{AVE}$, $^\circ G_{AEA}$, $^\circ G_{EAA}$ and $^\circ G_{EEA}$) are obtained from reciprocal reactions, where all reactions usually are assumed to have $\Delta G = 0$. 

3.3. The spinel phase
The database consists of a number of model parameters which are able to reproduce a large amount of experiments, both thermochemical data and phase diagram data.

4.1 Phases within the database

The solid solution phases in this system are modelled using the CEF. The liquid phase is modelled using the ionic two-sublattice liquid model. The same model is used both for metallic and oxide melts. At low levels of oxygen, the model becomes equivalent to a substitutional solution model between metallic atoms.

4.1.1 Ionic liquid

Two sublattices are assumed, one containing charged cations and one containing charged anions, neutrals and vacancies:

\[(Cr^{+3},Fe^{+2},Mn^{+2},Ni^{+2})_P(O^{-2},Va^{-Q},C,FeO_{1.5},MnO_{1.5})_Q\]

4.1.2 Corundum

Hematite (Fe$_2$O$_3$) and eskolaite (Cr$_2$O$_3$) are isomorphous with the generic phase name corundum (Strukturbericht D$_5$$_1$). No or very small solubility of nickel in hematite and eskolaite were reported in the literature. Eskolaite contains only small amount of Mn, while hematite can dissolve more than 10% Mn. Both hematite and eskolaite are modelled with a small deviation from stoichiometry by introducing an
additional interstitial sublattice with $\text{Cr}^{+3}$ and $\text{Fe}^{+3}$ respectively and vacancies. To maintain electroneutrality divalent ions are introduced to the first sublattice:

$$(\text{Cr}^{+2}, \text{Cr}^{+3}, \text{Fe}^{+2}, \text{Fe}^{+3}, \text{Mn}^{+3})_2 (\text{Cr}^{+3}, \text{Fe}^{+3}, \text{Ni}^{+2}, \text{Va})_1 (\text{O}^{-2})_3$$

Hematite and eskolaite undergo magnetic transitions at 946 and 303 K, respectively.

### 4.1.3 Halite

Wustite ($\text{FeO}$), manganosite ($\text{MnO}$) and bunsenite ($\text{NiO}$) are isomorphous with the generic phase name halite (Strukturbericht B1). Both wustite and manganosite have a considerable solid solubility due to the oxidation of $\text{Fe}^{+2}$ to $\text{Fe}^{+3}$ and $\text{Mn}^{+2}$ to $\text{Mn}^{+3}$ and the formation of cation vacancies. The solubility of $\text{Cr}$ in halite is modelled using $\text{Cr}^{+3}$ on the cation lattice. The phase is thus represented as:

$$(\text{Cr}^{+3}, \text{Fe}^{+2}, \text{Fe}^{+3}, \text{Mn}^{+2}, \text{Mn}^{+3}, \text{Ni}^{+2}, \text{Ni}^{+3}, \text{Va})_1 (\text{O}^{-2})_1$$

Bunsenite undergoes a magnetic transition at 519 K.

### 4.1.4 Pyrolusit and $\text{Ni}_6\text{MnO}_8$

Pyrolusite ($\text{MnO}_2$) with the generic name rutile (Strukturbericht C4) and $\text{Ni}_6\text{MnO}_8$ with an ordered NaCl-type structure are described as stoichiometric phases.

