

Thermodynamics of the γ/ε Martensitic Transformation in Fe-Mn Alloys: Modelling of the Driving Force, and Calculation of the M_S and A_S Temperatures

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Abstract: By using recent measurements of the martensitic transformation temperatures in the Fe-Mn system we perform an evaluation of the Gibbs energy (G_m) difference between fcc (γ) and hcp (ε) as a function of temperature and composition. The approach involves the use of thermodynamic models that account for the magnetic contribution to G_m , and the evaluation of a set of optimum model parameters. Among the quantities evaluated by us there is one related to the entropy of antiferromagnetic ordering in fcc, and parameters representing the Gibbs energy barriers for the start of the transformation. The calculated driving forces are confronted with results from other authors. A detailed comparison is reported with the usual thermodynamic evaluation method that relies on the estimation of T_0 temperatures as the average of M_S and A_S .

1. INTRODUCTION

The alloys formed by adding a metallic or non-metallic element to the Fe-Mn system have been a subject of great interest in connection with the so-called shape-memory effect (SME). This effect is governed by a martensitic transformation between an fcc (γ) structure and an hcp (ε) structure. A considerable amount of experimental work has been performed in these systems, but in order to characterize the relative stability of the γ and ε phase in complex alloys it would be useful first to establish this in the basic binary system, viz. the Fe-Mn system. This problem is studied in the present work by relying on models for the molar Gibbs energy (G_m). The models are phenomenological and contain parameters which are to be evaluated by analysing experimental information. The properties of γ can be taken from direct measurements at high temperatures, but the metastable ε phase is poorly known, and the evaluation must rely on information about the $\gamma \rightarrow \varepsilon$ (i.e. M_S) and the $\varepsilon \rightarrow \gamma$ (i.e. A_S) transformation temperatures. This led us to a critical analysis of the traditional approach to extracting thermodynamic values from A_S and M_S data, which is also reported in the present paper.

2. THERMODYNAMICS OF THE γ/ε TRANSFORMATION IN Fe-Mn

The thermodynamic analysis of martensitic transformation temperatures at a given pressure is often performed by using what we shall refer to in this paper as the Kaufman-Cohen [1] method, which is based on the concept of T_0 temperature. In the present case, the T_0 temperature of an alloy with an atomic fraction x_{Mn} of Mn is defined by the equation

$$G_m^\gamma(T_0, x_{Mn}) = G_m^\varepsilon(T_0, x_{Mn}) \quad (1)$$

where G_m is the integral Gibbs energy per mole of atoms. The T_0 temperature could be calculated from Eq.(1) only if a complete thermodynamic description is available, which is usually not the case. Therefore various estimation methods for T_0 have been proposed, which use experimental values of M_S and A_S . In particular, non-thermoelastic martensitic transformations in Fe-based alloys are often treated by estimating T_0 as

