

Electronic and Magnetic Structure of Ordered Fe-Ni Alloys

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Received March 2, 1993

Self-consistent band-structure calculations were performed for ordered ferromagnetic Fe-Ni alloys, using the Linear Muffin-tin Orbital Method. In particular, three compounds are analyzed, namely Ni_3Fe , NiFe and NiFe_3 . In order to obtain magnetic and cohesive properties our calculations were carried out at several lattice constants for each compound. The results for the internal excess energy show the stability of these alloys, with respect to the pure elemental solids. The dependence of the magnetic moments with the lattice parameter is investigated and calculated for NiFe_3 . The results show a collapse of its magnetic moment (Invar effect) as a function of the sample volume.

I. Introduction

Alloys of Fe-Ni have a continuous range of solid solubility which includes several compounds. Some of these compounds can be prepared in various degree of order, from completely disordered to totally ordered phases. The Fe-Ni system is of considerably interest, both for their mechanical and magnetic properties and have been extensively studied by many authors. Our interest in this system is based on the fact that recent theories of alloys phase stability, as well as first principles calculations of phase diagrams, have been phrased in terms of the alloy's underlying electronic structure^[1-4]. Since here we perform an "ab initio" band structure calculations of FeNi_3 , FeNi and Fe_3Ni in their ordered phases, the present work may be considered as a testing ground for these theories.

FeNi_3 has been the object of many experimental studies of magnetic^[5-9] and thermal^[10] properties and its nitride was investigated by Mossbauer spectroscopy^[11,12]. Its electronic structure was investigated both in its ordered and disordered phase^[13,14]. In its ordered phase, FeNi_3 has the well known Cu_3Au structure, which corresponds to a f.c.c. lattice, with Fe atoms located in the corners and Ni atoms at its face centers. The experimental lattice parameter is $a = 3.556 \text{ \AA}$ ^[15]. FeNi ordered compound has the CuAuI superstructure, and was obtained by high flux neutron irradiation of the corresponding disordered alloy and

by electron irradiation of FeNi invar alloys^[17]. In this structure Fe atoms are located at the origin and Ni atoms at (0.0, 0.5, 0.5). We notice that FeNi structure no longer has the cubic symmetry, but is in fact, tetragonal. Since this distortion is small^[18], in this work it was modeled as having cubic structure with experimental lattice parameter $a = 3.579 \text{ \AA}$ ^[19]. Fe_3Ni in its ordered phase has the Cu_3Au structure with Ni atoms located in the corners and Fe atoms at its face centers. Mossbauer spectra were obtained for Fe-Ni alloys, rich in iron, from a sample of the Santa Catharina meteorite^[20], and recently the nitride Fe_3NiN was obtained^[12] by co-reduction of oxides and direct nitridation of alloys. An interesting feature of the Fe_3Ni ordered compound comes from the fact that it has an electron per atom ratio $c/a \approx 8.5$. Since it is well known for decades that some Fe alloys with c/a in the range 5.4 to 8.7 show a very striking behavior known as "invar effect"^[20], ordered Fe_3Ni is within the class of invar alloys. In this work it is shown that this compound has a collapse of magnetic moment as a function of pressure.

We have employed the spin density functional theory within the von Barth-Hedin approximation^[21] for the exchange-correlation energy of the electron gas. The Linear Muffin-tin Orbital Method (LMTO) of Andersen^[22] was used to calculate the electronic structure of FeNi_3 , FeNi and Fe_3Ni . As the LMTO method has been described in great detail in many

publications^[23,24], we confine ourselves to a description of particular details of the present LMTO calculation. In the present calculation we did not consider the spin-orbit interactions but included the combined corrections terms. The solutions of the Schrödinger equation used s, p, d and f LMTO basis functions, and the self-consistency cycles were carried out until energy convergent on a scale better than 0.5 mRy was achieved. The one-electron potentials were self-consistently obtained using reciprocal sums with 364k points. The density of states were calculated as sum of delta functions convoluted with Gaussians functions for a fixed number of energy mesh points in each case.

Self-consistency was first achieved for the potential on 120k points and 500 energy points. Final DOS were calculated for 1500 energy points. Self-consistent field calculations within the Local Density Approximation (LDA) were performed for these three compounds in their ferromagnetic phase, for seven lattice parameters for each compound to obtain a clear understanding of the volume dependence of the ground state properties. In the next sections we present a discussion of the main results obtained for the three compounds under study in this work.

II. Results and Discussion

II.1 Bonding

Formation and stability of ordered phases can be studied by calculation of the excess internal energies. For isostructural $A_{1-x}B_x$ binary systems this quantity, for a given state of order a , is given by^[25-27]

$$\Delta E = E(\sigma, V) - \left(\frac{N_A}{N}\right) E_A(V_A) - \left(\frac{N_B}{N}\right) E_B(V_B), \quad (1)$$

where N_A and N_B are the numbers of A and B atoms in the ordered $A_{1-x}B_x$ compounds, whose state of order is a , V is the volume and E_A , E_B are the total energy functions of the elemental A and B solids respectively, at their V_A and V_B equilibrium volumes. The calculated total energies for three compounds as well as for the pure Fe and Ni solids in the f.c.c. structure were obtained as functions of the lattice parameter giving their theoretical equilibrium volume.