### 4.1.5 Cubic Spinel

Spinels (Strukturbericht H1) are a mineral with the general formula $\text{AE}_2\text{O}_4$ that crystallise in the cubic structure with metallic ions on tetrahedral and octahedral interstitial sublattices. $A$ and $E$ could be divalent, trivalent or tetravalent. A 2-3 spinel has $A = 2$ and $E = 3$ and a 4-2 spinel $A = 4$ and $E = 2$. A perfectly normal 2-3 spinel has all divalent ions on tetrahedral sites and the trivalent ions on the octahedral sites. However, the distribution $(E)(AE)\text{O}_4$ is also possible, and is referred to as an inverse spinel. The spinels comprise a large group of binary and ternary oxides, such as $\text{Cr}_3\text{O}_4$, $\text{FeCr}_2\text{O}_4$, $\text{Fe}_3\text{O}_4$, $\text{FeMn}_2\text{O}_4$, $\text{Mn}_3\text{O}_4$, $\text{MnCr}_2\text{O}_4$, $\text{NiCr}_2\text{O}_4$, $\text{NiFe}_2\text{O}_4$, $\text{NiMn}_2\text{O}_4$ and mixtures of these. Most of the simple spinels above have a cation distribution somewhere between the normal and inverse structure, thus the cations occupy both tetrahedral and octahedral sites. To be able to model deviation from stoichiometry vacancies are introduced to the octahedral sublattice and an extra interstitial sublattice normally filled with vacancies are added. The cubic spinel is modelled as:
4.2. References for all subsystems

(Cr\(^{+2}\),Cr\(^{+3}\),Fe\(^{+2}\),Fe\(^{+3}\),Mn\(^{+2}\),Ni\(^{+2}\))\(_1\) (Cr\(^{+3}\),Fe\(^{+2}\),Fe\(^{+3}\),Mn\(^{+3}\),Mn\(^{+4}\),Ni\(^{+2}\),Va)\(_2\)
(Cr\(^{+2}\),Fe\(^{+2}\),Mn\(^{+2}\),Va)\(_2\)(O\(^{-2}\))\(_4\)

There is a large variation in the critical temperature for magnetic transition for these spinels, from Fe\(_3\)O\(_4\) and NiFe\(_2\)O\(_4\) at \(\approx 850\) K to Mn\(_3\)O\(_4\) and NiMn\(_2\)O\(_4\) at \(\approx 40\) K.

### 4.1.6 Tetragonal Spinel

Mn\(_3\)O\(_4\) transforms from tetragonal \(\alpha\)-Mn\(_3\)O\(_4\) to cubic \(\beta\)-Mn\(_3\)O\(_4\) at increasing temperature. The low-temperature phase is distorted from cubic to tetragonal structure due to the cooperative Jahn-Teller effect. \(\alpha\)-Mn\(_3\)O\(_4\) dissolves only small amounts of other elements and are modelled as:

(Cr\(^{+2}\),Cr\(^{+3}\),Fe\(^{+2}\),Fe\(^{+3}\),Mn\(^{+2}\),Mn\(^{+3}\),Ni\(^{+2}\))\(_1\) (Cr\(^{+3}\),Fe\(^{+2}\),Fe\(^{+3}\),Mn\(^{+3}\),Mn\(^{+4}\),Ni\(^{+2}\),Va)\(_2\)
(Cr\(^{+2}\),Fe\(^{+2}\),Mn\(^{+2}\),Va)\(_2\)(O\(^{-2}\))\(_4\)

The magnetic transition is modelled the same way as for the cubic spinel.

### 4.1.7 Bixbyite

\(\alpha\)-bixbyite (\(\alpha\)-Mn\(_2\)O\(_3\)) transforms to \(\beta\)-Mn\(_2\)O\(_3\) (Strukturbericht D5\(_3\)) at around 300 K. The \(\alpha\)-modification was not considered due to the low transformation temperature. Mn\(_2\)O\(_3\) have a large solubility of Cr, Fe and Ni, especially Fe with a solubility of 70 % in certain conditions. Bixbyite is represented as:

(Cr\(^{+3}\),Fe\(^{+3}\),Mn\(^{+3}\),Mn\(^{+4}\),Ni\(^{+2}\))\(_2\)(O\(^{-2}\))\(_3\)

### 4.1.8 Ilmenite

NiMnO\(_3\) with ilmenite structure has some solubility of manganese. According to Mehandjiev et al. [43] both Ni\(^{+2}\) and Mn\(^{+4}\) are in octahedral positions. NiMnO\(_3\) is thus modelled as:

(Mn\(^{+3}\),Mn\(^{+4}\),Ni\(^{+2}\))\(_2\)(O\(^{-2}\))\(_3\)

### 4.2 References for all subsystems

The Fe-C-Cr-Mn-Ni-O database includes the assessments listed in Table 4.1. The unary data are evaluated by the Scientific Group Thermodata Europe (SGTE) and are compiled by Dinsdale [44].
Table 4.1: Assessed subsystems within the Fe-Cr-Mn-Ni-O system.

