Phase Equilibria and Thermodynamics of Rare Earth-Iron Systems

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Doctoral Thesis

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Abstract
The present thesis was initiated by a quest for knowledge about the Fe-Tb-Dy system and is focused on the basic thermodynamics of the rare-earth systems with primarily iron. The final aim is to create a thermodynamic database for rare earth-iron systems, a database from which all phase diagrams and thermodynamic properties of interest may be calculated. The emphasis is on the iron-rare earth systems but occasionally other systems are considered, e.g. when a more systematic study is performed in order to extrapolate necessary properties.

In the thesis calculations, empirical predictions, e.g. based on the atomic number, and assessments are combined with experimental investigations. During this work many questions of more fundamental nature appeared and some of them are tackled in the thesis. One may mention particularly:

- In the Fe-Dy and Fe-Tb systems, the lack of thermodynamic data led to several questions. For example, is it possible to obtain reliable values for the enthalpies of formation for the intermetallic phases by considering trends in the periodic table? Thus a systematic study, to predict the enthalpies of formation of the Laves phases, including the rare earth-iron, cobalt and nickel systems was performed, and the enthalpies for the intermetallic phases in the Fe-Dy and Fe-Er systems were measured.

- The solubility of Fe in Dy and Dy in Fe are determined by the so-called lattice stabilities. These quantities are predicted in the thesis by assessing intra rare earth systems.

- The transformation between the different close-packed structures, e.g. dhcp and hcp, is controversial. Is there a two-phase field between dhcp and hcp in the phase diagram or can the two phases gradually transform into each? According to the latest review article in the field such a gradual transformation is indeed possible. However, when critically examining the crystallographic relations and studying the early articles on the Nd-Sc system the present author concluded that the transformation must always be first order, i.e. there must be a two-phase field.

- The Fe$_2$Dy phases is a ferrimagnetic compound. The effect of the magnetism on the thermodynamic properties is considered.

Key Words: Rare earth metals, Terfenol-D, Laves phase, Enthalpy, experiment, Magnetostrictive material, intra rare earth systems, Fe-Tb, Dy-Fe, Dy-Fe-Tb, Er-Ho, Dy-Ho, Ho-Tb, Er-Tb, Dy-Er, Gd-Sc, Nd-Sc, Sc-Y, Heat capacity, Thermodynamic, Phase Equilibria
Reports

This thesis is based on the following papers:

I. Susanne Landin and John Ågren
Thermodynamic Assessment of the Fe-Dy and Fe-Tb Phase Diagrams and Prediction of the Fe-Tb-Dy Phase Diagram.

II. Susanne Norgren and John Ågren
Enthalpies of Formation of Transition-Metal Lanthanide Laves Phases with the MgCu2 Structure

III. Susanne Norgren, Fickerie Hodaj, P. Azay and Catherine Colinet
Experimental Investigation on the Enthalpies of Formation of the DyFe2, DyFe3, Dy2Fe17, ErFe2 and ErFe3 Intermetallic Compounds.

IV. Susanne Norgren and John Ågren
Heat Capacity of DyFe2

V. Susanne Norgren
Thermodynamic Assessment of the Ho-Tb, Ho-Dy, Ho-Er, Er-Tb and Er-Dy Systems.
To be published in Journal of Phase Equilibria.

VI. Susanne Norgren and John Ågren
On the dhcp-hcp Transformation in the Nd-Sc System.
To be submitted to Acta Materialia
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1. Introduction

Alloys based on the rare earth metals are a relatively new group of materials. Although the elemental metals were chemically separated already in 1907 (1) they were regarded as those “odd difficult ones at the bottom of the periodic table” (1) for many years. Not until more recently the technological and industrial potential of the rare earth metals have been explored. Despite their name they are not rare in the earth crust. For instance, cerium is as common as nickel or copper and the least abundant lanthanide is more plentiful than silver.

This thesis is concerned with the novel iron-rare earth alloys. Today such alloys have many applications as functional materials, most of them based on unique magnetic properties. One may mention, for example, information storage components on mini-discs, magnets, actuators for motors, micro-positioners, sensors for marine devices and ultrasonic equipment for medical diagnoses (1,2).

The strongest known (Super) magnet and the material with the highest known magnetostriction are found among the ferrous rare-earth alloys. A magnetostrictive material changes shape when it is exposed to a magnetic field (3,4,5), Figure 1.