Fig. 1 shows the internal excess energy, ΔE , for the compounds as a function of the lattice parameter. It is clear that FeNi₃, FeNi and Fe₃Ni are stable compounds with respect to the pure elemental solids and that FeNi₃ has the high energy formation. The calculated minimum data point in Fig. 1 correspond to the following lattice parameters, $a = 6.5807$ a.u., $a = 6.6287$ a.u. and $a = 6.6287$ a.u. for FeNi₃, FeNi and Fe₃Ni, respectively, which, as can be seen from Table I, do not differ appreciably from those obtained through an analytical fitting of the calculated total energies.

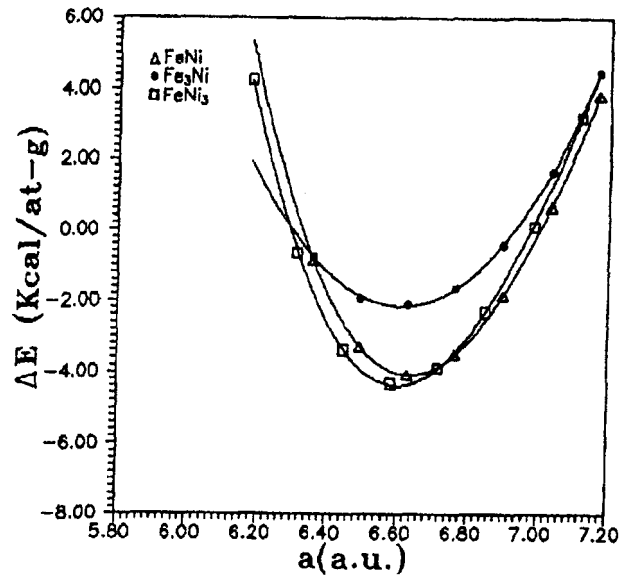


Figure 1: Internal excess energies as a function of the lattice parameter for FeNi₃, FeNi and Fe₃Ni ordered compounds.

The equilibrium lattice parameters, whose values were obtained by fitting the calculated total energy data points to a third degree polynomial, the bulk modulus and the energy formation for the compounds are given in Table I. The results are shown for the Barth-Hedin (vBH) approximation to the LDA. A parallel calculation using the Vosko-Wilk-Nussair (VWN) approximation^[28] to the LDA, for these compounds, gives results that do not differ appreciably from the results shown in Table I. The same was already verified in a previous calculation for Fe-Pd alloys^[29] where we have obtained a weak dependence of these properties on the type of approximation used. Here our calculations for both vBH and VWN approximations for f.c.c. Fe and Ni pure solids give results that show differences which are much less pronounced than the results for pure elemental metals studied by Jansen et al.^[30]. The

theoretical values for the Bulk modulus (B) in Table I are obtained from a numerical five points differentiation of the calculated total energies. An analytical calculation by fitting the total energies with a third degree polynomial gives practically the same values for B.

The theoretical equilibrium volumes (Table I) for FeNi_3 agrees well with the experimental values, the deviation in the lattice parameter being less than 1.5%. The same is true for FeNi ordered compound in which the deviation in the lattice parameter is about 2%. For FeNi and Fe_3Ni our results for the lattice parameter is in agreement with the recent results of Moroni et al^[31] and Mohn et al^[32-33], the difference being less than 0.5%. On the other hand we can estimate our result for Fe_3Ni from the lattice parameter given by Rochegude^[12] for the nitride Fe_3NiN which is $a \approx 3.783$ Å. It is known^[12,34,35] that the insertion of nitrogen leads to an expansion of the cell volume of an f.c.c. type-lattice. This expansion increases the lattice parameter about 8-10%. Considering this fact, our calculation gives a theoretical lattice parameter that is 1.5% larger than the experimental value. To show the Invar properties of Fe-Ni system in the iron-rich region we give in Table I the results of a paramagnetic calculation for the three compounds. Clearly, the difference in the energy formation between ferro and paramagnetic states is very small for the Invar alloy Fe_3Ni which shows magnetoelastic effects. We comment about this fact in Section 11.4.

TABLE I – Ground state properties for the three compounds. Theoretical lattice parameters in atomic units. Internal excess energies (AE) in Kcal/at-g, and Bulk modulus in Giga Pascal.

	Fe_3Ni	FeNi	FeNi_3
a (a.u.)	6.6101	6.6357	6.6012
AE (Kcal/at-g)	-2.15	-4.06	-4.36
B (GPa)	135.90	232.13	247.28
paramagnetic phase			
a (a.u.)	6.4903	6.5147	6.5325
AE (Kcal/at-g)	-1.57	-0.31	-0.53

II.2 Results for FeNi_3

In this section we discuss results of a ferromagnetic self-consistent calculation for FeNi_3 within the vBH approximation. For the lattice parameter we take $a =$

6.6012 a.u. which gives the minimum for AE in Fig. 1, and is very close to the experimental value for this compound. The Wigner-Seitz spheres around Fe and Ni atoms are taken to be of equal size, with radii $a \approx 2.6270$ a.u.. The results are displayed in Table II. At Ni site the magnetic moment agrees well with the experimental value which is 0.68 Bohr magnetons^[36]. On the other hand, at the Fe sites, the theoretical value for the magnetic moment is smaller than in the experiment, which is $3.107\mu_B$ ^[36]. A Real-Space LMTO-ASA calculation for this compound gives^[37] $2.87\mu_B$ for Fe and $0.53\mu_B$ for Ni, and a DVM cluster calculation^[38] gives $3.1\mu_B$ for Fe and $0.82\mu_B$ for Ni. A LMTO calculation by Jepsen et al^[39] gives $2.85\mu_B$ for Fe and $0.57\mu_B$ for Ni. Therefore, our result for Ni sites agrees well with other calculations. Notice however that agreement is not good for Fe sites and we relate the relative lower value obtained for the magnetic moment at these sites to the degree of population of the spin-down d-states. In Fig. 2 we can see that the magnetization at Fe sites is a smooth increasing function of its volume. We found the same behavior at Ni sites, but with less variation in the magnetic moment.

