Magnetic component of mixing enthalpy for BCC Fe-Cr alloys: ab initio based model

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Abstract. The standard magnetic model in the current CALPHAD modelling is based on the Inden–Hillert–Jarl model and can be used to ferromagnetic and antiferromagnetic alloys. In this work, we demonstrate that this model can also be applied to alloys with more complicated forms of magnetism. The concept of ‘effective magnetic moment’ has been introduced as a measure of the maximum magnetic entropy. To calculate this quantity, it is necessary to know the local magnetic moments on the atoms of the components. A case study on the Fe –Cr system has been performed by Density Functional Theory (DFT) formalism at 0 K. It is shown that the CALPHAD modelling using the concept of effective magnetic moment leads to good agreement with the data of ab-initio modeling of the magnetic contribution to the mixing energy of Fe-Cr alloys.

1. Introduction

Alloys of magnetic metals, one of which shows a tendency to ferromagnetic (FM), and the other to antiferromagnetic (AF) ordering often have complex magnetic properties. Typical examples of this kind are bcc alloys of the Fe–Cr system. Ferritic steels with a high chromium content are of considerable technological interest because of the beneficial effects of chromium on their corrosion and radiation resistance and are considered as potential structural materials for nuclear reactors. The enthalpy of mixing for the bcc phase of this system was determined at 1529 K using adiabatic high-temperature calorimetry by W.A. Dench [1]. The Dench data served as the basis for the widely known thermodynamic model of Andersson and Sundman [2].

The second reason for the increased interest in the Fe-Cr system is the change in the sign of the mixing enthalpy from negative to positive at 0 K for the ferromagnetic bcc phase in alloys with a chromium content of less than 10 at.% [3,4]. Since at low temperatures the study of phase equilibria is practically impossible, the experimental confirmation of this effect is the experimentally detected short range inversion at 703 K in alloys with 11 at. % Cr [5].

A number of studies have shown that a change in many thermodynamic properties of this system with a change in composition is due to a fundamental connection with the magnetic characteristics of the Fe – Cr alloy [4,6,7]. In particular, it was shown in the work [7] that the enthalpies of formation of random Fe – Cr alloys differ significantly in the ferromagnetic and paramagnetic states. The origin of strong concentration dependence of magnitude and short-range order of the magnetic moments in iron-chromium alloys is explained by the effects of frustration in the magnetic interactions of the components. Cr atoms interact antiferromagnetically with each other and with the Fe atoms. Therefore, as soon as two or more Cr impurities in bcc Fe become nearest neighbors, there will be a
frustration and as a result the Cr atoms decrease their magnetic moments [4,8]. This frustration leads to a strong dependence of the chromium atom’s moment on the number of Cr atoms in its neighbourhood.

Inversion of the sign of mixing enthalpy questioned the conventional thermodynamic CALPHAD-model of Andersson and Sundman. In thermodynamic modelling, the semi-empirical approximation introduced by Inden [9] is used to describe the jump in the magnetic heat capacity $C_{\text{mag}}$ near the critical point. In case of a pure element it is assumed that $C_{\text{mag}}$ is a function of the reduced temperature $T/T_c$ ($T_c$ is the critical temperature of the magnetic transition) which satisfies the relation

$$S(T >> T_c) = \int_0^\infty \frac{C_m}{T} dT = R \cdot \ln(\beta + 1)$$

(1)

where $\beta$ is the average magnetic moment. When using this approach for binary magnetic alloys, it is necessary to take into account the concentration dependence of the parameters $\beta$ and $T_c$. In this case, usually, the value of $\beta$ is interpreted as the average magnetic moment of the alloy (that is, the average magnetization per atom), which can be easily measured by conventional magnetometry methods. However, this approach leads to a significant error if the magnitude of the magnetic moments of the alloys are differ substantially, as in the case of the Fe – Ni alloy [10]. Such an approach can lead to an even greater error in the case of antiferromagnetic ordering of magnetic moments, which is observed in the Fe – Cr system [11]. For such cases, Inden [9] proposed to write down the expression (1) for the alloy as the maximum magnetic entropy for ferromagnetic ordering:

$$S(T >> T_c) = R \cdot \sum x_i \ln(\beta_i + 1)$$

(2)

where $x_i$ and $\beta_i$ are the concentration and magnitude of the local magnetic moments of the atoms of the $i$-th alloy component, the magnitude of which can be determined by ab initio methods.