$$T_0 = \frac{A_S + M_S}{2} \quad (2)$$

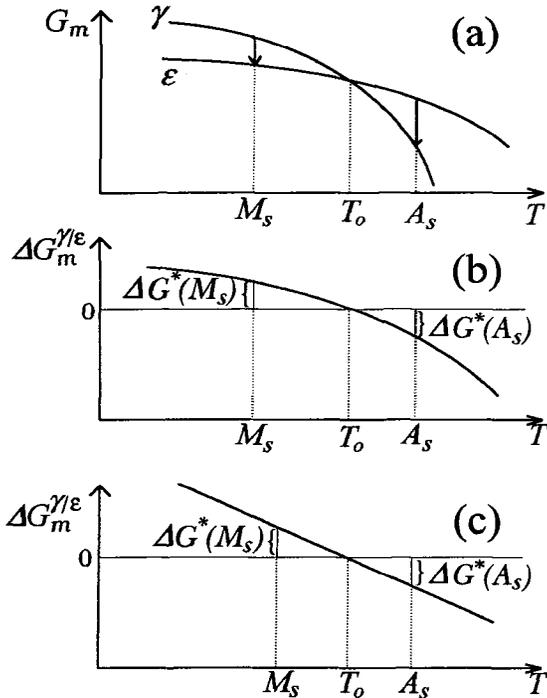


Fig. 1. Schematic isobaric diagram showing: (a) G_m for the γ and ϵ phase, A_S , M_S , and the T_0 temperature for an alloy, (b) the difference $G_m^\gamma - G_m^\epsilon$ and the resistances to the $\gamma \rightarrow \epsilon$ and $\epsilon \rightarrow \gamma$ transformations, and (c) the particular case in which Eq.(2) holds exactly.

Early measurements by Kaufman and Cohen [1] in the Fe-Ni and other systems lent experimental support to this approximation, but in the present paper we shall focus on its theoretical basis, which can be discussed by referring to Fig.1. There we schematize (Fig.1(a)) the variation with temperature of G_m^γ and G_m^ϵ at constant pressure for a given composition. In addition, in Fig.1(b) we show schematically the difference in G_m between γ and ϵ , $\Delta G_m^{\gamma/\epsilon}$. This difference provides the so-called driving force for the direct ($\gamma \rightarrow \epsilon$) transformation, whereas $\Delta G_m^{\epsilon/\gamma}$ does it for the retransformation ($\epsilon \rightarrow \gamma$). The driving force is, by definition, zero at $T = T_0$, but $\Delta G_m^{\gamma/\epsilon}$ and $\Delta G_m^{\epsilon/\gamma}$ are positive at the temperatures for the start of the $\gamma \rightarrow \epsilon$ and $\epsilon \rightarrow \gamma$ transformations, respectively. In particular, in Fig.1(b) it has been assumed that the driving force amounts to $\Delta G_m^*(M_S)$ and $\Delta G_m^*(A_S)$ at the onset of the $\gamma \rightarrow \epsilon$ and $\epsilon \rightarrow \gamma$ transformation, respectively. Thus the positive quantities $\Delta G_m^*(M_S)$ and $\Delta G_m^*(A_S)$ will represent the resistance to the start of these transformations. Figure 1(b) represents a general situation, and Fig 1(c) the particular case in which Eq.(2) applies. Simple geometrical considerations show that Eq.(2) will hold exactly only if the following two conditions hold: (i) the ΔG_m vs. T function remains linear between M_S and A_S , and (ii) the resistances $\Delta G_m^*(M_S)$ and $\Delta G_m^*(A_S)$ are equal.

Condition (i) will, in turn, hold exactly only if the entropy difference between the γ and ϵ phase is independent of T for $M_S < T < A_S$. Otherwise this can only be an approximation, which might be justified if $C_p^\gamma = C_p^\epsilon$, or when the difference between A_S and M_S is very small. In the Fe-Mn system such a difference is large, viz. about 100 K. In addition, the γ phase orders antiferromagnetically on cooling, at a temperature T_N^γ , and, in particular, for alloys with Mn contents such that $23\text{wt}\% < \% \text{Mn} < 28\text{wt}\%$ we find that $M_S < T_N^\gamma < A_S$ (see Figs. 2 (a) and (b)). In that range the magnetic ordering reaction is expected to decrease the entropy of γ more rapidly than that of ϵ , which remains paramagnetic down to much lower temperatures [2]. Since assumption (i) does not hold exactly in the Fe-Mn case, we shall consider Eq.(2) only as an approximation. Assumption (ii) about the ΔG_m^* quantities is evidently another approximation, but one cannot judge it *a priori* without a detailed structural model for the transformation.