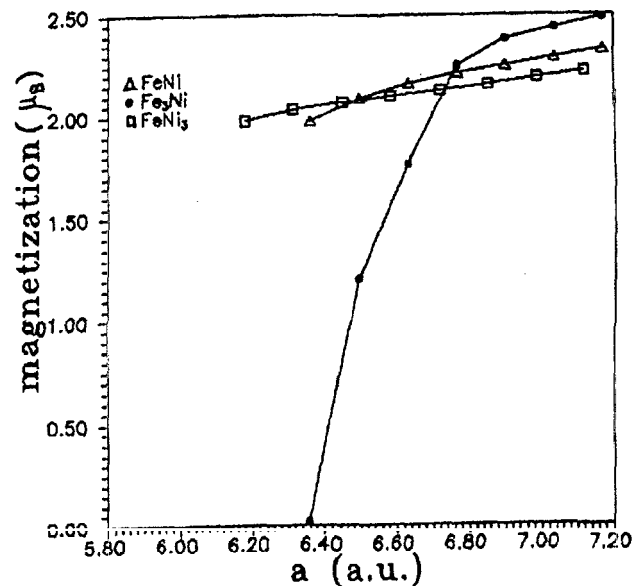


Figure 2: Magnetic moments at Fe sites for the three compounds as a function of the lattice parameter.

From Table II the main contribution for the DOS at the Fermi level (E_F) is due to d-electrons, and for both sites the spin-down states give a higher value for

TABLE II - Calculated parameters of spin-polarization FeNi₃ using the self-consistent potentials, with $a = 6.5807$ a.u.

	Fe		m	Ni		m
	↑	↓	↑ - ↓	↑	↓	↑ - ↓
n (electrons/spin)	4.92	2.83	2.09	5.46	4.64	0.82
n_s (electrons/spin)	0.30	0.29	0.01	0.33	0.33	0.00
n_p (electrons/spin)	0.35	0.34	0.01	0.38	0.40	-0.02
n_d (electrons/spin)	4.24	2.17	2.07	4.71	3.88	0.83
n_f (electrons/spin)	0.03	0.03	0.00	0.04	0.03	0.01
$N(E_F)$ (states/spin Ry)	1.58	21.10		2.07	11.38	
$N_s(E_F)$ (states/spin Ry)	0.19	0.07		0.21	0.04	
$N_p(E_F)$ (states/spin Ry)	0.43	0.16		0.42	0.29	
$N_d(E_F)$ (states/spin Ry)	1.25	20.85		1.43	10.91	
$N_f(E_F)$ (states/spin Ry)	0.01	0.02		0.02	0.14	
$N(E_F)$ (states/atom Ry)		22.98			13.45	
$N(E_F)$ (states/Unit cell Ry)			63.33			
γ (mJ/mol K ²)			10.98			
E_F (Ry)			0.744			
AQ (electrons)		-0.25060			0.05353	

the DOS at E_F . This leads to the calculated value for the electronic specific heat coefficient shown in Table II. Charge transfer (Table II) for the equilibrium lattice parameter gives 0.083 electrons as excess charge at Ni sites. The results for the charge transfer at Fe sites for different lattice parameters are displayed in Fig. 3.

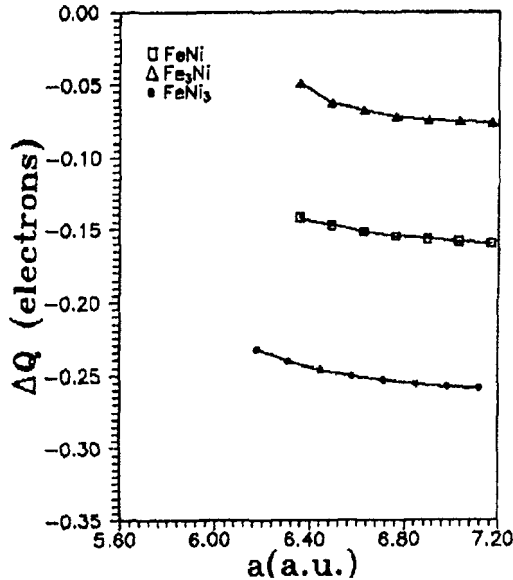


Figure 3: Charge transfer at Fe sites as a function of the lattice parameter for the three ordered compounds.

Clearly it is a smooth function and practically does not vary for the lattice parameters considered. Thus the electron transfer from one site to the other does not

have a strong dependence with the lattice spacing between Fe-Ni atoms, contrary to the results of a previous calculation^[29] for Fe-Pd alloys where we found a more pronounced variation of the charge transfer with lattice spacing.

The density of states at Fe and Ni sites for both spin directions is shown in Fig. 4. Clearly, the spin-up d-electrons form a common d-band. Further, the spin-down electrons are almost excluded from Fe sites, which results in the formation of localized magnetic moments. This fact was reported in prior calculations^[29,40-41] in Fe-Pd alloys and by Kubler et al^[42] for Heusler alloys. Spin polarization results in a splitting of up and down bands putting the Fermi level in a valley between the DOS of up and down spins as can be seen from Fig. 4. This reduces the density of states $N(E_F)$ tending to put it in agreement with the experimental value for the linear coefficient of the specific heat (γ). From the total DOS obtained from up and down projected densities of states we found that the value of $N(E_F)$ is increased if the Fermi level moves in the direction of low or high energies, and this is exactly what happens when the sample volume is changed. Clearly this is not only a simple rigid shift of the DOS, but contrary as the volume changes, some features of the DOS are subtly altered. However, since there is no remarkable alterations we do not make more comments about this fact here.

