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# Thermodynamic analysis using experimental magnetization data of the austenite/ferrite phase transformation in Fe-xNi alloys ( $x = 0, 2, 4$ wt %) in strong magnetic field

T Garcin, S Rivoirard and E Beaugnon

CNRS/CRETA, 25 rue des martyrs BP166, 38042 Grenoble cedex9, France

Email: thomas.garcin@grenoble.cnrs.fr

**Abstract.** The effect of strong magnetic field on the transformation temperature from ferrite to austenite and from austenite to ferrite is examined in Fe-xNi alloys ( $x = 0, 2, 4$  wt%). Alloy magnetization measurements are used to calculate the magnetic contribution to the driving force and to account thermodynamically for the field dependence of the transformation temperatures. The predicted shift of the transformation temperatures is compared with experimental dilatometry measurements of transformation temperatures, up to 16T. The use of experimental magnetization measurements is found to be an accurate alternative to the Weiss Molecular Field theory for the prediction of the magnetization of ferrite close to its Curie point.

## 1. Introduction

Thermo-magnetic processing can be considered as a new technology for modifying phase equilibria and phase transformation kinetics in steels, with the goal of developing novel microstructures and properties unattainable through conventional thermo-mechanical processing. From a thermodynamic point of view, magnetic field is considered as an intensive parameter, like pressure or temperature. It can influence phase equilibria through its contribution to the free energy of the system and thus be useful for practical purposes in functional materials. The phase transformations in metallic materials are generally affected by the application of an external magnetic field if the magnetic susceptibilities of the parent and product phases are different [1]. Fe-based alloys clearly fit into this category, ferrite ( $\alpha$ ) being ferromagnetic at a temperature below its Curie point ( $T_C$ ) and paramagnetic above, whereas austenite ( $\gamma$ ) is always weakly paramagnetic. In order to quantify the effect of a high magnetic field on the  $\gamma/\alpha$  transformation in Fe-based alloys, the commonly used method is to calculate the phase boundaries from proper expressions of the Gibbs free energies of

ferrite and austenite as a function of the applied magnetic field and of the magnetization behaviour of the different phases. Several equilibrium phase diagrams in magnetic field have been calculated with various models [2-6] in which the Weiss Molecular Field (WMF) theory is generally used to describe the magnetization of ferrite at high temperatures and under strong magnetic fields [7]. Therefore, experimental measurements of phase transformation temperatures under magnetic field are highly needed to examine the validity of these calculated phase diagrams.

Up to now, it was reported in literature that the  $\gamma/\alpha$  equilibrium transformation temperature for pure iron [8-10], for the eutectoid composition Fe-0.8C (wt%) [9, 11] and for Fe-xCo alloys with  $x = 10, 20, 30$  wt% [8] was increased with increasing magnetic field intensity. The change in the transformation temperature was either proportional to the magnetic field strength when the ferrite phase is ferromagnetic at the transformation temperature or proportional to the square of the magnetic field when the ferrite phase is paramagnetic. Although the above mentioned experimental measurements were performed during continuous heating and cooling, i.e. under non-equilibrium conditions, the  $\gamma/\alpha$  transformation temperature was defined as the average value of the transformation temperature during heating and cooling and was compared to the calculated  $\gamma/\alpha$  equilibrium temperature. In this way, the hysteresis of the transformation temperature was neglected. However, in most Fe-based alloy compositions, the  $\alpha \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transformation temperatures are quite different and the average of the  $\gamma/\alpha$  transformation temperature is no longer suitable to describe the boundaries of a two phase region. Recently, another approach was proposed to account for non-equilibrium conditions and to treat the two transformations separately. This method was successfully applied to calculate the non-equilibrium  $\gamma \rightarrow \alpha$  and  $\alpha \rightarrow \gamma$  transformation temperatures under magnetic field in Fe-xRh alloys [14] and Fe-xC-Mn alloys [15].

Fe-xNi alloys ( $x \leq 4$  wt%) are specially interesting to extrapolate this new approach to the general case where the transformation may occur below or above the Curie point of the  $\alpha$ -phase, depending on the Ni content. The addition of Ni to the Fe matrix decreases the Curie point of the  $\alpha$ -phase [2]. At the same time, Ni addition influences both the  $\alpha \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transformation temperatures, since

Ni enlarges the stability domain of austenite [16]. Consequently, depending on the Ni content,  $T_C$  can be found below, within or above the  $\alpha+\gamma$  stability region. In a previous paper, the  $\alpha\rightarrow\gamma$  and  $\gamma\rightarrow\alpha$  transformation temperatures were measured using dilatometry in a magnetic field of 16 T [17]. The effect of magnetic field on the transformation temperatures ( $T_{\alpha\rightarrow\gamma}$  and  $T_{\gamma\rightarrow\alpha}$ ) was found to be different, depending on the magnetic state of the  $\alpha$ -phase when the transformation occurs. All possible variations from a linear to a quadratic behaviour of the transformation temperature versus field were observed.