**Figure 1.**

The magnetostriction is defined as the fractional change in length when the applied field is rotated from perpendicular to parallel with the measurement direction. (3)
In 1971 Clark and Belson (6), at Naval Ordnance Laboratory in White Oak, Maryland-USA, discovered that the Fe$_2$Tb Laves phase has a giant magnetostriction. They named the new alloy Terfenol, composed of the words for TERbium, FErum, and Naval Ordnance Laboratory. It was later found that an addition of dysprosium to Terfenol improved the magnetic properties further. The most favourable composition was Fe$_{1.95-2.0}$Dy$_{0.73}$Tb$_{0.27}$ and the alloy was named Terfenol-D, where D stands for Dysprosium.

In 1981 Croat (7), discovered the Fe-Nd super magnets and Koon and Das (8) the even stronger Fe-Nd-B magnets. Even though strong Sm-Co magnets were known since the late sixties the new Fe-Nd-B became technologically very important due to the much lower price. Today the development of Fe-Nd alloys with boron or nitrogen additions has resulted in magnets that are even stronger than the Sm-Co magnets (1) at room temperature. However, for high temperature applications the Co based alloys are still preferred since they have a higher Curie temperature.

Rare earth metals are also technologically important in other applications often based on their high affinity to oxygen rather than on their magnetic properties. For example, they are added as misch-metal in high-alloy steels, Y and Dy are used in doping of high-temperature superconductors and Ce is used with Fe in lighter flints and as oxygen getters in order to lower the oxygen partial pressure. Rare earth metals are also added in aluminium alloys for a grain refining effect. Moreover, in 1997 Gschneidner patented a method utilising the magnetic ordering energy in these metals to construct a new generation of freon-free refrigerators (9).

The physical properties of a material are intimately related to its microstructure and an important task thus is to control and design the microstructure to achieve optimal properties and performance. The microstructure depends on temperature, pressure, chemical composition and thermal history of the material. Fortunately, there are several techniques available to control and design the microstructure. One of the most important guides for the materials scientist is the appropriate phase diagram. The phase diagram may be regarded as a map, describing the state of equilibrium in the system under various experimental conditions, i.e. temperature, pressure and chemical
composition. According to thermodynamics, the lowest Gibbs energy determines the equilibrium state at given conditions, and the phase diagram thus represents the thermodynamic properties of the system with the lowest Gibbs energy. During the last decades the SGTE (Scientific Group Thermo-data Europe), which is a collaboration between different European groups, has presented a set of thermodynamic databases from which phase diagrams and other thermodynamic properties can be calculated.

Unfortunately, not much research is reported on the thermodynamic properties of the rare earth-iron systems compared to other metallic systems. Thus research in this field is much needed and the task is not so much to find an interesting question but rather to choose one. Fortunately, the rare earth elements are chemically very similar and often one can make good predictions by studying tendencies in the periodic table.

Consequently, the present research was initiated by an urge for more information about the phase relations of the Fe-Tb-Dy system in particular and rare earth systems in general. The objective is to create a thermodynamic database for these systems, a database from which all phase diagrams and thermodynamic properties of interest may be calculated. The emphasis is on the iron-rare earth systems but occasionally other systems may be considered, e.g. when a more systematic study is performed in order to extrapolate necessary properties.

2. History of the rare earth metals

From a Swedish perspective the history of the rare earth metals is very interesting and is described in e.g. “Jordens grundämnen” volume 2 by Enghag (2). For the convenience of the reader a short résumé is given in this section.

In 1787 Arrhenius discovered a black mineral in the feldspar mine of Ytterby on the island of Resarö in Sweden (2). He called the black mineral ytterbit. The Finish scientist Gadolin at Uppsala University made the first analysis of the black mineral in 1794 and concluded (in Swedish) that it
contained “31 delar kiseljord, 19 delar alun, 12 delar järnkalk and 38 delar av okänd jordart”. The last two words are Swedish for unknown earth. This statement and the common belief that this “okänd jordart” was rare led to the name “Rare Earths” (10). Ytterbit was renamed to Gadolinit and was later shown to be a mixture of many rare-earth metal oxides. The names of many rare earth metals for example Erbium, Terbium, Yttrium and Ytterbium, (Ytterby), Scandium (Scandinavia), Thulium (Thule) and Holmium (Stockholm) reflect, where they were first found. In 1989 The ASM classified the mine at Ytterby as “Historical Landmark” in the history of metals.