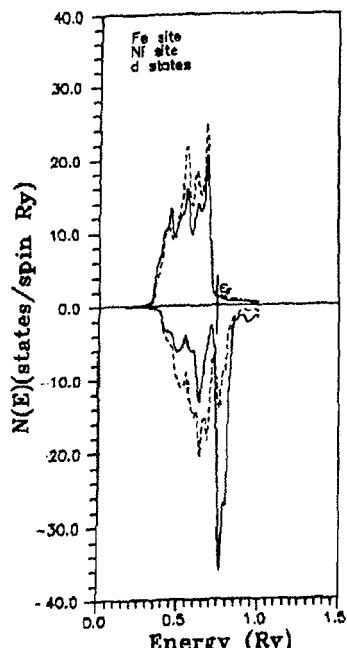


Figure 4: The d-projected densities of states for spin-up and spin-down at Fe sites (solid line) and Ni sites (dashed line) of the FeNi₃.

11.3 Results for FeNi

In this section we discuss the results of our calculation for the case of ordered FeNi. Here we used the lattice parameter $a \approx 6.6357$ a.u. which gives the minimum in Fig. 1 (equal-size Wigner-Seitz spheres with radii $s = 2.6408$ a.u.). Our results for this lattice parameter are displayed in Table III (with vBH approximation). It shows an increase in the atomic moments at Fe and Ni sites. Again, a comparison with the results of a DVM cluster calculation^[38,43], shows a good agreement for the magnetic moment at Ni sites and a fair agreement for Fe sites, since the calculation^[43] gives $0.79\mu_B$ for Ni and $3.33\mu_B$ for Fe. Also the values of the magnetic moments for this compound calculated by Jepsen et al^[39] with the LMTO method gives $2.59\mu_B$ for Fe and $0.59\mu_B$ for Ni, which shows again the fair agreement of our results for Fe sites. Here the magnetization at Fe sites is a smooth increasing function of the volume, as seen in Fig. 2. Since the magnetic moment at Ni sites shows less variation, here as for FeNi₃ compound, the most important contribution for the behavior of the total magnetization is due to changes in the magnetic moment at Fe sites. This result shows that the magnetization at Fe sites, in Fe-Ni alloys, is

most sensitive to lattice spacing variation (volume effects). From Table III we note that the main contribution is due d-electrons for both sites but now we found an abrupt decrease in $N(E_F)$ for spin-down d-electrons for both sites. This fact is discussed in terms of the projected DOS below. Therefore, the calculated value of γ for this compound is much smaller than the value obtained for FeNi₃ (see Table II). For this compound we obtain 0.150 electrons as the excess charge at Ni sites. Fig. 3 shows that the charge transfer at Fe sites, as the volume is decreased, follows the same trends as FeNi₃. However, in this case the Fe sites lose less electrons than in FeNi₃ when increasing the iron concentration.

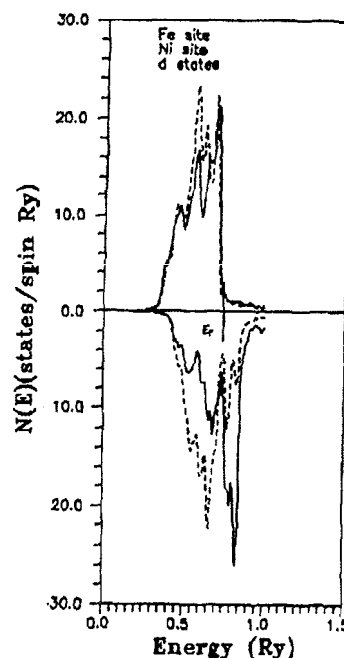


Figure 5: The d-projected densities of states for spin-up and spin-down at Fe sites (solid line) and Ni sites (dashed line) of the FeNi.

In Fig. 5 the density of states are displayed for up and down electrons at Fe and Ni sites. The main contribution for the total DOS comes from d-electrons and the formation of the magnetic moments follows the same trends discussed for FeNi₃. Also it is easy to see from Figs. 4 and 5 that Fe and Ni atoms have, in general, similar DOS, apart from small subtle alterations in their features. This leads to smooth change of the DOS with composition as well as a small variation in the atomic moments in agreement with the description provided by the Slater-Pauling curve^[5,44,45]. Notice that

TABLE III - Calculated parameters of spin-polarized FeNi using the self-consistent potentials, with $a = 6.6287$ a.u.

	Fe		m		Ni	
	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$
n (electrons/spin)	5.01	2.85	2.16	5.53	4.61	0.92
n_s (electrons/spin)	0.30	0.30	0.00	0.33	0.34	-0.01
n_p (electrons/spin)	0.36	0.36	0.00	0.39	0.42	-0.03
n_d (electrons/spin)	4.31	2.16	2.15	4.77	3.82	0.95
n_f (electrons/spin)	0.04	0.03	0.01	0.04	0.03	0.01
$N(E_F)$ (states/spin Ry)	3.57	6.80		2.02	5.10	
$N_s(E_F)$ (states/spin Ry)	0.18	0.06		0.18	0.04	
$N_p(E_F)$ (states/spin Ry)	0.41	0.30		0.37	0.47	
$N_d(E_F)$ (states/spin Ry)	2.97	6.36		1.46	4.53	
$N_f(E_F)$ (states/spin Ry)	0.01	0.08		0.04	0.03	
$N(E_F)$ (states/atom Ry)		10.37			7.12	
$N(E_F)$ (states/Unit cell Ry)			17.49			
γ (mJ/mol K ²)			3.03			
E_F (Ry)			0.743			
AQ (electrons)	-0.15090			0.15090		

when the iron concentration is increased (e.g. going from FeNi₃ to FeNi) there is a great charge transfer to Ni sites, which populates the spin-down states at these sites. Hence an abrupt decrease in the DOS at E_F occurs. Also, for Fe sites, the Fermi level (Fig. 5) is located in a valley of the DOS for spin-down states lowering the value for $N(E_F)$ at these sites.