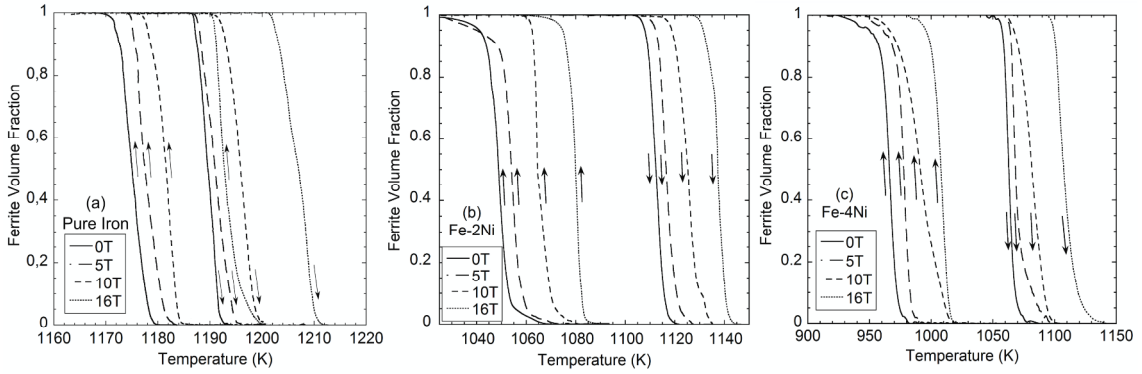
This work has two main purposes. First, to test the validity of the new approach proposed in [14, 15] in the case of Fe-xNi alloys ( $x \leq 4$  wt%) by quantifying the magnetic contribution to the  $\alpha\rightarrow\gamma$  and  $\gamma\rightarrow\alpha$  transformations respectively. The second aim is to validate the use of the WMF theory for the calculation of the ferrite magnetization by experimental magnetic measurements under high magnetic field. For that purpose, magnetic measurements at high temperatures are realised. Finally,  $\alpha\rightarrow\gamma$  and  $\gamma\rightarrow\alpha$  transformation temperatures, previously measured by dilatometry in [17], are compared with calculated values based either on the WMF theory or on experimental magnetization data.

## 2. Experimental

The preparation of Fe-Ni alloys with Ni contents of 0, 2 and 4 wt% and the experimental transformation temperatures from ferrite to austenite and from austenite to ferrite measured by dilatometry up to 16T can be found in [17]. The home-made dilatometer setup consists of a resistive furnace inserted into the 32 mm room temperature bore of a superconducting magnet, coupled with a high resolution Michelson laser interferometer [18]. Magnetic measurements are performed under a magnetic field up to 3.8 T using a high temperature device based on the Faraday method as described in [19]. In this method, the magnetization per unit volume is measured by the magnetic force exerted on the sample placed in the z-axis field gradient of the magnet.

