Fe-Ni system: thermodynamic modelling assisted by atomistic simulations

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1. Introduction

Fe-Ni is a key system for different technologically relevant materials such as invar alloys, permalloys, inconel alloys, etc.

From a fundamental point of view it is interesting for the peculiar interplay between chemical and magnetic ordering phenomena.

Fe-Ni phase diagram has been studied for more than a century. Nevertheless some uncertainty still affect low temperature phase relations mainly because of the difficulty in reaching stable equilibrium at temperatures lower than about 300°C. Atomistic calculations may complement experimental investigation of phase equilibria and thermodynamics, especially at low temperature.

A recent critical assessment [2005Cac] pointed out the need for a complete re-evaluation of the system taking into account not only stable phase equilibria, but also metastable ordering equilibria, especially between fcc-based ordered structures. This is in progress and preliminary results have already been used in the thermodynamic assessment of the Fe-Ni-Ti ternary system [2007Cac].

The present status of the evaluation, also supported by new atomistic calculations, is presented and discussed.

4. Fe-Ni phases

Stable and metastable Fe-Ni phases modelled in this work are listed in the Table here below.
Liquid and **bcc** (cI2-W, A2) have been modelled as disordered solutions.
The disordered **fcc** (cF4-Cu, A1) solid solution and the related ordered phases (cP4-AuCu$_3$ L1$_2$ and tP4-AuCu L1$_0$) have been modelled as a single four sublattice phase where each sublattice corresponds to a different crystallographic site in the fcc lattice. In this way the different fcc–based structures result from the different occupancy of the four sublattices:

    (A)(A)(A)(A)   cF4-Cu (A1)
    (A)(A)(B)(B)   tP4-AuCu (L1$_0$)
    (A)(B)(B)(B)   cP4-AuCu$_3$ (L1$_2$)

Mixing of several atomic species in the same sublattice can describe compositional variations in the same phase.
This allowed us to correctly reproduce either first and second order transitions between ordered and disordered structures.

Magnetic interactions in both bcc and fcc phases play an important role in this system and have also been considered.

Formula	Structure	Phase	Sublattice model	Remarks
Liquid		Liquid	(Fe,Ni,Ti)	disordered solution
γ-(Fe,Ni)	A1, cF4-Cu, Fm-3m	A1	(Fe,Ni,Ti)	disordered part of FCC4 magnetic
Fe$_3$Ni	cP4-AuCu$_3$, Pm-3m			
FeNi	tP4-AuCu, P4/mmm	FCC4	(Fe,Ni,Ti)$_{1/4}$ (Fe,Ni,Ti)$_{1/4}$ (Fe,Ni,Ti)$_{1/4}$ (Fe,Ni,Ti)$_{1/4}$	ordered phases related to A1 magnetic
Fe$_3$Ni	cP4-AuCu$_3$, Pm-3m			
α-(Fe,Ni) δ-(Fe,Ni)	cI2-W, Im-3m	A2	(Fe,Ni,Ti)	disordered solution magnetic

5. Results: first-principles calculations

First principles calculations have been carried out in order to determine thermodynamic and magnetic properties of several structures in the Fe-Ni system.
A full structure minimization at the ground state (0 K) has been carried out using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) with plane wave basis sets [1993Kre, 1996Kre1/2]. The calculations employed the generalized gradient approximation (GGA) of Perdew and Wang [1992Per] and valence electrons were explicitly represented with projector augmented wave (PAW) pseudopotentials. The plane wave cut-off energy was set to 450 eV for all structures. k-point meshes were created by a Monkhorst-Pack scheme [1976Mon]. The ground state structure was determined by minimizing the Hellmann-Feynman forces with conjugate gradient algorithm, until all ionic forces were less than 0.01 eV/A. For magnetism, collinear magnetic configurations have been considered, although spin flips were allowed. Harmonic and anharmonic contributions at higher temperature have been neglected in the present calculations.
The complete list of the results obtained in this work is reported in the Table here below.