11.4 Results for Fe₃Ni

In this section we discuss the results for Fe₃Ni, which is an Invar alloy^[20]. In fact Fe₃Ni is the most interesting of the three investigated alloys in the present work since it shows magnetoelastic effects, with a collapse of its magnetic moment with pressure, an effect that can be seen reflected in its electronic structure. We modeled the Fe₃Ni as having the f.c.c. structure with Ni atoms at the corners and Fe atoms at its face centers. We took: $a = 6.6101$ a.u. as the lattice parameter (this value gives the minimum AE in Fig. 1), and the Wigner-Seitz around Fe and Ni atoms are taken with same radii, $s = 2.6306$ a.u..

Table IV displays the calculated parameters for Fe₃Ni with vBH approximation for exchange-correlation. At the theoretical equilibrium volume the magnetic moments for both Fe and Ni are less than the magnetization for the other two compounds, that is, Fe atoms show a weak ferromagnetism in Fe₃Ni (a deviation in the Slater-Pauling curve). A comparison of our calculated magnetic moments for this compound

with previous calculations shows a good agreement. For example a prior ASW calculation of Williams et al^[46] gives $2.0\mu_B$ and $0.5\mu_B$ at Fe and Ni sites respectively, and a recent calculation by Jepsen et al^[39] gives $1.66\mu_B$ and $2.29\mu_B$ for Fe, $0.37\mu_B$ and $0.59\mu_B$ for Ni at 2.60 and 2.65 Wigner-Seitz radii respectively. Note however that the behavior of magnetization with respect to the change in volume is quite different (Fig. 2). As we vary the lattice parameter in direction to high volumes the magnetization at Fe sites increases smoothly but more rapidly than in the other two compounds. At Ni sites the atomic moments follows the same behavior. From Fig. 2 we see that the magnetization for low volumes shows a drastic variation, going abruptly to zero for a variation of 4% in the lattice parameter. This was already observed for f.c.c. iron in a ferromagnetic calculation^[47-51] and was first described theoretically by Madsen and Andersen^[52]. Such behavior, the magnetic collapse or a breakdown of ferromagnetism, indicates particularly^[49,50,53] for f.c.c. iron the existence of more than one magnetic phase. The existence of these different magnetic phases for f.c.c. Fe, Co and Ni was treated by the fixed spin-moment method by Moruzzi et al^[54]. In the present work we relate this behavior of the magnetization to specific features of the densities of states.

From Table IV we see an increasing in $N(E_F)$ due to a much larger contribution of spin-up states at Fe and Ni sites which raises the value of γ for this compound.

TABLE IV - Calculated parameters of spin-polarized Fe₃Ni using the self-consistent potentials, with $a = 6.6287$ a.u.

	Fe		m		Ni		m
	↑	↓	↑ - ↓	↑	↓	↑ - ↓	
n (electrons/spin)	4.80	3.13	1.67	5.49	4.71	0.78	
n_s (electrons/spin)	0.30	0.31	-0.01	0.34	0.35	-0.01	
n_p (electrons/spin)	0.37	0.37	0.00	0.42	0.44	-0.02	
n_d (electrons/spin)	4.09	2.42	1.67	4.70	3.89	0.81	
n_f (electrons/spin)	0.04	0.03	0.01	0.04	0.02	0.02	
$N(E_F)$ (states/spin Ry)	9.98	15.74		9.42	11.50		
$N_s(E_F)$ (states/spin Ry)	0.08	0.14		0.03	0.13		
$N_p(E_F)$ (states/spin Ry)	0.53	0.32		0.65	0.24		
$N_d(E_F)$ (states/spin Ry)	9.24	15.21		8.66	11.08		
$N_d(E_F)$ (states/spin Ry)	0.12	0.06		0.08	0.05		
$N(E_F)$ (states/atom Ry)		25.72			20.92		
$N(E_F)$ (states/Unit cell Ry)			98.07				
γ (mJ/mol K ²)			17.00				
E_F (Ry)			0.768				
ΔQ [electrons]		-0.06729			0.20187		

A comparison with FeNi₃ compound shows that the contribution of spin-down electrons to $N(E_F)$ is smaller due to the high degree of population of the spin-down states at Fe and Ni sites. In Fig. 3 we see the charge transfer at Fe sites for various lattice parameters. The behavior of the charge transfer follows the trends of

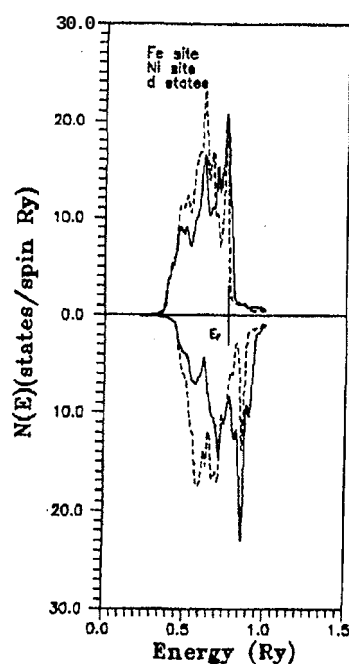


Figure 6: The d-projected densities of states for spin-up and spin-down at Fe sites (solid line) and Ni sites (dashed line) of the Fe₃Ni.

other two compounds but here Fe atoms loose less electrons due to an increase in iron concentration. This

charge transfer gives 0.2018 electrons as the excess charge at Ni sites at the equilibrium volume.