In the Swedish village of Bastnäs, not far from Riddarhyttan, Cronstedt, found another black mineral in 1751, which he first thought was tungsten. Fifty years later Berzelius and Hisinger discovered that the main component was cerium-oxide and they thus called the mineral Cerit. In 1850 the rare earths Y, Er and Tb were extracted from Gadolinit. This mineral contains almost all the heavy rare earth metals, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y, while Cerit mainly contains the light rare earth metals La, Ce, Pr, Nd, Sm and Sc. The pioneering work by Mosander, Berzelius, Cleve, Nilson, de Boisbaudran, Urbain, de Marignac and von Welsbach made it possible to refine all the rare earth metals already in 1907, except Pm which was not discovered until 1947 (2).

In 1948 Ce misch-metal additions, were used to produce nodular cast iron but was later replaced by the less expensive Mg. Today rare earth misch-metal is primarily added to high-temperature alloys to improve their corrosion resistance.

The rare earth metals have among the highest known oxygen affinity and consequently oxygen impurity levels were high in the early days. Other impurities are nitrogen, iron and other rare earth elements. Not until 1966 the first really pure rare earth metal, Yttrium, was produced by solid state electrolysis. This process could operate on a larger scale and the market price, on most of the rare earth metals, dropped (1).
3. Thermodynamics of the Rare earth systems

Computer aided phase diagram calculations, based on thermodynamic data, have been used for more than two decades. In this thesis the CALPHAD method (CALculation of PHAse Diagrams) is applied to describe the alloy systems considered. This method originates from the work by Kaufman and Bernstein (11), Hillert (12) and others. For a more detailed description the reader is referred to the recent book by Saunders and Miodownik (13). In the CALPHAD method the individual phases in a system are assigned Gibbs energy expressions.

The Gibbs energies of the liquid and solid solution phases in the Fe-R systems, where R is any of the trivalent rare earths, are described with a substitutional solution model based on random mixing of the different atoms. The molar Gibbs energy for the liquid thus is expressed as:

\[ G_m^L = x_A^o G_A^L + x_B^o G_B^L + RT (x_A \ln x_A + x_B \ln x_B) + x_A x_B I^L \]  \hspace{1cm} (1)

where \( g^o_i \) is the Gibbs energy in a non-magnetic state of the pure component, \( x_i \) is the composition of \( i \) in atomic percent, \( R \) is the gas constant and \( T \) is the temperature. \( I^L \) is a regular solution parameter. The composition dependence of \( I^L \) is represented by a Redlich-Kister polynomial:

\[ I^L = \sum_{k=0}^k L_{AB}^L (x_A - x_B)^k \]  \hspace{1cm} (2)

where \( L_{AB}^L \) are adjustable parameters that may depend on temperature. The same thermodynamic model as for the liquid phase is used for the solid solution phases but with an additional term, \( G_m^{mag} \), which is the contribution to the Gibbs energy from the magnetic ordering. The magnetic contribution is described by the model by Inden (14) and Hillert and Jarl (15). The intermetallic phases are described with two substitutional sublattices one for iron atoms and one for rare earth atoms.

The adjustable parameters in the Gibbs energy expressions are optimised to fit various pieces of experimental information such as, for example, phase diagram data, enthalpies, heat capacities and activities. The procedure of
critically selecting data, choosing thermodynamic models, i.e. the Gibbs energy expressions and to evaluate the model parameters to fit the experimental data is often called an assessment. There are several software tools available for this procedure. In this work the Parrot (16) optimising module within the Thermo-Calc (17) software has been used. The optimal parameters are found by a non-linear least square optimisation procedure. An assessment is a time consuming task and it requires the skill and ability to select reliable data when data from various sources are contradictory.

Generally speaking, the experimental phase diagram and thermodynamic data are sparse in the iron-rare earth systems and intra rare earth systems. Moreover, in the iron-rare earth alloys the existing enthalpy measurements are contradictory as discussed by Norgren and Ågren (paper II). One question for these systems concerns the magnetic contribution to the Gibbs energy from the 4f electrons. Schön and Inden (18) showed that for pure Gd there is an extra contribution to the heat capacity from the 4f electrons. The question then is whether the Hillert-Jarl (15) and Inden model (14), used in the SGTE-databases, is capable or not of representing this effect.

In the next section some questions, uncertainties and limitations on the phases in the rare earth-iron systems will be discussed in more detail.