| Formula	Structure	Lattice	ΔH (kJ/mol at)	a$_0$ (nm)	M (μ$_B$/at)
Fe	A2 cI2-W	bcc	0	0.2826	2.156
Fe [a]	A1 cF4-Cu	fcc	9.3	0.345	0.090
Fe [a]	A1 cF4-Cu	fcc	16.3	0.365	2.553
Fe$_3$Ni	L1$_2$ cP4-AuCu$_3$	fcc	5.2	0.3560	1.834
Fe$_3$Ni	D0$_3$ cF16-AlFe$_3$	bcc	4.3	0.5705	2.127
FeNi	L1$_0$ tP4-AuCu	fcc	-5.5	0.3547 [b]	1.606
FeNi	B2 cP2-CsCl	bcc	8.9	0.2844	1.707
FeNi	B32 cF16-NaTl	bcc	2.9	0.5668	1.611
FeNi$_3$	L1$_2$ cP4-AuCu$_3$	fcc	-7.7	0.3539	1.182
FeNi$_3$	D0$_3$ cF16-AlFe$_3$	bcc	2.8	0.5637	1.100
Ni	A2 cI2-W	bcc	9.2	0.2800	0.537
Ni	A1 cF4-Cu	fcc	0	0.3518	0.618

a) two minima have been found as a function of lattice parameter
b) f.c.c. distorted, c= 0.3585 nm

The present ab initio results are in agreement with previous calculations produced by several authors [2005 Lec, 2005Mis, 2005Moh, 2006Kis, 2007Abr] using different methods. As evidenced in the Table, most binary Fe-Ni structures have been found to be unstable with respect to Fe-A2 and Ni-A1. Magnetism plays an important role in this system and all structures have been found to be ferromagnetic at 0 K. For Fe-A1, two minima in energy have been found as a function of lattice parameter, one at a lower a$_0$ which is essentially non magnetic and another one at higher a$_0$ which is magnetic.