### 3. Results

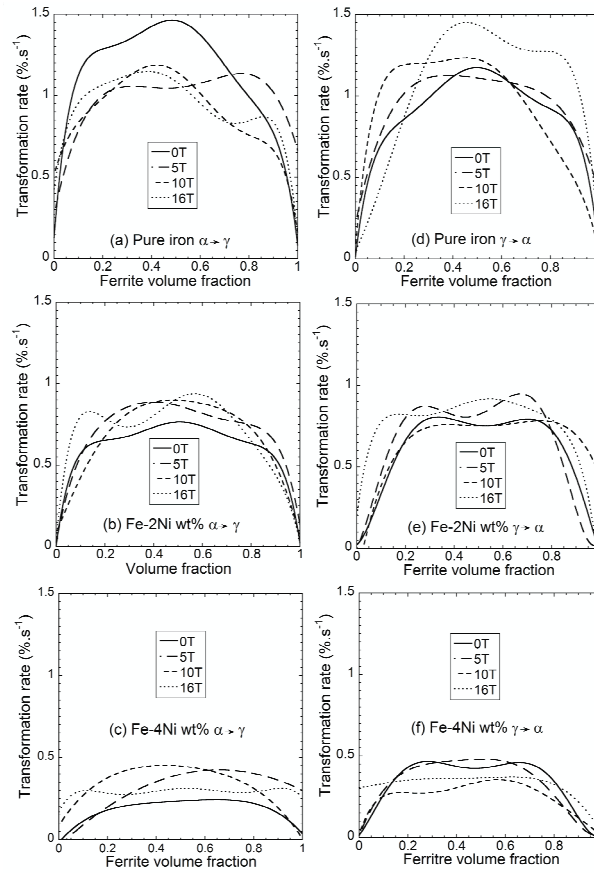
As detailed in [17], the  $\alpha \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transformation temperatures are calculated as the average value of the onset of the transformation temperature ( $T_S$ ) and the end of the transformation temperature ( $T_E$ ) and are referred to as  $T_{\alpha \rightarrow \gamma}$  during heating and  $T_{\gamma \rightarrow \alpha}$  during cooling. The volume fraction of ferrite is systematically deduced from the dilatometry signal using the lever rule method [20] and is plotted in Figure 1 as a function of temperature during heating and cooling for the three Fe-xNi alloys ( $x = 0, 2, 4$  wt%). It is shown that both  $T_{\alpha \rightarrow \gamma}$  and  $T_{\gamma \rightarrow \alpha}$  are shifted towards higher temperatures when the magnetic field is increased.



**Figure 1.** Ferrite fraction deduced from dilatometry measurements for the Fe-xNi alloys ( $x = 0, 2, 4$  wt%) treated under the influence of a 0, 5, 10 and 16 T magnetic field.

Moreover and for each studied composition, the hysteresis between the transformation temperatures during heating and cooling, as well as the time needed to achieve the complete transformation are found to be independent of the magnetic field intensity. As a quantitative illustration, the rate of transformation obtained by the time derivative of the phase fraction is shown for each transformation condition in Figure 2. The interaction between the migrating interface and the Ni component in the alloy gives rise to a migration resistance. This phenomenon, associated to solute drag, is observed in Figure 2 through the reduction of the transformation rate by the Ni addition for both the  $\alpha \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transformation. Assuming no segregation of Ni in the parent and product phase, the transformation can be considered as interface-controlled and its rate or more strictly the kinetics of the ferrite interface is defined as the product of the driving force by the

interface mobility [21]. It has been recently shown that the interface mobility is not influenced by an external magnetic field in the case of the austenite to ferrite interface-controlled reaction in iron [22]. In addition, Figure 2 shows that the variations in the transformation rates between 0 and 16T are random and not significant as compared to the effect of the Ni content. Consequently, it is assumed in the following analysis, that the driving force for transformation is the same irrespective of a magnetic field during continuous heating, respectively cooling.



**Figure 2.** Transformation rates measured during  $\alpha \rightarrow \gamma$  and  $\gamma \rightarrow \alpha$  transformations for (a, d) pure iron, (b, e) Fe-2Ni and (c, f) Fe-4Ni (wt%) under 0, 5, 10 and 16 T.

### 3. Discussion

The effect of a magnetic induction  $B$  on the non-equilibrium  $T_{\alpha \rightarrow \gamma}^B$  and  $T_{\gamma \rightarrow \alpha}^B$  transformation temperatures is calculated applying a thermodynamic analysis. The phase transformations during heating and cooling occur under non-equilibrium conditions since a driving force is required for the

creation of interfaces and their migration. This driving force can be calculated by the quantification of the total Gibbs free energy change  $\Delta G_{tot}^B$  between the two phases  $\alpha$  and  $\gamma$  at the transformation temperature. In the present approach,  $\Delta G_{tot}^B$  is expressed as the sum of a chemical term,  $\Delta G_{chem}$  and of a magnetic term  $\Delta G_{mag}$  as:

$$\Delta G_{tot}^B = \Delta G_{chem} + \Delta G_{mag} \quad (1)$$

According to the definitions of the chemical and magnetic free energies, the total Gibbs free energy change can be written as:

$$\Delta G_{tot}^B = \Delta H_{i \rightarrow j} - T_{i \rightarrow j}^B \Delta S_{i \rightarrow j} - \frac{M^{mol}}{\rho \mu_0} \int_0^B (M_i^B - M_j^B) dB \quad (2)$$