4. The Terfenol-D systems.

4.1 The Fe-Dy binary system

The Fe-Dy system was investigated by Van Der Goot and Buschow (18), Figure 2. They showed that four intermetallic phases existed and indicated that Fe$_{23}$Dy$_6$ melts peritectically at 1290 °C. In their phase diagram, the liquidus curve in the vicinity of the Fe$_3$Dy phase shows a very asymmetric shape indicating that the properties of the liquid is very different on either side of the Fe$_3$R phase.

This behaviour of the liquid is not seen in the other iron-rare earth systems. Thus this asymmetric shape in the Fe-Dy system does not seem reasonable
and Landin and Ågren, (paper I), instead assumed a more symmetric liquidus curve of the Fe₃R phase. In their assessment it was impossible to treat the Fe₂₃R₆ phase as formed through a peritectic reaction. It was instead suggested to form by a peritectoid transformation a few degrees below the originally proposed peritectic temperature, Figure 3.

Figure 2.
The Fe-Dy phase diagram hand drawn by Van Der Goot and Buschow including their experimental points (18).

Figure 3
The Fe-Dy phase diagram as assessed by Landin and Ågren (paper I).
4.2 The Fe-Tb-Dy ternary system.

A calculated phase diagram section in the Fe-Tb-Dy system is shown in Figure 4, together with the only experimental information available (20). In this calculation no ternary interaction parameters were used since these binary systems are very similar indicating that only very small or no ternary interactions should be needed.

The agreement between the experiments and the calculation, Figure 4, is despite this fairly good, except for the liquidus curve between 0.3-0.5 mole fraction Fe. However, it is not reasonable to assess ternary interaction parameters in order to fit one single experimental point. It should be mentioned that the thermodynamic data, by Landin and Ågren, paper I, is only valid above 800 K where the magnetic contribution to the Gibbs energy can be neglected.

![Figure 4](image)

Section of the Fe-Tb-Dy ternary system calculated with the assumption that the Fe$_{23}$R$_6$ phase is present, paper I.

As seen in Figure 4 all the intermetallic phases are stochiometric. However, a recent experimental investigation by Mei et al. (21) shows that there is a 2 at%-narrow homogeneity range for iron at high temperatures in the Laves
phase. This is important as it allows for a slight variation in composition when producing Terfenol-D. To achieve optimal magnetostriction a single-phase material is preferred, as additional phases will hinder the domain wall motion. Today, Terfenol-D is produced with a slight excess of rare earth metals, in order to avoid of the adjacent Fe₃R phase with less good properties.

4.3 Stability of the Fe₂₃Dy₆ phase

The rare earth-iron systems from Gd to Lu, with the exception of Yb, form several intermetallic compounds, namely Fe₂R, Fe₃R, Fe₂₃R₆ and Fe₁₇R₂. The existence of Fe₂₃R₆ is somewhat controversial. Although, this phase is reported in almost all the early heavy rare earth-iron phase diagrams, i.e. the Gd-, Tb-, Dy-, Ho-, Er-, Tm- and Lu-Fe, many authors think that it might be stabilised by impurities relying on an article by Gschneidner (22). This effect is known in the R₃Al series where all the heavy-R₃Al phases are stabilised by impurities and therefore not present in the pure binary systems (23). Van der Goot and Buschow (19) obtained a one-phase Fe₂₃Dy₆ structure by heat treating the composition at 1250 °C for 4 weeks. Norgren et al., (paper III), also tried to synthesise this compound by heat treating at 1200 °C for 3 weeks. They found a Fe₂₃Dy₆ single-phase structure in the SEM and by x-ray diffraction. It should be mentioned that they did not analyse the impurity levels after this long heat treatment. The phase was not investigated further as it was very brittle and hard to handle. However, the Fe₂₃R₆ phase is still a puzzle. Gschneidner (22) proposed, as mentioned, that some phases in the rare earth systems could be stabilised by impurities. On the other hand, Henig and Grieb (24) investigated the Fe-Tb-B ternary phase diagram and did not succeed in synthesising Fe₂₃R₆ at all. Of course it may still exist in other impurity systems. In conclusion whether Fe₂₃R₆ is a high temperature phase in binary Fe-R systems or if it is stabilised by impurities is still an open question.
5. Enthalpies of formation

5.1 Systematic studies

When calculating phase diagrams the enthalpy of formation of the intermetallic compounds is an important quantity. It is then important to consider how the sparse experimental information available should be used and how contradictory information should be treated. In general, the rare earth elements are believed to have very similar properties as they differ from each other only in the number of f-electrons. Often this is true but there are exceptions, (25). For instance, there is a span in melting points of 750 K between La (1193 K) and Lu (1936 K).