<table>
<thead>
<tr>
<th>System</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Cr</td>
<td>Andersson [45], Lee [46]</td>
</tr>
<tr>
<td>C-Fe</td>
<td>Gustafson [47], Andersson [48], Franke [49]</td>
</tr>
<tr>
<td>C-Mn</td>
<td>Huang [50], Franke [49]</td>
</tr>
<tr>
<td>C-Ni</td>
<td>Gabriel et al. [51], Lee [46], Franke [49]</td>
</tr>
<tr>
<td>C-O</td>
<td>SGTE [52]</td>
</tr>
<tr>
<td>Cr-Fe</td>
<td>Andersson and Sundman [53], Lee [54]</td>
</tr>
<tr>
<td>Cr-Mn</td>
<td>Lee [54]</td>
</tr>
<tr>
<td>Cr-Ni</td>
<td>Dinsdale and Chart [55], Lee [54]</td>
</tr>
<tr>
<td>Cr-O</td>
<td>Taylor and Dinsdale [6, 7], Kowalski and Spencer [56], Kjellqvist et al. [41]</td>
</tr>
<tr>
<td>Fe-Mn</td>
<td>Huang [57]</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>Dinsdale and Chart [58], Lee [54]</td>
</tr>
<tr>
<td>Fe-O</td>
<td>Sundman [23], Selleby and Sundman [24], Kowalski and Spencer [56], Kjellqvist et al. [41]</td>
</tr>
<tr>
<td>Mn-Ni</td>
<td>NPL [59]</td>
</tr>
<tr>
<td>Mn-O</td>
<td>Grundy et al. [26], Kjellqvist and Selleby [27]</td>
</tr>
<tr>
<td>Ni-O</td>
<td>Taylor and Dinsdale [7], Kowalski and Spencer [56]</td>
</tr>
<tr>
<td>C-Cr-Fe</td>
<td>Andersson [48], Lee [46, 54]</td>
</tr>
<tr>
<td>C-Cr-Mn</td>
<td>Lee [60]</td>
</tr>
<tr>
<td>C-Cr-Ni</td>
<td>NPL [61], Lee [46]</td>
</tr>
<tr>
<td>C-Cr-O</td>
<td>Kjellqvist and Selleby [62]</td>
</tr>
<tr>
<td>C-Fe-Mn</td>
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<tr>
<td>C-Fe-Ni</td>
<td>Gabriel et al. [51], Lee [46]</td>
</tr>
<tr>
<td>C-Fe-O</td>
<td>Kjellqvist and Selleby [62]</td>
</tr>
<tr>
<td>C-Mn-Ni</td>
<td>extrapolation from binaries</td>
</tr>
<tr>
<td>C-Mn-O</td>
<td>extrapolation from binaries</td>
</tr>
<tr>
<td>C-Ni-O</td>
<td>Kjellqvist and Selleby [62]</td>
</tr>
<tr>
<td>Cr-Fe-Mn</td>
<td>Lee [54]</td>
</tr>
<tr>
<td>Cr-Fe-Ni</td>
<td>Lee [63], [54]</td>
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<tr>
<td>Cr-Fe-O</td>
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<td>Taylor and Dinsdale [7], Kjellqvist et al. [41]</td>
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<td>Mn-Ni-O</td>
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<tr>
<td>C-Cr-Fe-Ni</td>
<td>Lee [63]</td>
</tr>
<tr>
<td>Cr-Fe-Ni-O</td>
<td>Kjellqvist et al. [41]</td>
</tr>
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4.3 Oxidation of an austenitic Fe-Mn-Cr stainless steel