where  $M^{mol}$ ,  $\rho$  and  $\mu_0$  are the atomic weight, the density and the magnetic permeability of vacuum respectively.  $T_{i \rightarrow j}^B$  is the transformation temperature from  $i$  to  $j$  under a magnetic induction  $B$ , with  $i$  and  $j$  being  $\alpha$  or  $\gamma$ .  $\Delta H_{i \rightarrow j}$  and  $\Delta S_{i \rightarrow j}$  are the enthalpy and entropy changes accompanying the transformation. Finally,  $M_i^B$  and  $M_j^B$  are the magnetizations of the phase  $i$  and  $j$  respectively. In the present analysis, the magnetic term in equation (2) is defined as the additional contribution provided by the external magnetic field at the temperature at which the transformation occurs without the presence of magnetic field. Therefore, the magnetisation values are determined at the temperature  $T_{i \rightarrow j}^{B=0}$  and under a magnetic induction  $B$ . Table 1 reports the values of  $T_{i \rightarrow j}^{B=0}$  measured in [17] for both the austenite to ferrite and ferrite to austenite transformations and the corresponding equilibrium temperatures  $T_{i \rightarrow j}^{equ}$  obtained from thermodynamic databases (Thermocalc<sup>®</sup>). In the various cases, the transformations temperature  $T_{i \rightarrow j}^{B=0}$  is relatively close to the equilibrium temperature  $T_{i \rightarrow j}^{equ}$  because of the low heating and cooling rate (3 K/min) imposed during the experiments in [17]. Close to the equilibrium, the variations of  $\Delta H_{i \rightarrow j}$  and  $\Delta S_{i \rightarrow j}$  are negligibly small. Therefore, these two parameters are determined at the corresponding equilibrium temperature and are assumed equal to  $\Delta H_{i \rightarrow j}^{equ}$  and

$\Delta S_{i \rightarrow j}^{equ}$  respectively. In the present approach, the entropy and enthalpy changes do not contain any magnetic field influence as both the temperature dependence of the magnetisation as well as the change in the magnetic ordering due to the application of a magnetic field are already accounted for in the definition of  $\Delta G_{mag}$  given above. Therefore, at the equilibrium temperature, the total Gibbs free energy  $\Delta G_{tot}^B$  is zero, so that the entropy change is expressed by:

$$\Delta S_{i \rightarrow j}^{equ} = \frac{\Delta H_{i \rightarrow j}^{equ}}{T_{i \rightarrow j}^{equ}} \quad (3)$$

The enthalpy change  $\Delta H_{i \rightarrow j}^{equ}$  for the various transformations is obtained from thermodynamic databases (Thermocalc<sup>®</sup>) and the values are reported in Table 1.

**Table 1.** Equilibrium temperature  $T_{\alpha \rightarrow \gamma}^{equ}$  ( $T_{\gamma \rightarrow \alpha}^{equ}$ ), corresponding enthalpy change  $\Delta H_{\alpha \rightarrow \gamma}^{equ}$  ( $\Delta H_{\gamma \rightarrow \alpha}^{equ}$ ) and experimentally measured transformation temperatures  $T_{\alpha \rightarrow \gamma}^{B=0}$  ( $T_{\gamma \rightarrow \alpha}^{B=0}$ ) [17] for the Fe-xNi alloys with x = 0, 2, 4 wt%; Curie temperatures  $T_C$  and average magnetic moments  $m$  of ferrite introduced in the WMF model for the corresponding composition.

Fe-Ni (x wt%)	0	2	4
$T_{\alpha \rightarrow \gamma}^{equ}$ (K)	1183	1107	1056
$T_{\alpha \rightarrow \gamma}^{B=0}$ (K)	1189	1113	1061
$\Delta H_{\alpha \rightarrow \gamma}^{equ}$ (kJ.mol <sup>-1</sup> )	1.026	1.605	1.646
$T_{\gamma \rightarrow \alpha}^{equ}$ (K)	1183	1040	902
$T_{\gamma \rightarrow \alpha}^{B=0}$ (K)	1175	1048	968
$\Delta H_{\gamma \rightarrow \alpha}^{equ}$ (kJ.mol <sup>-1</sup> )	1.026	2.364	4.637
$T_C$ (K)	1043	1036	1029
$m$ (Bohr magnetons)	2.20	2.23	2.25