The similarity between the different rare earth elements allows reasonably accurate estimations of unknown properties to be made from known properties. Systematic studies are often used to derive the properties from one rare earth to the other. The studies are often based on the atomic number, which directly reflects the number of f-electrons for these trivalent rare earth metals. It is believed that the f-electrons have little, if any effect on the lanthanide structural sequence (1, 25). If a property, e.g. the molar volume or the enthalpy of formation of a compound is plotted versus atomic number one expects a smooth variation, except for Pm, Eu and Yb. The exceptions are due to that the Pm nucleus is unstable and data is consequently missing. Yb and Eu are divalent and their phase diagrams are not consistent with the other trivalent rare earths. Plotting the trivalent rare earths like this is equivalent with the inverse Mendeleev number sequence as suggested by Pettifor (26). However, it is always important to know the nature of the studied group of metals when a plot like this is made. When plotting a property, for example the enthalpy of formation of a given compound, versus the atomic number, Ce often deviates. This behaviour is caused by the valence of cerium that fluctuates between 3 and 4 while the others are trivalent. When comparing the rare earth metals at room temperature it is important to keep in mind that Gd has a magnetic transition just below room temperature (27).
5.2 The Reduced Volume

The atomic volume decreases smoothly with 7.6% from La to Lu. This is called the lanthanide contraction and was discovered by Goldschmidt (28) for the oxides and shown by Klemm and Bommer (29) for the pure elements. Kubaschewski et al. (30) showed that there is a correlation between enthalpy of formation and relative volume contraction, although there are numerous exceptions. They (30) defined a volume parameter \( f \), as:

\[
f = \frac{V[Me_xR_y]}{x\cdot V[Me] + y\cdot V[R]} - 1
\]

where \( V[Me_xR_y] \) is the experimental volume of the compound and \( x\cdot V[Me] + y\cdot V[R] \) is the calculated volume of the pure elements in stoichiometric amounts. If the compound formation yields no volume change \( f = 0 \). A strongly negative \( f \) would indicate a strongly negative enthalpy of formation, i.e. a more stable compound. Gschneidner (31) suggested a method to compensate for the lanthanide contraction based on the correlation found by Kubaschewski et al. (30). He introduced the reduced volume, \( V_{\text{Red}} \).

\[
V_{\text{Red}} = \frac{V[Me_xR_y]}{V[Me_xLa_y]} \frac{V[La]}{V[R]}
\]

and proposed that the enthalpy of formation for the compound \( Me_xR_y \) would have similar variation with atomic number of \( R \) as the reduced volume. If the reduced volume decreases as a function of atomic number then the enthalpy of formation also becomes more negative when going from \( Me_xLa_y \) to \( Me_xLu_y \) and vice versa. Gschneidner (31) was indeed able to demonstrate the applicability of his correlation for a number of compounds. This method holds for the \( Al_2R \) and \( Mg_2R \) series as shown by Ferro et al. (32). Jacob and Pandit (33) argued that the correlation does not hold for the \( RPt_5 \) compounds at 1000 K. Here there is an increase in the reduced volume \( V_{\text{red}} \), while emf- measurements (33) are almost independent of lanthanide atomic number. As pointed out by the present author, (paper II), there is not necessarily a contradiction because Gschneidner considered the enthalpy at low-temperatures while Jacobs and Pandit (33) regarded the total Gibbs energy.
at very high temperatures. At 1000K the entropy of formation may have a considerable effect on the result. However, in the present thesis, paper II, it is concluded that Gschneidner’s correlation does not hold for the Fe$_2$R-, Co$_2$R- and Ni$_2$R-series.

In Figure 5, $V_{\text{red}}$ is plotted versus the atomic number of the lanthanide in the Laves phase and in Figures 6 and 7 the existing measurements of the enthalpy of formation in the Co$_2$R and Ni$_2$R Laves phases are plotted.

**Figure 5**
Reduced volume $V_{\text{red}}$ for the Fe$_2$R, Co$_2$R, Ni$_2$R and Mn$_2$R Laves phases, after paper II.

**Figures 6 and 7.**
Experimental enthalpy of formation at 298 K in the Co$_2$R and Ni$_2$R phases as a function of the lanthanide atomic number, after paper II.
As can be seen, the reduced volume increases and according to Gschneider’s correlation the enthalpy of formation would become more positive. Although from Figures 6 and 7 it is evident that the enthalpy of formation is almost independent of atomic number or even decreases. In the Fe$_2$R Laves phase series only two contradictory investigations are performed and in the Mn$_2$R series no there were no accessible enthalpy measurements, hence these plots are not shown here.