Douglass et al. [65] studied the oxidation in air of an austenitic Fe-Mn-Cr stainless steel containing 17.8 mass-% Mn, 9.5 Cr, 1.0 Ni, 0.27 C and 0.03 N. The samples were oxidized over the temperature range 700-1000°C for 24 hours and studied as the oxidation progressed from transient to steady-state mode. However, it seemed like equilibrium between the surface and the atmosphere was not reached for the samples at low temperatures (700-750°C). At low temperatures the only oxide formed in their experiments after 24 hours is Mn$_2$O$_3$, while at higher temperatures, a more complex scale consisting of halite, spinel, corundum and Mn$_2$O$_3$ is formed. A sample oxidized for 15 days at 750°C resulted in an oxide scale similar to those at high temperatures. The suspicion that the oxidation experiments at low temperatures does not reach equilibrium after only 24 hours is strengthened by the calculations performed using the database developed in this work. The calculations gave similar results over the whole temperature range, corresponding to the experimental result for high temperatures.

The oxide scales formed at high temperatures (800-1000°C) were thick and complex according to Douglass et al. [65]. The outermost oxide was always Mn$_2$O$_3$ with some iron in solution. In some cases, a thin layer of Fe$_2$O$_3$ with dissolved manganese was found beneath the Mn$_2$O$_3$. Below the outer scale an Fe-Mn spinel is formed and closest to the substrate a layer with manganowustite and a Cr-containing spinel. No chromium was found in the outer two layers.

A calculation at 900°C is shown in Fig. 4.1. The nitrogen in the steel is ignored. The composition of the spinel and halite phases is seen in Figs. 4.2(a) and 4.2(b). The spinel phase formed has a composition very close to MnCr$_2$O$_4$ at low P$_{O_2}$, with an increasing amount of Fe at higher P$_{O_2}$. The composition of the halite phase varies between MnO at low P$_{O_2}$ and a more Fe-rich phase at high P$_{O_2}$. The corundum phase is very close to Fe$_2$O$_3$ with small amounts of Mn and Cr. Mn$_2$O$_3$ is only stable in the calculations at oxygen pressures higher than in air or at high temperatures (>1225 K).

It should be remembered that this is a simple equilibrium calculation i.e. no diffusion is taken into account and the relative amounts of all the elements except oxygen, are constant. Because of this, the observed compositional variations in the oxides cannot be exactly reproduced. In order to be able to describe reality more closely a kinetic description of the system is also needed in addition to the present thermodynamic one. Models to describe diffusion in oxides are being developed in a parallel project [66] and mobility data are being assessed. Once this is available it will be possible to simulate the formation of oxides scales on a metallic surface including the thickness of the different layers as well as the variation in composition.
Chapter 4. The Fe-Cr-Mn-Ni-O database

Figure 4.1: Oxidation of a steel (17.8% Mn, 9.5 Cr, 1.0 Ni, 0.27 C) at 900°C.

Figure 4.2: Calculated composition of spinel and halite in the oxide scale.

(a) Composition of the β-spinel phase.  
(b) Composition of the halite phase.
Chapter 5

Concluding remarks

5.1 Summary of appended papers

Paper I. Parameters in the compound energy formalism for ionic systems
The compound energy formalism involves many model parameters, which are evaluated to give the best fit to the experimental information. The optimisation is simpler if less parameters need to be adjusted. The maximum number of independent parameters that can be evaluated depends on the information available. The best choice of parameters is first discussed for simple ionic substances with an internal variable, then for solutions of two or four such substances. To reduce the number of parameters, independent parameters are conveniently defined as combinations of primary model parameters. That may be possible when there is an internal variable, which can take only one value, the value that minimizes the Gibbs energy. Such combinations may be regarded as the true optimisation parameters and they may be used actively during an optimisation. The discussion in this paper deals with substances with an internal variable and mixtures, which may have more than one internal variable. The conclusions apply equally well to non-ionic systems if the information is limited to stoichiometric compositions.