The density of states, for each spin direction, at Fe and Ni sites is shown in Fig. 6. We see that, for the ordered Fe₃Ni, the spin-up electrons form a common d-band as in the case of FeNi₃ and FeNi ordered compounds the main difference arising at Ni sites where we note that the peaks in the DOS, for spin-down electrons moves to low energies. Fig. 6 shows, as for the other two compounds the splitting of the d-bands, but here it occurs an increase in the population of the spin-down states which gives the calculated magnetic moments (Table IV). A comparison between Figs. 4, 5 and 6 shows a smooth change in the DOS, with iron concentration (one resembles another) in agreement with the fact that these ordered compounds are superimposed on the Slater-Pauling curve⁵.

The influence of pressure on the magnetization for the Fe₃Ni (Fig. 2) can be analyzed in terms of the electronic structure. To clarify this point, results for Fe₃Ni are given for two different lattice parameters, $a = 6.4934$ a.u. and $a = 6.3581$ a.u.. These values correspond to a deviation in a of -2%. and -4% respectively, from its equilibrium volume (here, as before, we take equal-size Wigner-Seitz spheres in each case corresponding to $s = 2.5376$ a.u. and $s = 2.4847$ a.u. respectively). Table V gives a clear idea of what happens with the electronic distribution when interatomic spac-

ing is reduced. For both sites as the volume is decreased there is an increasing number of spin-down d-electrons with a decreasing number of spin-up d-electrons, which reduces their difference. Hence, small magnetic moments are obtained. From Table V(b) we see that, for the corresponding pressure, the compound makes a transition to the paramagnetic phase, which has low volume. In fact, Table I shows that the paramagnetic phase has a low volume, and that the volume difference between para and magnetic states is higher for iron-rich region (Invar alloys), being very small for pure nickel.

From the curve for Fe₃Ni in Fig. 1 we can estimate the difference in the energy formation between para and ferromagnetic states since, for a deviation of -4% in the lattice parameter, the Fe₃Ni compound goes abruptly to the paramagnetic phase. This difference is 3.80 mRy/atom, which is greater than the value obtained from a paramagnetic calculation (see Table I) that gives 1.32 mRy/atom. From Table I we see that this difference is very small as compared with the values 11.97 mRy/atom and 12.21 mRy/atom for FeNi and FeNi₃ compounds. These results are in good agreement with recent results on Fe₃Ni obtained via the spin-fixed moment method^[33]. The small energy difference between para and magnetic states is a feature of the Invar alloys and recent band structure calculations together with a Landsu expansion of the total energy allows to calculate the magnetic contribution to the thermal expansion coefficient, to investigate the Invar anomalies at finite temperature.

The abrupt change in the magnetization can be viewed as a "population effect" of the spin-down d-states at Fe sites. This can be clarified through Figs. 7 and 8, where we show the d-DOS at Ni and Fe sites for two different lattice parameters. At Ni sites (Fig. 7) the general features of the DOS for spin-up states are much more altered when compared with the DOS for equilibrium volume. It resembles the structure of spin-down DOS, and this occurs also at Fe sites (Fig. 8). Therefore, although we observe an entire shift of the DOS, some alterations in its features occurs, which indicates a modification on the self-consistent potentials felt by the electrons due to the reduction of lattice spacing. One remarkable aspect of these figures is that for both sites, the structure of the DOS for up and down

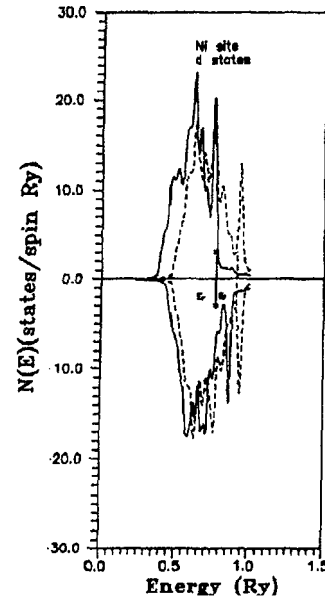


Figure 7: The d-projected densities of states for both spin directions at Ni sites for two different lattice parameters of Fe₃Ni. Solid line: $a = 6.6287$ a.u.; dashed line: $a = 6.3581$ a.u.. The Fermi energies are $E_F = 0.768$ Ry and $E_F = 0.912$ Ry, respectively.