According to the negligible impact of magnetic field on the transformation rate evidenced in Figure 2 and in agreement with previous works [13-15, 22], the total driving force is assumed to be unchanged by the application of a magnetic field as:



$$\Delta G_{tot}^B = \Delta G_{tot}^{B=0} \quad (4)$$

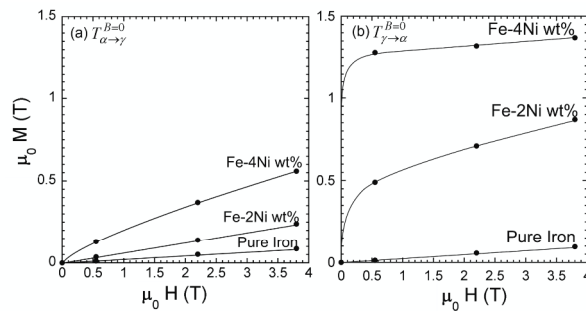
The substitution of equations (2) and (3) in equation (4) leads to:

$$\Delta H_{i \rightarrow j}^{equ} \left( 1 - \frac{T_{i \rightarrow j}^B}{T_{i \rightarrow j}^{equ}} \right) - \frac{M^{mol}}{\rho \mu_0} \int_0^B (M_i^B - M_j^B) dB = \Delta H_{i \rightarrow j}^{equ} \left( 1 - \frac{T_{i \rightarrow j}^{B=0}}{T_{i \rightarrow j}^{equ}} \right) \quad (5)$$

From this expression, the change in the transformation temperature  $T_{i \rightarrow j}^B$  is deduced as a function of the magnetic field, magnetizations of phases and enthalpy changes during transformations as:

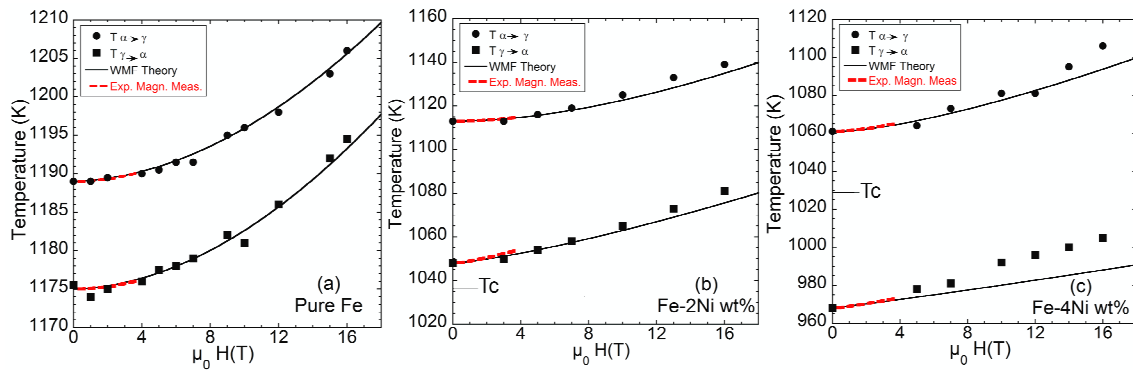
$$T_{i \rightarrow j}^B = T_{i \rightarrow j}^{B=0} + \frac{T_{i \rightarrow j}^{equ}}{\Delta H_{i \rightarrow j}^{equ}} \frac{M^{mol}}{\rho \mu_0} \int_0^B (M_i^B - M_j^B) dB \quad (6)$$

To solve this final expression, the respective magnetizations of ferrite and austenite are required together with the parameters given in table 1. The magnetization of ferrite is evaluated in two different ways: from theoretical calculation using the WMF theory and from experimental magnetization measurements shown in Figure 3. The temperature and magnetic field dependence of the ferrite magnetisation in the WMF theory is evaluated with the method proposed in [3] which accounts for the influence of alloying elements in the magnetic properties of Fe. The respective Curie temperatures  $T_C$  and average magnetic moments  $m$  of ferrite in the alloys are reported in table 1. The magnetization of austenite is taken from the data of Arajs et al. [23] and the effect of the addition of Nickel in the susceptibility data of austenite is neglected.



**Figure 3.** Magnetization of ferrite  $M_{\alpha}^B$  in the Fe-xNi alloys with x = 0, 2, 4 wt% measured at their respective  $T_{\alpha \rightarrow \gamma}^{B=0}$  and  $T_{\gamma \rightarrow \alpha}^{B=0}$  reported in table 1.