### 5.3 Measurement of the enthalpy of formation in the Fe-Dy and Fe-Er systems

As a part of this thesis the enthalpies of formation of all the intermetallic phases in the Fe-Dy and Fe-Er systems, except the Fe$_{23}$R$_6$ phase were measured by indirect solution calorimetry, paper III. The Fe-Dy system was an obvious choice since it is one of the components in Terfenol-D. The Fe-Er system was included in the measurements as it contains the same intermetallic compounds as the Fe-Dy system and is one of the heavy rare earth metals. The measured enthalpies are shown in Figure 8.

![Figure 8.](image)

Experimental values of the enthalpies of formation of the intermetallic compounds in the Gd-Fe, Dy-Fe and Er-Fe systems, after paper III.
The enthalpy measurements shown in Figure 8 indicate that the enthalpy is constant or slightly becomes more negative when going from Fe$_2$Gd to Fe$_2$Er in agreement with the trend shown for the Co$_2$R and Ni$_2$R series. It is clearly shown in the plot that the enthalpy of formation becomes more negative in the order from Fe$_{17}$R$_2$, Fe$_3$R and Fe$_2$R. As seen the Fe$_{17}$Dy$_2$ phase has a very low enthalpy of formation and the error for this value is therefore as large as 25%, paper III.

6. Lattice stabilities, phases and structures of pure elements

In our first assessment, paper I, of the Fe-Tb-Dy system the low solubilities of rare earth in iron and iron in rare earth were neglected. In order to describe these solubilities with the Calphad method it is necessary to know the so-called lattice stability (11) of the rare earth structure where it is not stable. To clarify which lattice stabilities that are needed for the rare earth metals, a short summary of the existing phases and structures is done.

Jayaraman and Sherwood (34) presented the close packed sequence of the rare earth metals, starting from fcc - dhcp - Sm-type to hcp. All the heavy rare earth elements have the close packed hexagonal structure, Mg-type, with ABAB stacking. The light rare earth metals, Nd and Pr, have the double close packed hexagonal structure with ABAC-stacking, La-type, at room temperature and atmospheric pressure. La and Ce have both the latter, at high temperatures, and the fcc stacking at room temperature. Sm has the unique Sm-type structure that is close packed hexagonal with ABCAB stacking. All the rare earth elements transform to bcc at high temperatures except Er, Tm and Lu and maybe Ho. The fcc structure is only found in La and Ce at atmospheric pressure. Consequently when performing assessments of these systems there is a need for reliable predictions of the lattice stability for the hypothetical structures, such as Ho, Tm and Lu as bcc and Pr through Lu as fcc. It is helpful to study trends in the periodic table when estimating properties not previously measured. In this case the intra-rare earth systems are very suitable since these metals are very similar making it possible to extrapolate properties from one system to another. In paper V,
Norgren estimated lattice stabilities for hypothetical bcc Holmium and bcc Erbium and the enthalpy part are shown in Figure 9, as black triangles.

![Figure 9.](image)

The enthalpy difference of Bcc/α-Ho and Bcc/α-Er, where α denotes a stable close packed phase, are shown as black triangles, after paper V.

The black points in Figure 9 are ab initio calculations of the enthalpy of formation at 0 K (35). These calculations often overestimates the real experimental value (35) but the common trend is the same as for experimentally obtained values as seen in Figure 9. These values were included here for comparison with estimates of bcc-Ho and bcc-Er. These estimates are in line with the trend for the rare earth elements. However, in Figure 9 there is also a SGTE-pure enthalpy value for Ho, $\Delta H_{m}^{\alpha/bcc}$ (36), one should keep in mind that it was not completely clear if Ho transforms to bcc just below the melting point or not. Consulting, binary intra rare earth data in the Ho-Er, Ho-Dy and Ho-Tb systems the present author’s opinion is that it melts as hcp. This is discussed in paper V.
7. The Sc-Nd system

The intra rare earth diagrams, with one end member having the hcp and one the dhcp structure are puzzling. The common opinion seems to be that these structures can gradually transform into each other, even though, the stacking sequence is different. This belief stems from a very thorough investigation of the Sc-Nd phase-diagram by Beaudry et al. (37), Figure 10.