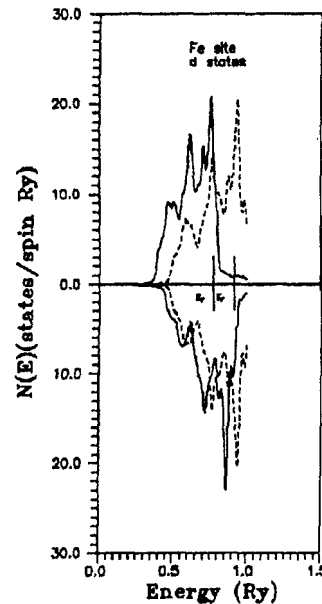


Figure 8: The d-projected densities of states for both spin directions at Fe sites for two different lattice parameters of Fe₃Ni. Solid line: $a = 6.6287$ a.u.; dashed line: $a = 6.3581$ a.u.. The Fermi energies are $E_F = 0.768$ Ry and $E_F = 0.912$ Ry, respectively.

spins, for low volumes, become equal and thus the system is driven to the paramagnetic phase. For Fe sites

TABLE V - Calculated parameters of Fe_3Ni for two different lattice parameters near and at the magnetic collapse. (a) lattice parameter $a = 6.4934$; (b) lattice parameter $a = 6.3551$.

(a)	Fe		m		Ni	
	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$
n (electrons/spin)	4.57	3.37	1.20	5.31	4.88	0.43
n_s (electrons/spin)	0.30	0.30	0.00	0.34	0.35	-0.01
n_p (electrons/spin)	0.37	0.37	0.00	0.42	0.44	-0.02
n_d (electrons/spin)	3.86	2.66	1.20	4.51	4.06	0.45
n_f (electrons/spin)	0.04	0.03	0.01	0.04	0.03	0.01
$N(E_F)$ (states/spin Ry)	10.34	19.75		6.18	18.45	
$N(E_F)$ (states/Unit cell Ry)			114.88			
E_F (Ry)			0.830			
ΔQ (electrons)		-0.06300			0.18900	

(b)	Fe		m		Ni	
	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$	$\uparrow$	$\downarrow$	$\uparrow - \downarrow$
n (electrons/spin)	3.99	3.96	0.03	5.07	5.07	0.00
n_s (electrons/spin)	0.30	0.30	0.00	0.34	0.34	-0.00
n_p (electrons/spin)	0.37	0.37	0.00	0.44	0.44	-0.00
n_d (electrons/spin)	3.29	3.26	0.03	4.25	4.25	0.00
n_f (electrons/spin)	0.04	0.04	0.00	0.04	0.04	0.00
$N(E_F)$ (states/spin Ry)	13.90	14.36		4.75	5.13	
$N(E_F)$ (states/Unit cell Ry)			94.66			
E_F (Ry)			0.912			
ΔQ (electrons)		-0.04920			0.14761	

(Fig. 8) we see that, as the volume decreases, the spin-up DOS is shifted to higher energies emptying up states, and at the same time populating spin-down states, since Fermi energy moves to high energies. Therefore the magnetic breakdown comes from two factors, an inversion of the spin-up into spin-down stateç, as well as the population of spin down states by the excess electrons at Fe sites, since for low volume Fe sites loose less electrons than in the equilibrium volume (Table V).

III. Conclusion

The electronic structures of ferromagnetic FeNi_3 , FeNi and Fe_3Ni ordered compounds were studied using a fully self-consistent band-structure calculation within the LMTO method. From the analysis of the results it was found that electronic and magnetic properties are sensitive to the iron content in iron-nickel alloys. We found for these alloys a common behavior of the electronic states that explains the formation of localized magnetic moments from an itinerant electron point of view which is similar to the case of Heusler alloys. Some theoretical results agree well with experimental values and our calculated lattice parameters for FeNi_3

and FeNi agree within 1.5% with respect to the experimental results. Further, for Fe_3Ni our theoretical value for lattice parameter is within 0.5% with respect to others calculations found in the literature.

The electronic structure of these compounds was studied as function of the lattice parameter with the aim of understanding the dependence of the ground-state properties (charge transfer, magnetization) with volume. The calculation for the internal excess energy show the stability of these compounds, with energies of -4.36 Kcal/at-g, -4.06 Kcal/at-g and -2.15 Kcal/at-g for FeNi_3 , FeNi and Fe_3Ni respectively. Our paramagnetic results give small energy difference (about 1.8 mRy/atom) between para and ferromagnetic states for Fe_3Ni and a large volume difference between these states. This is a characteristic feature of an Invar alloy and is in agreement with recent results of Mohn et al^[32,33] and Moroni et al^[31]. We found also that the total magnetization for FeNi_3 and FeNi are smooth increasing functions of the lattice parameter. For the Fe_3Ni alloy a collapse of the magnetic moment for both Fe and Ni sites occurs as sample volume is decreased about 4%. This magnetic breakdown was explained by

subtle changes in the DOS accompanied by inversion of spin populations.

Acknowledgements

One of us (J. B. Filho) acknowledges financial support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq.