In the present evaluation the $\Delta G_m^{\gamma/\varepsilon}$ vs. T functions for the Fe-Mn system are established without applying Eq.(2), but using the measured M_S and A_S as input data. These are taken as the temperatures at which $\Delta G_m^{\gamma/\varepsilon} = \Delta G_m^*(M_S)$ and $\Delta G_m^{\varepsilon/\gamma} = \Delta G_m^*(A_S)$, respectively, in accord with Fig.1. Thus by analysing the data we extract information on the $\Delta G_m^{\gamma/\varepsilon}$ difference as a function of T and x_{Mn} , as well as the ΔG_m^* quantities. Our $\Delta G_m^{\gamma/\varepsilon}$ function accounts for magnetic effects, i.e. we are not forcing $\Delta G_m^{\gamma/\varepsilon}$ to be linear at all temperatures. In addition, by systematically analysing the experimental data we can test whether assumption (ii) is at least compatible with the trends of the M_S and A_S measurements.

3. GIBBS ENERGY MODELLING AND EXPERIMENTAL DATABASE

The G_m function of the γ or ε phase was described by resolving it into a magnetic ΔG_m^{mg} and a non-magnetic contribution, according to the following expression

$$G_m^\phi = x_{Fe} {}^0G_{Fe}^\phi + x_{Mn} {}^0G_{Mn}^\phi + RT(x_{Fe} \ln x_{Fe} + x_{Mn} \ln x_{Mn}) + {}^E G_m^\phi + \Delta G_m^{mg,\phi} \quad (3)$$

where x_i is the atomic fraction of the element i ($i = \text{Fe, Mn}$) and 0G_i is the Gibbs energy of the element i , with the structure of the phase ϕ ($\phi = \gamma, \varepsilon$) in a non-magnetic state, and ${}^E G_m$ is the excess Gibbs energy. All necessary information about 0G_i was taken from assessments of the thermodynamic properties of Fe [3] and Mn [4,5]. The magnetic contribution to G_m was described by using the Hillert-Jarl [6] phenomenological model, which gives

$$\Delta G_m^{mg,\phi} = RT \ln(\beta^\phi + 1) f^\phi(\tau) \quad (4)$$

where β^ϕ is a composition dependent parameter that is related to the total magnetic entropy, i.e. the quantity $\Delta S_m^{mg,\phi}(\infty) - \Delta S_m^{mg,\phi}(0)$, as follows

$$\Delta S_m^{mg,\phi}(\infty) - \Delta S_m^{mg,\phi}(0) = R \ln(\beta^\phi + 1) \quad (5)$$

The variable τ is defined as T/T_N^ϕ where T_N^ϕ is the Néel temperature of ϕ (γ or ε), as a function of composition, and $f^\phi(\tau)$ represents the polynomial of Hillert and Jarl [6]. T_N^γ and T_N^ε , as a function of composition were taken from refs.[5] and [2], respectively. The composition dependence of β^γ was described by adopting the phenomenological expression

$$\beta^\gamma = x_{Fe} {}^0\beta_{Fe}^\gamma + x_{Mn} {}^0\beta_{Mn}^\gamma - \frac{1}{3} x_{Fe} x_{Mn} \beta_{Fe,Mn}^\gamma \quad (6)$$

where the quantities ${}^0\beta_{Fe}^\gamma$ and ${}^0\beta_{Mn}^\gamma$ refer to $\gamma\text{-Fe}$ [3] and $\gamma\text{-Mn}$ [4]. The quantity $\beta_{Fe,Mn}^\gamma$, which describes the deviations of the β^γ value from the linear interpolation between the pure elements, it is not known from direct measurements, but preliminary calculations by us [7] suggest that it should be of the order of 3. This quantity will be determined in the present work. Lacking experimental information β^ε was estimated [7] by using the Weiss and Tauer approximation and the experimental magnetic moment. We remark that this will not affect our results, because they are restricted to temperatures higher than the known $T_N^\varepsilon = 230\text{K}$ [2]. The excess Gibbs energy term ${}^E G_m$ in Eq.3 was treated in the so-called subregular approximation of the Redlich-Kister [8] formalism, viz.

$${}^E G_m^\phi = x_{Fe} x_{Mn} [{}^0L^\phi + {}^1L^\phi (x_{Fe} - x_{Mn})] \quad (7)$$

The parameters ${}^0L^\gamma$ and ${}^1L^\gamma$, which account phenomenologically for the interaction between Fe and Mn atoms in the γ phase, were taken from the analysis by Huang [5], but ${}^0L^\varepsilon$ and ${}^1L^\varepsilon$ were treated as independent of temperature and determined in the present work.