The corresponding results of the magnetic field dependence of  $T_{\alpha \rightarrow \gamma}^B$  and  $T_{\gamma \rightarrow \alpha}^B$  are shown in Figure 4. The black lines correspond to the calculation from the WMF theory and the dotted red lines are evaluated by using experimental magnetic measurements. In this Figure, experimental values of  $T_{\alpha \rightarrow \gamma}$  and  $T_{\gamma \rightarrow \alpha}$ , determined by dilatometric analysis and reported in [17] for the three alloy compositions, are plotted with solid marks for comparison. Depending on the Ni content, the variation of the transformation temperature shows various dependences with the magnetic field intensity. When the  $\gamma \rightarrow \alpha$  transition occurs below the Curie temperature of ferrite, the magnetization of the ferrite phase  $M_{\alpha}^B$ , is rapidly saturated so that the magnetic energy has a linear dependence on the applied magnetic field value. On the contrary, when the  $\gamma \rightarrow \alpha$  transition occurs above the Curie temperature, the ferrite is formed in the paramagnetic state and hence  $M_{\alpha}^B$  is almost linearly dependent on  $B$ . Since the magnetic energy is proportional both to the applied field and to the magnetization, the temperature shift is roughly proportional to the square of the field value. In the Fe-2Ni wt% alloy, intermediate field dependences are observed.



**Figure 4.** Change in the transformation temperature in (a) pure iron (b) Fe-2Ni wt% and (c) Fe-4Ni wt% in the presence of magnetic field.

The calculated data are in good agreement with the transformation temperatures measured experimentally by dilatometry in [17]. The use of experimentally measured  $M_{\alpha}^B$  to calculate the magnetic contribution to the total free energy of the transformation constitutes a very accurate

approach, however, limited to 3.8 T in this work. In the case of the  $\gamma \rightarrow \alpha$  transition in the Fe-4Ni wt%, an underestimation of the transformation temperature is observed and the transformation occurs close to the Curie temperature. According to [24], this discrepancy could be ascribed to an improper quantification of the interactions between magnetic moments at the Curie transition in the WMF theory.

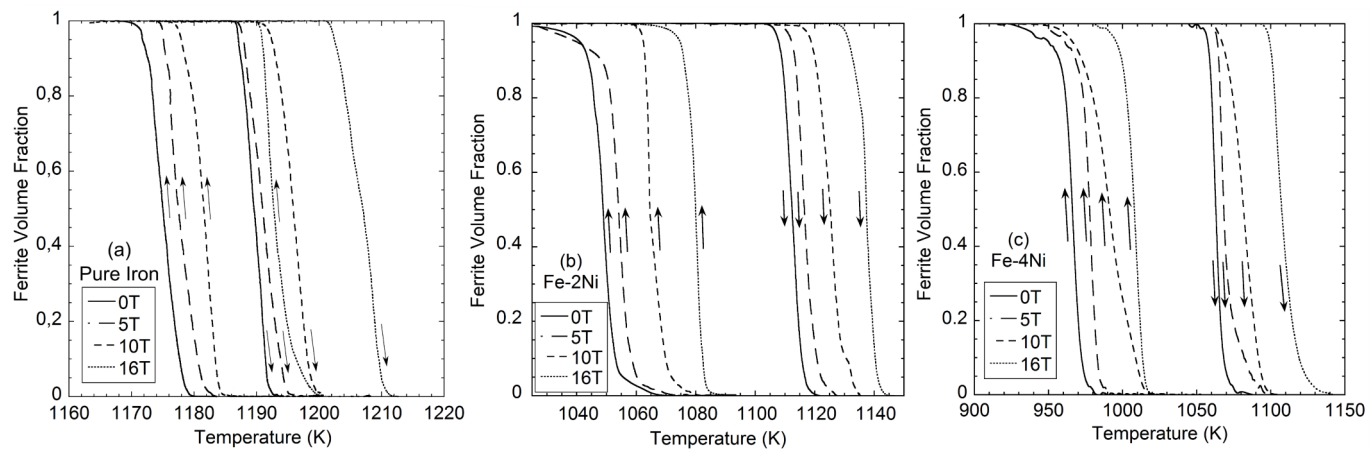
#### 4. Conclusion

The effect of magnetic field on the non-equilibrium ferrite-austenite and austenite-ferrite transformation temperatures is examined in Fe-xNi alloys (with  $x = 0, 2, 4$  wt%). A thermodynamic analysis is proposed to calculate the shift of the transformations upon higher temperatures under magnetic field. This approach is based on both experimental measurements and theoretical calculations. A good agreement is found between the expected magnetic field dependence of the transformation temperatures and experimental dilatometry measurements previously performed up to 16 T. This work demonstrates that the use of experimental magnetization measurements to calculate the magnetic contribution to the total free energy of the transformation constitutes an accurate alternative to the WMF theory.