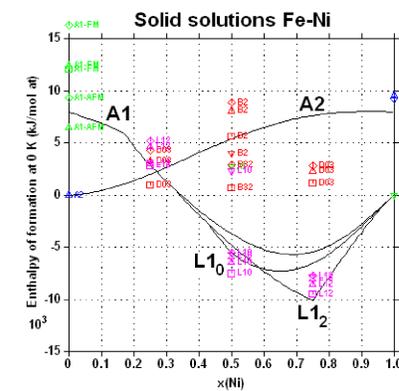## 5. Results: Thermodynamic modelling

Preliminary results of the Fe-Ni thermodynamic modelling are summarised in the figures here below.
A general good agreement between computed and experimental data has been obtained. Nevertheless low temperature phase equilibria may be improved. Additionally, on the basis of the available ab-initio results, metastable bcc ordered phases may also be modelled.
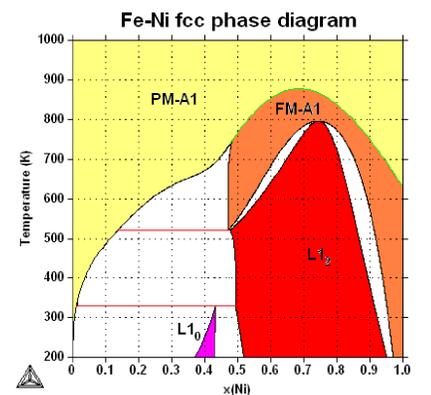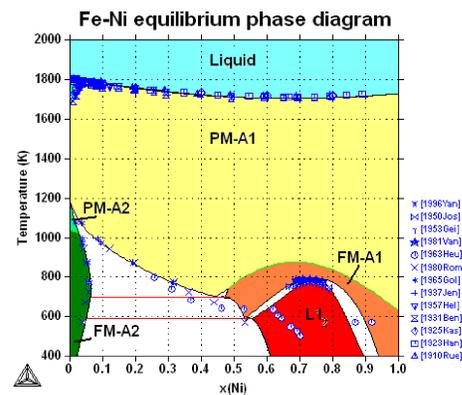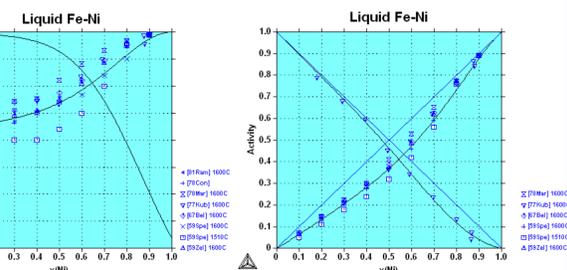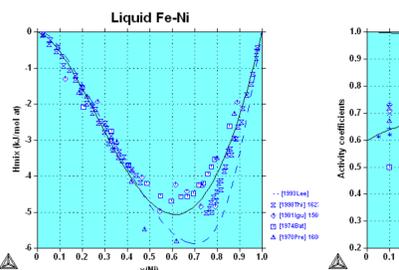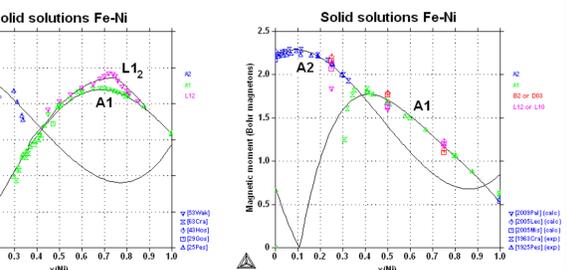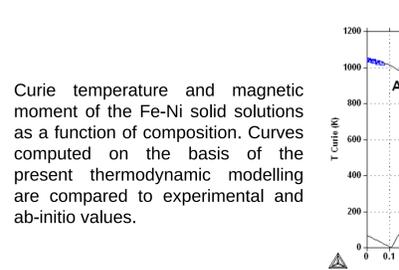

In agreement with previous predictions a tricritical point and a monotectoid equilibrium related to the magnetic transition in the fcc A1 phase have been obtained.
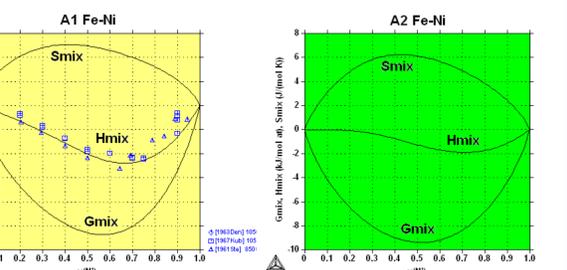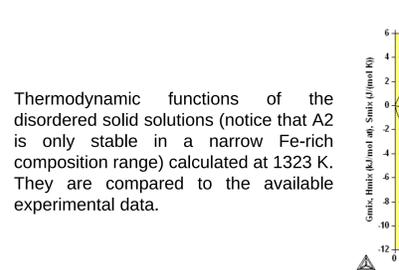

In the metastable fcc phase diagram the controversial L1$_0$ phase appears. It has been observed in meteoric samples and, according to [1996Yan], it is a metastable phase in the system.

Enthalpy of formation of the solid phases at 0 K. Reference states are A2-Fe and A1-Ni. The curves computed on the basis of the thermodynamic models are compared to the results of ab-initio ground state calculations. bcc ordered phases (B2, B32 and D0$_3$) have not been modelled yet.

Curie temperature and magnetic moment of the Fe-Ni solid solutions as a function of composition. Curves computed on the basis of the present thermodynamic modelling are compared to experimental and ab-initio values.

Selected thermodynamic functions of the liquid phase compared to the available experimental information.

Thermodynamic functions of the disordered solid solutions (notice that A2 is only stable in a narrow Fe-rich composition range) calculated at 1323 K. They are compared to the available experimental data.

Entropy of mixing of the solid solutions referred to the SER state for both elements as a function of temperature. For each temperature two curves are calculated, corresponding to the paramagnetic (PM) and ferromagnetic (FM) states respectively. The important role of magnetism in this system is evident.