In summary, the present evaluation comprised three parameters of the Gibbs energy model, one of them describing the magnetic entropy of the γ phase (viz., $\beta_{Fe,Mn}^\gamma$), and the other two the non-magnetic part of G_m^ε (viz. ${}^0L^\varepsilon$, ${}^1L^\varepsilon$). In addition we determined the ΔG_m^* quantities (see Section 4) which account for the resistance to the start of the transformation. These various quantities were determined simultaneously by searching for the best fit to measured values of M_S and A_S for Fe-Mn alloys. The information available about these temperatures was critically analysed by us, and it was concluded [7] that the experimental scatter band is too large to be used in a thermodynamic evaluation. Thus a new experimental study of the M_S and A_S temperatures in the system was carried out [7] by using dilatometric and electrical resistivity

methods, and alloys with Mn contents between 10 wt% and about 30 wt% Mn. For each binary composition Cotes et al. [7] studied two thermal cycles, starting with the retransformation of a previously quenched alloy, i.e., four transformation temperatures were determined, in a sequence which we shall refer to as $A_S(2) \rightarrow M_S(3) \rightarrow A_S(4) \rightarrow M_S(5)$. Here $A_S(2)$ denotes the measured temperature for the start of the second phase transformation that occurred in the specimen, which involved a change from ε to γ . The present evaluation will be based on the A_S and M_S temperatures reported by Cotes et al. [7], and the reader is referred to their paper for a detailed comparison with the results of previous studies.

4. CALCULATION OF DRIVING FORCES, M_S AND A_S TEMPERATURES

The evaluation of the various parameters was performed step-wise. In step 1, the data by Cotes et al. [7] corresponding to the first cycle (i.e., the $A_S(2)$ and $M_S(3)$ temperatures) amounting to 36 data values were analysed. In addition to the three model parameters referred to above we then explored the possibility of $\Delta G_m^*(M_S)$ being equal to $\Delta G_m^*(A_S)$, but in order to reduce the number of free parameters we treated that ΔG_m^* as independent of composition. In step 2 the measured values for $A_S(4)$ and $M_S(5)$ were incorporated to the database, which then amounted to 61 values. A new set of three thermodynamic model parameters were evaluated, while keeping the tentative approximation of ΔG_m^* being independent of x_{Mn} . However, in

accord with Section 2 we considered ΔG_m^* as a structure-dependent parameter, which should be affected by the density of crystal defects in the material, and thus with the number of thermal cycles. This possibility was accounted for by letting the ΔG_m^* value for the transformations in the second thermal cycle to be different from the value for the first cycle. Finally, in step 3 the same database was analysed, and the study of the sensitivity of ΔG_m^* to microstructure was taken one step further, by allowing $\Delta G_m^*(M_S)$ and $\Delta G_m^*(A_S)$ to be different. All parameter values determined in each step, which determine what we shall refer to as model 1, 2 and 3, respectively, are listed in Table 1. In Figs. 2(a) and 2(b) a comparison is presented between calculated values for M_S and A_S and those determined by Cotes et al. [7] in the first and second thermal cycle, respectively. All three models account very well for the observed values. The strong decrease in the M_S temperatures which is observed to the right of the Néel temperature line reflects the rapid stabilization of the γ phase which is caused by the magnetic ordering reaction. Preliminary calculations using the present model [7] suggested that the magnetic entropy of γ is strongly coupled to the observed decrease in M_S , but according to the ideas in Section 2