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**Figure 1 (Figure1a\_1c.tif)**

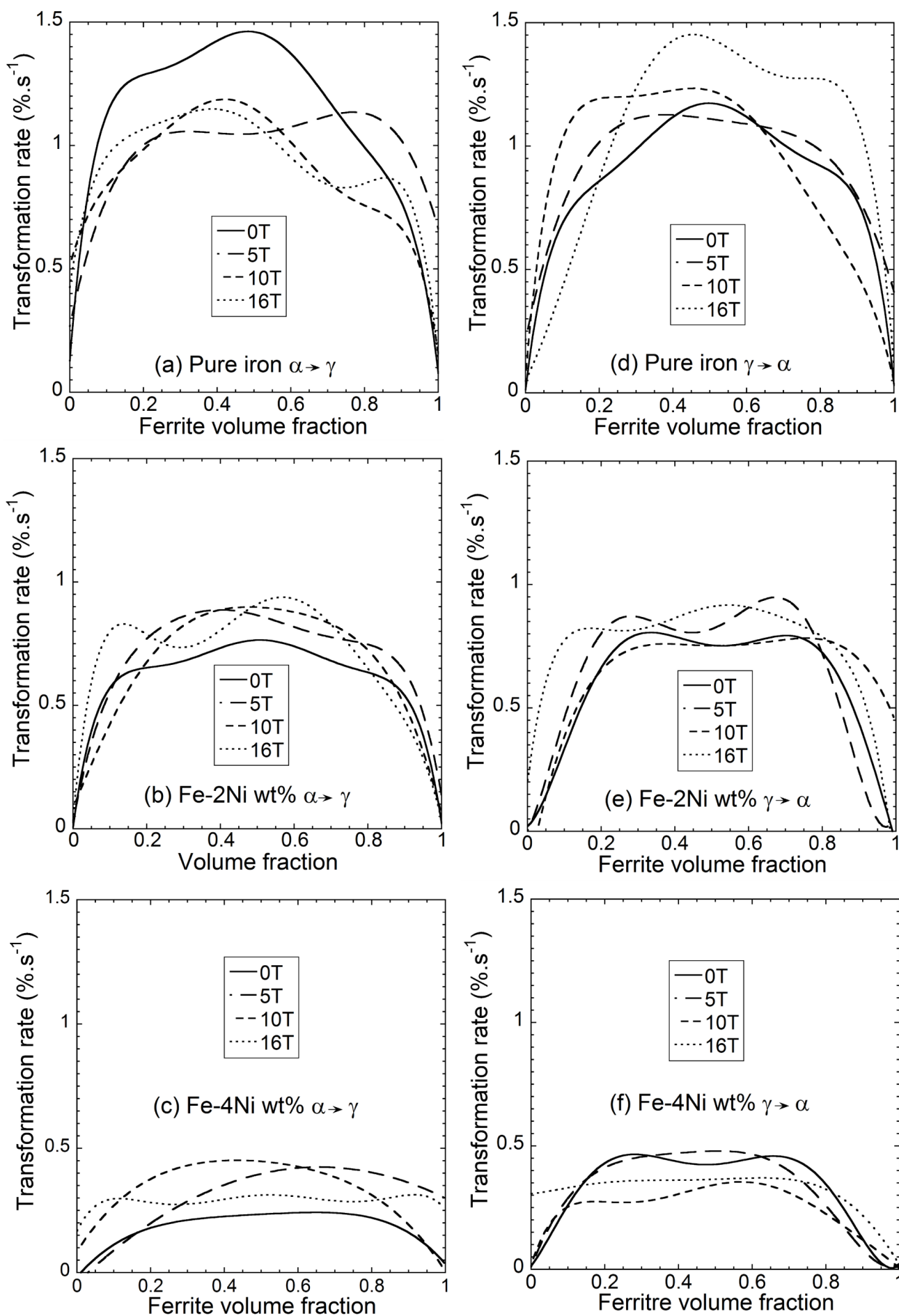


Figure 2 (Figure2a\_2f.tif)