Paper II. Thermodynamic modelling of the Cr-Fe-Ni-O system
There is a need to describe the influence of oxygen on high alloyed steels, both regarding oxidation processes like the formation of oxide layers and regarding steel/slag processes in a metallurgical context. As a first step in order to be able to perform calculations and simulations on these different processes, the thermodynamic properties need to be described. The core system for high alloyed steels is the Fe-Cr-Ni-O system, which is thermodynamically described in this paper. Previous attempts have been made to describe this system but resulted in an in-
consistent description, more specifically concerning the spinel phase. The aim of the present study was to obtain a consistent thermodynamic database for the Cr-Fe-Ni-O system with an emphasis on the modelling of the spinel phase. The solid phases are described using the compound energy formalism and the metallic and ionized liquid is modelled using the ionic two-sublattice model. The only quaternary parameters used are interaction parameters to model the miscibility gap in the NiCr$_2$O$_4$-NiFe$_2$O$_4$ spinel system. Otherwise, the description of the quaternary system is obtained by extrapolation of the ternary systems and the agreement with the limited experimental data on the quaternary system is quite good.

**Paper III. Adding C to the thermodynamic description of the Cr-Fe-Ni-O system**

The aim of this study was to include also carbon in the description of Fe-Cr-Ni-O, with an emphasis on the modelling of the liquid phase. The liquid phase is assessed in the C-Fe-O and C-Ni-O systems using the ionic two-sublattice model and good agreement between calculated and experimental data is achieved in the C-Fe-O system. The available experimental data in the C-Ni-O system could not be reproduced. The calculated oxygen solubility in liquid C-Ni is considerably lower than the reported value. This kind of disagreement has been discussed before for systems with a very low oxygen solubility in liquid iron. Based on C-Ni-O in this work and other systems from literature, it is suggested that the calculated solubility of oxygen is more reliable than the experimental one. The C-Cr-O system is extrapolated from the binaries since no experimental information was found. The model parameters in this paper together with the previous description of the Cr-Fe-Ni-O system [41], give a consistent thermodynamic description of the C-Cr-Fe-Ni-O system.

**Paper IV. Assessment of the Fe-Mn-O system**

In this paper the ternary Fe-Mn-O system is assessed and part of the binary Mn-O system is reassessed as the first step towards a Fe-Cr-Mn-Ni-O database. α- and β-hausmannite (Mn$_3$O$_4$) were earlier described as stoichiometric phases, but are here described using the compound energy formalism with a four sublattice model to be consistent with our previous work on the Cr-Fe-Ni-O spinel. The new model describes the cation distribution of ions between tetrahedral and octahedral sites and the nonstoichiometry of α- and β-hausmannite. Mn with oxidation state +4 is introduced to the octahedral sublattice in β-spinel to conform with the experimental information from Dorris and Mason [67]. The liquid phase is assessed using the ionic two-sublattice model, where the Mn$^{2+}$ ion has been replaced by a neutral MnO$_{1.5}$ species equivalent to the Fe-O system.

**Paper V. Assessment of the Cr-Mn-O system**

The assessment in this paper gives a good description of the available experimental information in the ternary Cr-Mn-O system. The C-Cr-Fe-Ni-O and Fe-Mn-O systems have been studied in earlier work with the intention to thermodynamically describe the influence of oxygen on high alloyed steels. No heat capacity measurement...
ments have been performed for the MnCr$_2$O$_4$ spinel and the enthalpy and entropy at 298 K is not known. The Gibbs energy of MnCr$_2$O$_4$ is evaluated based on phase diagram data and reported values for the Gibbs energy of formation at some temperatures. The description of the spinel phases in the Cr-Mn-O system is included in the same description as the Fe-Cr-Ni-O and Fe-Mn-O spinels. The liquid phase is assessed using the ionic two-sublattice model. Good agreement between calculated and experimental values is achieved.