They reported a wide two-phase mixture at low temperatures but a homogeneous solution at high temperatures. However, to accomplish a transformation from hcp to dhcp structure an entire atomic plane needs to be moved but it is hard to visualise how this can be achieved gradually as a homogeneous transformation. Hence, Norgren and Ågren, (paper VI), assessed this phase diagram and presented a different solution with a very narrow two-phase region at high temperatures, Figure 11.

It is interesting to notice that in many other intra rare earth systems with one end member being dhcp and the other hcp, there is an intermediate phase named d-phase, which is formed by a peritectic reaction. At temperatures
above this phase a two-phase, dhcp-hcp, region is indicated (38-41). In the most recent compilation of the intra rare earth systems (42) this possible two-phase region is not shown as they thought the transformation is gradual. The d-phase is not treated in this thesis but it can be mentioned that it has the Sm-type structure and has been observed in most of the heavy-light intra rare earth systems. When and how it forms is not exactly known. It may form by a peritectoid reaction at low temperatures as first suggested by Spedding (38). Koch (43) on the other hand suggests that it form martensitically due to strains set up in the alloy.

![Figure 11](image)

Nd-Sc phase diagram assessed by Norgren and Ågren, (paper VI), treating the dhcp and hcp phases as separate phases.

8. Magnetic transition and heat capacity

Our first assessment of the Fe-Tb-Dy system, see paper I, is only valid above 800 K. In order to extend the diagram to lower temperatures, the magnetic contribution to the Gibbs energy must be taken into account. The Fe$_2$Tb and Fe$_2$Dy phases are magnetic at room temperature. The rare earth Fe$_2$Dy compound is a ferrimagnet and has a critical temperature of 362 °C.
The magnetic model used in assessments, so far, is developed for ferromagnets by Inden (14) and Hillert-Jarl (15). This model is also applied to antiferromagnets. The question is how it applies to a ferrimagnet as Fe$_2$Dy. Norgren and Ågren, (paper V), calculated the heat capacity of Fe$_2$Dy using the Einstein model for the nonmagnetic part and the Inden-Hillert-Jarl model for the magnetic contribution. No quantitative measurements of the heat capacity above 300 K were reported in the literature and thus the present author recently applied DSC to measure it.

![Figure 12.](image)

*Figure 12.*  
+ Heat capacity measured in this work; thick solid lines are the Neumann-Kopp kombination with the magnetic contribution according to the Inden-Hillert-Jarl (14,15) model. The thin solid line consists of the Einstein model with two optimised additional terms (+AT+BT$^2$), and the Inden-Hillert-Jarl model for the magnetic contribution.

In Figure 12, the calculated and experimental heat capacity is plotted. Unfortunately, the scatter of the experimental data is rather high, indicated by the dashed lines, but nevertheless, it seems too early to rule out the applicability of the Inden-Hillert-Jarl model in the present case. However, one may notice that the observed effect of short-range order, i.e. above the critical
temperature is larger than predicted from the calculations. This parameter should thus be adjusted in the model.

9. The present reports

A short comment on the reports in this thesis is given and the pertinence to the development or knowledge of new materials. The present author’s contribution to each work is outlined.

9.1 Thermodynamic Assessment of the Fe-Dy and Fe-Tb phase diagrams and prediction of the Fe-Tb-Dy Phase diagram

In this work thermodynamic assessments of the Fe-Dy and Fe-Tb binary systems are presented together with a calculation of the ternary Fe-Tb-Dy system assuming that the Tb-Dy system is ideal. These phase diagrams are useful when, for example, studying the melting behaviour, explaining the microstructure or when trying to synthesise an alloy with specific properties at the lowest cost and best result.

The present author performed the calculations and wrote the report, under supervision of Ågren.

9.2 Enthalpies of Formation of Transition-Metal Lanthanide Laves Phases with the MgCu₂ Structure

In this work a systematic study to derive realistic values for the enthalpies of formation of the lanthanide Laves phases are presented. These quantities have not been measured earlier. The study included the Ni₂R, Co₂R and Fe₂R Laves phases.

The present author performed the simulations and wrote the report. The work was supervised by Ågren.
9.3 Experimental Investigation on the Enthalpies of Formation of the DyFe$_2$, DyFe$_3$, Dy$_2$Fe$_{17}$, ErFe$_2$ and ErFe$_3$ Intermetallic Compounds.

In this work an experimental study of the enthalpies of formation using dissolution calorimetry in liquid aluminium is presented. The enthalpies are an important piece of information when assessing phase diagrams.