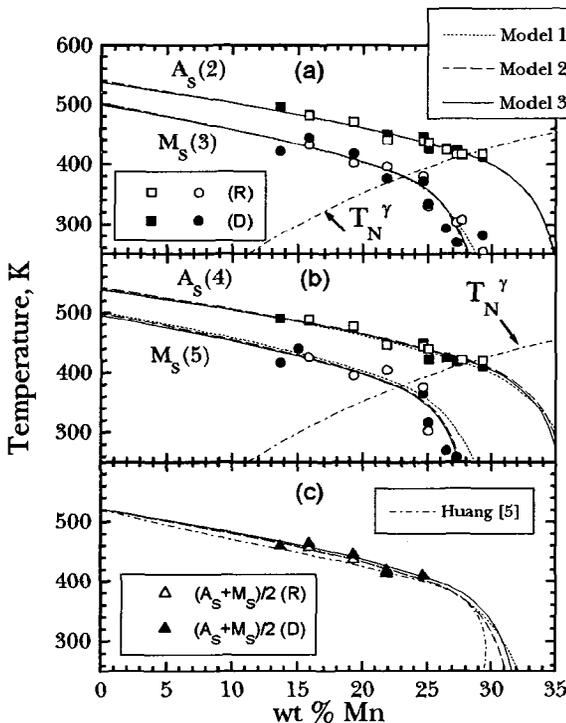


Fig. 2. Calculated A_S and M_S compared with experimental data, (a) for the 2nd and 3rd transformations, and (b) for the 4th and 5th, (R)=resistivity data, (D)=dilatometry data. (c) Calculated T_0 lines compared with Eq.(2) applied to experimental data [7]. T_N^γ is the Néel temperature of the fcc phase e.

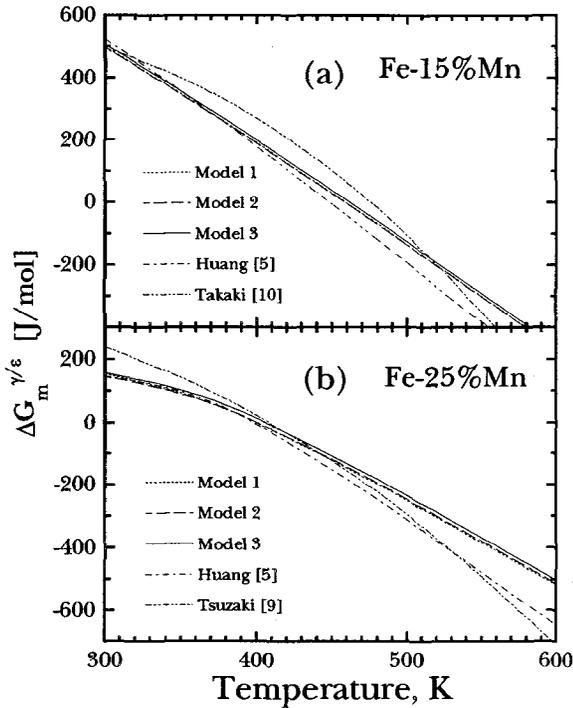


Fig. 3. Calculated $\Delta G_m^{\gamma/\epsilon}$ values with results from refs. [5,9,10] for Fe-Mn alloys with: (a) 15 wt% Mn and (b) 25 wt% Mn.

Fig.2(c) where a comparison is given between Cotes et al.'s [7] values for $(M_S + A_S)/2$ and the T_0 line calculated by using Eq.(1) and the three model descriptions. Our three calculated lines fall in the experimental scatter band. In Figs. 3(a) and 3(b) we compare the present $\Delta G_m^{\gamma/\epsilon}$ versus T functions for alloys with 15 and 25 wt% Mn, respectively, with results according to other authors[5, 9, 10]. It is evident that in general, the various sources agree reasonably well on $\Delta G_m^{\gamma/\epsilon}$ within the temperature range accessible to experiments, but larger discrepancies are observed at high temperatures. In particular Fig.3 demonstrates that the systematic difference which was noted in Fig.2(c) between our results and those by Huang [5] remains at higher temperatures.