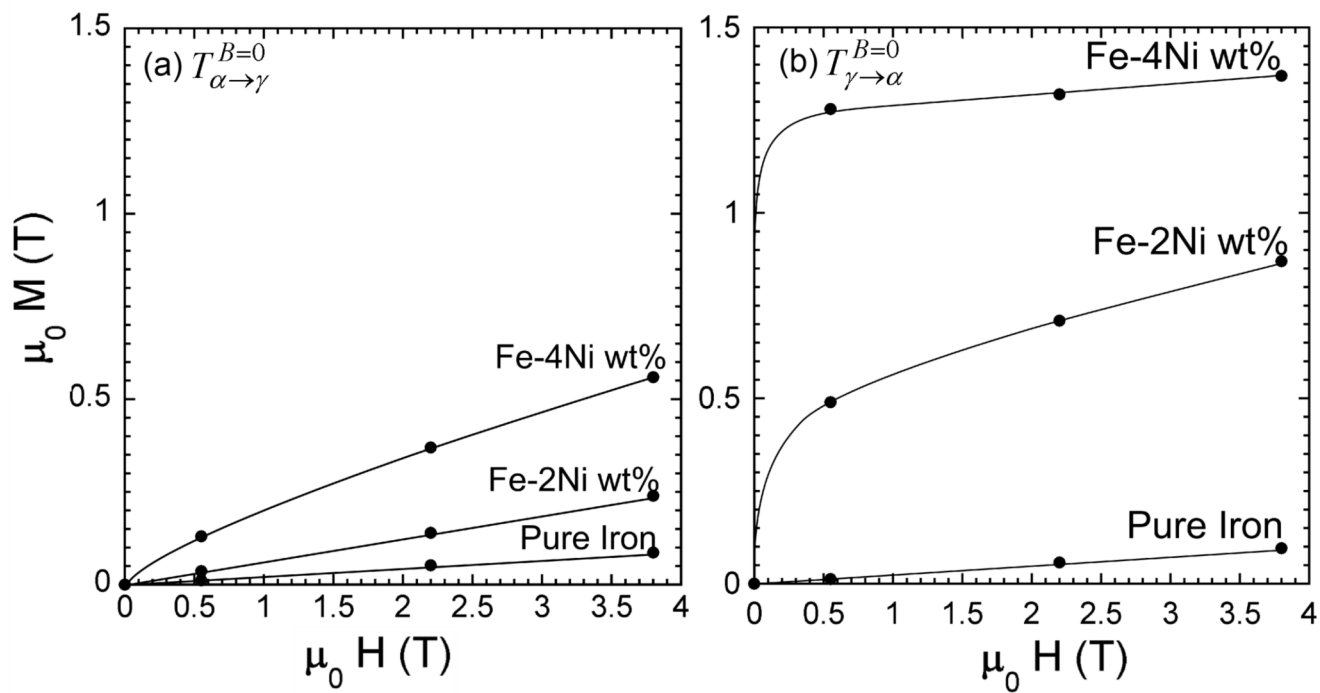


Figure 3 (Figure3a\_3b.tif)

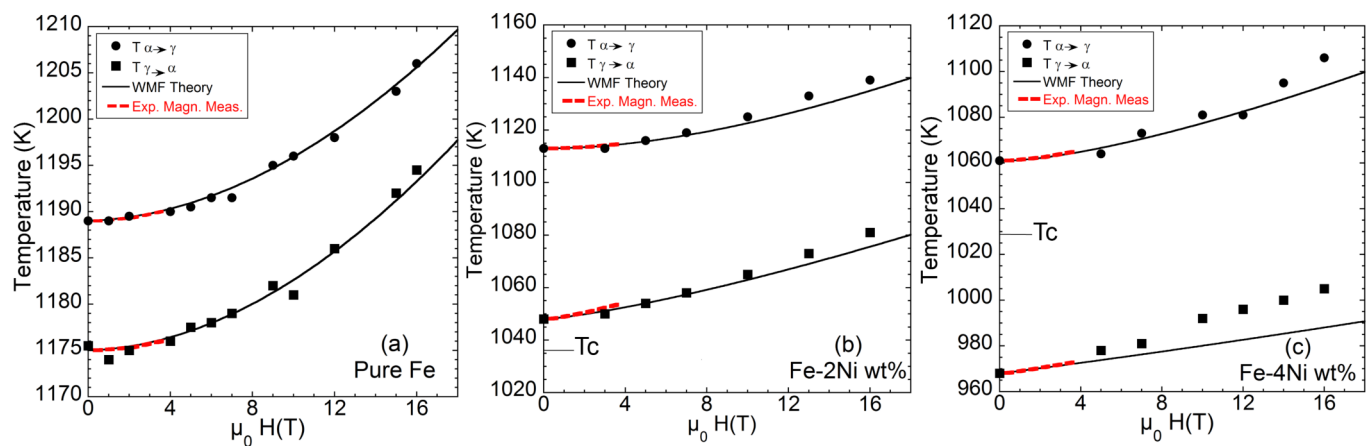


Figure 4 (Figure4a\_4c.tif)