The present author did most of the experimental work, under supervision of Colinet and Hodaj and wrote the report under supervision of Colinet and Ågren.

9.4 Heat Capacity of DyFe$_2$

In this work the effect of ferrimagnetic ordering on the heat capacity and the thermodynamic properties is studied. Applying existing models for the magnetic contribution, e.g. the Hillert-Inden-Jarl model developed to the fourth term in the series expansion and the Einstein model for the vibrational part of the heat capacity.

The work was performed by the present author who also wrote the report. The work was supervised by Ågren.

9.5 Thermodynamic Assessment of the Ho-Tb, Ho-Dy, Ho-Er, Er-Tb and Er-Dy Systems.

In this work the lattice stabilities of Ho and Er with a bcc structure and Nd and Gd with a fcc structure are predicted. An attempt to estimate the lattice stabilities of dhcp, Sm-type, hcp and fcc phases are also given. Moreover, the phase diagrams are assessed and calculated. It is discussed whether Ho is hcp structure up to the melting point or transforms to bcc just below the melting point.

The present author did the assessments and calculations and wrote the report. The work was supervised by Ågren.
9.6 On the dhcp-hcp transformation in the Nd-Sc system

In this work the crucial Nd-Sc system is assessed treating dhcp and hcp as separate phases. The wide two-phase region below 600 °C is accomplished by introducing a miscibility gap in the hcp phase.

The assessments and the experimental work were done by the present author who also wrote the report. Ågren was supervising.

10. Questions and some words about the future

In the binary rare earth-iron systems there is a need for a more thorough investigation of the Fe$_{23}$R$_{6}$ phase to verify under what circumstances it is stable.

The possible bcc region in Ho needs to be further investigated experimentally.

In the assessments the Fe and R atoms are assumed to form a substitutional solution even though the iron atom is much smaller than the R-atom and iron diffusion is very fast in most of the rare earth metals indicating diffusion via interstitial sites.

All the intra rare earth phase diagrams with one end member being hcp and the other dhcp should probably be redrawn or reassessed, as it is not possible to have a homogeneous transformation between the two different structures. In these systems the formation of the Sm-type phase needs to be further studied.

More studies on the effect of ferrimagnetic ordering on the heat capacity are needed, for example in Fe$_2$Dy. The hump in the heat capacity caused by the 4-f electrons must be included in the magnetic model.
11. Conclusions

This work was aimed at the phase relationships and thermodynamic properties of rare earth-iron alloys being the basis of many novel functional materials. It has resulted in a database covering the following binary systems: Fe-Tb, Fe-Dy, Ho-Er, Ho-Tb, Ho-Dy, Er-Tb, Er-Dy, Sc-Nd, Sc-Gd, and Sc-Y. The binary data can be combined to calculate phase diagrams or thermodynamic properties in binary and possibly in higher-order systems. In the thesis the ternary Fe-Tb-Dy liquidus surface is calculated as one example.

However, during the course of this work a number of issues have been addressed. A severe problem is the lack of experimental information. This work has contributed with measurements and estimates of thermodynamic properties necessary for reliable phase diagram assessments. For example, estimated values for the enthalpies of formation of the Me₄R Laves phases in the Fe, Co and Ni series are presented. Moreover, hypothetical lattice stabilities, necessary in phase diagram assessments to describe the solubility of R in Fe or Fe in R, for Ho-, Er-bcc and Nd-, Pr- and Gd-fcc, are predicted. A method to evaluate the lattice stabilities for the close packed structures is proposed and used for hcp-Nd and dhcp-Sc.

In this thesis an alternative interpretation to the Sc-Nd system containing a dhcp-hcp two-phase field is given. The general opinion seems to be that this transformation is gradual. However, available experimental data do not verify this experimentally, allowing for a different interpretation of the system including a narrow two-phase region.

The pure rare earth metals have been available for over 90 years and it is surprising that questions regarding the pure elements still are not answered or completely understood. For Ho the general opinion seems to be that it has a hcp structure up to the melting point and this is assumed in this thesis also. This assumption is based on three Ho-R phase diagrams. Despite this, there is a small possibility that Ho transforms to bcc just below the melting point and to the knowledge of the present author, this possibility has not been thoroughly investigated experimentally.
The effect of ferrimagnetic ordering on the heat capacity of the Fe$_2$Dy Laves phase is discussed and a qualitative plot of the heat capacity in the vicinity of the critical temperature is shown. More experimental investigations are needed to evaluate if the existing magnetic model is capable of describing the heat capacity or not.

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