The calculation of the magnetic component of the mixing energy using the expression (2) was proposed by the authors still in [12]. However, an article published in Russian turned out to be inaccessible to the majority of researchers, and discussions on the methods of thermodynamic evaluation of magnetic contribution continued [13]. In particular, [14] indicated a discrepancy in the values of the difference in the enthalpy of mixing for the high-temperature paramagnetic state and the low-temperature ferromagnetic state obtained from ab initio calculations and the CALPHAD method. In this regard, it seems to us useful to present our results to a wide circle of specialists.

2. Calculation of the magnetic contribution to the mixing energy of Fe-Cr alloys

The basis of our calculation is the expression for the energy of the magnetic ordering energy (the difference between the ferromagnetic and paramagnetic state) for the bcc alloys of the Fe-Cr system

$$E_f = -0.835 \cdot RT_c \ln(\beta + 1)$$

(3)

which can be obtained from the data of work [15].

We assumed that atoms of different types in the paramagnetic state of the alloy will have different magnetic moments, the magnitudes of which will be the same as for the ferromagnetic state at 0 K. In this case, the magnetic contribution to the mixing energy was calculated in accordance with the expression:

$$E_{\text{mix}}^{f} = -0.835 \cdot R \left[T_c(x) \left(x \cdot \ln(\beta_{Cr}+1)+(1-x) \cdot \ln(\beta_{Fe}+1)\right) T_c^{oP}(1-x) \cdot \ln(\beta_{Fe}^{oP}+1)-T_c^{oP} \cdot x \cdot \ln(\beta_{Cr}^{oP}+1)\right]$$

(4)

where $T_c(x)$, $\beta_{Cr}$, $\beta_{Fe}$ are the Curie point and local atomic magnetic moments of the components for Fe-Cr alloy with $x$ mole fraction Cr and $T_c^{oP}$, $\beta_{Cr}^{oP}$, $\beta_{Fe}^{oP}$ the same for pure bcc iron and chromium.

To carry out the calculations according to (4), where were used the data [15] for the Curie points (in Kelvin) of Fe-Cr $\alpha$-alloys:

$$T_c(x) = 1043 + 175.5 \cdot x - 2170.9 \cdot x^2 + 642.4 \cdot x^3$$

(5)
where $x$ is chromium concentration. The values of the atomic magnetic moments of the components for different concentrations alloys were taken from the first-principle calculation [4] and are shown in table 1. For pure bcc iron and chromium the following values of magnetization (in $\mu$B) were used:

$$\beta_{Cr}^0 = 0.4; \beta_{Fe}^0 = 2.216.$$  

### Table 1. Magnetic moments on atoms of iron and chromium in Fe-Cr alloys according to the work [4].

| Chrome concentration $x$, at% | Magnetic moments of atoms, $\mu_B$ |  |
|-----------------------------|----------------------------------|---|
|                            | Fe  | Cr  |  |
| 0                           | 2.23 | 1.17 |  |
| 0.019                       | 2.27 | 1.71 |  |
| 0.0625                      | 2.345 | 1.64 |  |
| 0.125                       | 2.29 | 1.01 |  |
| 0.1875                      | 2.37 | 0.72 |  |
| 0.25                        | 2.19 | 0.51 |  |
| 0.3125                      | 2.19 | 0.45 |  |
| 0.375                       | 2.15 | 0.24 |  |
| 0.4375                      | 2.08 | 0.072 |  |
| 0.5                         | 2.07 | 0.048 |  |
| 0.5625                      | 1.92 | 0.143 |  |
| 0.625                       | 1.94 | 0.035 |  |
| 0.6875                      | 1.97 | 0.155 |  |
| 0.75                        | 1.89 | 0.122 |  |

3. Discussion and conclusions

Comparison of the magnetic contribution to the mixing energy evaluated by (4) with the ab initio calculations of magnetic ordering energy of mixing (MOEM) is shown in figure 1. It can be seen that quite satisfactory agreement has been reached. This result demonstrates that the current CALPHAD modeling based on the Inden model can be also applied to alloys with more complicated forms of magnetism such as BCC Fe-Cr system. We employ an interpolation for composition dependence of the critical temperature $T_c$ in terms of polynomials (5). To describe the concentration dependence of the magnetic moments of the components, a more accurate description based on ab initio modelling was used.

Results allow us to formulate the following conclusions: a) the magnetic component of the mixing energy of ferromagnetic alloys can have a significant effect on the concentration dependence of the total mixing energy and even change its sign for a certain concentration range; b) magnetic ordering energy of mixing for Fe-Cr alloys as a function of concentration is a reasonably good described by the formula (3) where the atomic magnetic moments of the alloy components are computed by using ab initio simulations.
Figure 1. Comparison of MOEM between ab initio SQS, PAW-VASP calculations by Olsson [16] (bold line) and thermodynamic modeling by (3) (black circles).

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