References

1. K. M. Flabbe and J. D. Joannopoulos, Phys. Rev. Lett. **59** (1987).
2. K. Terakura, T. Oguchi, T. Mohri and K. Watanabe, Phys. Rev. **B35**, 2169 (1987).
3. S. H. Wei, A. A. Ubye, L. G. Ferreira and A. Zunger, Phys. Rev. **B36**, 4163 (1987).
4. J. E. Bernard, L. G. Ferreira, S. H. Wei and A. Zunger, Phys. Rev. **B38**, 6338 (1988).
5. C. G. Sauls and M. K. Wilkinson, Phys. Rev. **97** 304 (1955).
6. S. C. Ng, B. N. Brockhouse and E. D. Hallman, Mat. Res. Bull. **2**, 69 (1967).
7. A. I. Ushakov and V. V. Litvintsev, Fiz. Metal. Metall. **42**, 880 (1976).
8. J. M. Drijver, F. van der Wonde and S. Rodelaar, Phys. Rev. **B16**, 993 (1977).
9. T. E. Cranshaw, J. Phys. F: Met. Phys. **17**, 967 (1987).
10. E. A. Owen and E. L. Yates, Phys. Soc. **49**, 1 (1936).
11. G. Shirane, W. J. Takei and S. L. Ruby, Phys. Rev. **126**, 49 (1966).
12. P. Rogéude "Metastabilité et Equilibre de Solutions Solides à l'azote. Etudes par spectrométrie Mossbauer" (PhD Thesis, USTL, Lille, France, 1986).
13. D. D. Johnson "The Electronic and Energetic Study of Magnetic Random Substitutionally Disordered FeNi Alloys" (PhD Thesis, University of Cincinnati U.S., 1985).
14. D. D. Johnson, F. J. Pinski and G. M. Stocks, J. Appl. Phys. **57**, 3018 (1985).
15. P. Lambin and F. Herman, Phys. Rev. **B30**, 6903 (1984).
16. J. Paulevé, D. Dautreppe, J. Launquier and L. Néel, C. R. Acad. Sci. Paris **254**, 965 (1962).
17. A. Chamberod, J. Langier and J. M. Perrisson, J. Mag. Mag. Mater. **10**, 139 (1979).
18. J. Danon, R. B. Scorzelli, I. Souza Azevedo and M. Christophe-Michel-Levy, Nature **281**, 469 (1979).
19. J. Danon, R. B. Scorzelli, I. Souza Azevedo and K. Imakura, Phys. Scripta **21**, 223 (1980).
20. J. Danon, R. B. Scorzelli, I. Souza Azevedo, J. Langier and A. Chamberod, Nature **284**, 537 (1980).
21. U. von Barth and L. Hedin, J. Phys. **C5**, 1629 (1972).
22. O. K. Andersen, Phys. Rev. **B12**, 3060 (1975).
23. O. K. Andersen and O. Jepsen, Physica (Utrecht) **91B**, 317 (1977).
24. H. L. Skriver, *The LMTO Method: Muffin-Tin Orbitals and Electronic Structure* (Springer, New York, 1984).
25. L. G. Ferreira, A. A. Mbaye and A. Zunger, Phys. Rev. **B35**, 6475 (1987).
27. L. G. Ferreira, A. A. Mbaye and A. Zunger, Phys. Rev. **B40**, 3197 (1989).
28. S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
29. C. A. Kuhnen and E. Z. da Silva, Phys. Rev. **B** **46**, 8915 (1992).
30. H. J. F. Jansen, K. B. Hathaway and A. J. Freeman, Phys. Rev. **B30** 6177 (1984).
31. E. G. Moroni and T. Jarlborg, Physica **B161**, 115 (1989).
32. P. Mohn, K. Schwarz and D. Wagner, Physica **B161**, 153 (1989).
33. P. Mohn, K. Schwarz and D. Wagner, Phys. Rev. **B43**, 3318 (1991).
34. C. Cordier-Robert "Influence des Elements Substitutionnels sur les Distributions D'interstitiels et la Precipitation de Nitrures dans les Solutions Solides et les Composés du Fer et de l'Azote" (PhD Thesis, USTL, Lille, France, 1989).
35. C. A. Kuhnen, R. S. de Figueiredo, V. Drago and E. Z. da Silva, J. Magn. Magn. Mater. **111**, 95 (1992).
36. J. W. Cable and E. C. Wolhen, Phys. Rev. **B7**, 2005 (1973).
37. J. Duarte Jr., P. R. Peduto and S. Frota-Pessoa, Rev. Bras. Fis. **21**, 101 (1991).
38. D. Guenzburger, D. E. Ellis and J. Danon, J.

- Magn. Magn. Mater 59, 139 (1986).
39. O. Jepsen and F. Herman, Phys. Rev. B41, 6801B (1990).
40. C. A. Kuhnen and E. Z. da Silva, Phys. Rev. B35, 370 (1987).
41. C. A. Kuhnen and E. Z. da Silva, J. Mag. Magn. Mater. 67, 260 (1987).
42. J. Kubler, A. R. Williams and C. B. Sommers, Phys. Rev. B28, 1745 (1983).
43. D. Guenzburger and D. E. Ellis, Phys. Rev. B36, 6971 (1987).
44. J. C. Slater, J. App. Phys. 8, 385 (1937); S. Takizawa and K. Terakura, Phys. Rev. B39, 5792 (1989).
45. L. Pauling, Phys. Rev. 54, 899 (1938).
46. A. R. Williams, V. L. Moruzzi, C. D. Gelatt Jr., J. Kubler and K. Schwarz, J. Appl. Phys. 53, 2019 (1982).
47. U. K. Poulsen, J. Kollar and O. K. Andersen. J. Phys. F6, L241 (1986).
48. O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen and J. Kollar, Physica 86-88 B, 249 (1977).
49. J. Kubler, Phys. Rev. Lett. 81A, 81 (1981).
50. D. Bagayoko and J. Callaway, Phys. Rev. B28, 5419 (1983).
51. A. R. Williams, J. Kubler and C. D. Gellat Jr., Phys. Rev. B19, 6094 (1979).
52. J. Madsen and O. K. Andersen, in Proceedings of the 21st Annual Conference on Magnetism and Magnetic Materials, edited by J. J. Becker, G. H. Lander and J. J. Rhgne (AIP, N. York, 1976) p. 327.
53. D. M. Roy and D. G. Pettifor, J. Phys. F7, L183 (1977).
54. V. L. Moruzzi. P. M. Marcus, K. Schwarz and P. Mohn, Phys. Rev. B34, 1784 (1986).