5. CONCLUDING REMARKS

The present calculations demonstrate that very recent information about the γ/ϵ transformation temperatures can be accounted for in a reasonably accurate way by an approach where (i) the Gibbs energy of the solid phases is assumed to be treatable by standard thermodynamic models and (ii) the barriers to the transformation are described by a single, composition independent parameter. This approach has been tested in three ways, which differed in the number of free parameters allowed for. Indeed, the expected tendency was observed that increasing the number of parameters increases the goodness of the fit, but this is, obviously, a less relevant fact if one takes into account the scatter of the experimental data. It seems more significant that the energies extracted from the data (viz. $\Delta G_m^{\gamma/\epsilon}$ and ΔG_m^*) are essentially the same, in spite of varying the degrees of freedom allowed for in the fit. This adds to our confidence in the main

the measurements showing such magnetic effect should not be analysed using the concept of T_0 . This is the reason why our analysis in ref.[7] did not lead to a value for $\beta_{Fe,Mn}^{\gamma}$, but only a probable range where it should fall. With the more general method applied in the present work, these M_S data can be used to extract a $\beta_{Fe,Mn}^{\gamma}$ value, which should help in refining the entropy description for γ . Table 1 shows that the $\beta_{Fe,Mn}^{\gamma}$ value obtained in step 1 is the largest, which implies smaller magnetic effects and somewhat higher M_S temperatures for alloys placed to the right of the T_N^{γ} line. However such a prediction from model 1 (dotted line in Fig.2(b)) is not supported by the data obtained in the second cycle. Thus models 2 and 3, which are based on data from both cycles, yield $\beta_{Fe,Mn}^{\gamma}$ values which are almost identical, and fall in the expected [7] range. While the present study did not assume the validity of Eq.(2) we should now examine the general belief that this equation often gives reasonable estimates of T_0 . However, from the ideas in Section 2 we conclude that in the Fe-Mn system this approximation might be justified only outside the range where magnetic effects are important. This expectation is tested in

Table 1. Parameters values determined in the present work. The Standard deviation of the ΔG_m^* values are given in parentheses.

	Model 1	Model 2	Model 3
$^0I^E [J/mol]$	-3494	-3620	-3634
$^1I^E [J/mol]$	-580	-382	-482
$\beta_{Fe,Mn}^r$	4.56	3.94	3.96
$\Delta G_m^*(A_s(2))[J/mol]$	85(± 15)	81(± 16)	71(± 16)
$\Delta G_m^*(M_s(3))[J/mol]$	85(± 32)	81(± 32)	92(± 32)
$\Delta G_m^*(A_s(4))[J/mol]$	-	94(± 20)	79(± 20)
$\Delta G_m^*(M_s(5))[J/mol]$	-	94(± 39)	110(± 39)

trends shown by the calculations. In particular, our results indicate that the approximation $\Delta G_m^*(M_s) = \Delta G_m^*(A_s)$ might be used in estimating M_S and A_S temperatures in Fe-Mn alloys, but the structural implications of this relation should be fully explored. In addition, it seems necessary to establish whether the increase in $\Delta G_m^*(M_s)$, that is noted in Table 1, when going from the first to the second thermal cycle does reflect the effect of cycling upon the transformation temperatures. Further work along these lines is in progress in our laboratory.

ACKNOWLEDGMENTS

This work has been supported by the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina (CONICET) under grant PID No.3289/92. Financial support from Fundación Balseiro (Bariloche, Argentina) is also acknowledged. The work by A.Fernández Guillermet is part of a research project supported by CONICET under grant PIA-0028/92.

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