**Paper VI. Assessment of the Mn-Ni-O system**

In this paper the ternary Mn-Ni-O system is assessed. The thermodynamic properties of NiMn$_2$O$_4$ have been rarely studied. No heat capacity measurements have been performed, the enthalpy and entropy at 298 K is not known and no reported Gibbs energy of formation has been found. The Gibbs energy function of NiMn$_2$O$_4$ was evaluated using phase diagram data and one reported enthalpy of formation of NiMn$_2$O$_4$ from NiO and Mn$_2$O$_3$ at 970 K. A controversy exists about the cation distribution in NiMn$_2$O$_4$ despite a number of investigations. In this work it is modelled as an almost complete inverse structure at room temperature, with a more normal structure at increasing temperatures. The spinel Ni$_{3-x}$Mn$_x$O$_4$ ($1.725 \leq x \leq 3$) is modelled using Mn$^{4+}$ in order to dissolve more Ni than NiMn$_2$O$_4$. The liquid phase is assessed using the ionic two-sublattice model. With this ternary, the Fe-Cr-Mn-Ni-O database is complete.

### 5.2 Discussion and future work

The compound energy formalism was used to describe all solution phases and the ionic two-sublattice liquid model for the metallic and ionized liquid. A self-consistent database for the Fe-Cr-Mn-Ni-O system is obtained by critical assessment of the subsystems. The majority of the binary and some of the ternary systems have been described earlier using models compatible with the models used in the present work, and these descriptions are adopted. The available descriptions of the Cr-O, Fe-O and Mn-O systems are slightly changed in this work. The ternary systems C-Cr-O, C-Fe-O, C-Ni-O, Cr-Mn-O, Fe-Mn-O and Mn-Ni-O are assessed in the scope of this thesis. The cubic spinel phase in Cr-Fe-O, Cr-Ni-O and Fe-Ni-O systems is reassessed in order to be consistent and compatible with the four-sublattice model. In Cr-Fe-O and Cr-Ni-O also the liquid phase is reassessed to avoid the formation of miscibility gaps at high temperatures that were present in the original assessments. For the missing ternary, C-Mn-O, there seems to be no available experimental data, why the description for C-Mn-O is achieved only by extrapolations from its binary systems. Three of the metallic ternary systems, M-Mn-Ni (M=C, Cr, Fe), are also only described by extrapolations from its binary systems. These systems should be examined more carefully if one uses the database to calculate equilibria close to the Mn-Ni corner.
All simple spinels (Cr$_3$O$_4$, FeCr$_2$O$_4$, Fe$_3$O$_4$, FeMn$_2$O$_4$, Mn$_3$O$_4$, MnCr$_2$O$_4$, NiCr$_2$O$_4$, NiFe$_2$O$_4$, NiMn$_2$O$_4$) within this system are described using the same model. Even though the same model is used, inconsistencies could be found when merging two or more assessments to be used in the same database. This was the case for the Cr-Fe-Ni spinel in previous studies due to different choices of reference for charge, resulting in deviant values for some of the end-members common in more than one system. Only one reference for each phase can be chosen. For the spinel phase, the recommended reference is $^oG_{\text{Fe}^{+2}:\text{Fe}^{+3}:V_a:O^{-2}} = \frac{^oG_{\text{Fe}^{+3}:\text{Fe}^{+2}:V_a:O^{-2}}}$. The model for the Cr-Fe-Ni spinel was made consistent without any reassessment by introducing interaction parameters. The spinel phase is now consistent for the entire Cr-Fe-Mn-Ni-O system.

This work will contribute to the development of a larger oxide database able to treat high alloyed steels. The models in this work are compatible with the models used in a parallel work on the Al$_2$O$_3$-CaO-Fe-O-MgO-SiO$_2$ system [68,69]. Merging this description with the Fe-Cr-Mn-Ni-O system will be a huge work including many new assessments. More interesting alloying elements for high alloyed steels could also be added to the database eventually, e.g. Mo, Si, Co etc. The Fe-Cr-Mn-Ni-O database can be used with an appropriate thermodynamic software, e.g. Thermo-Calc, to calculate thermodynamic properties, equilibrium states and phase diagrams. In general, the agreement between calculated and experimental values is good. The database, combined with kinetic information together with a suitable software, e.g. Dictra, could be used to simulate diffusion in oxides [70].
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