Ab-initio electronic and magnetic properties of Fe-Al alloys

E. APIÑANIZ AND F. PLAZAOLA

Elektrika eta Elektronika Saila, Euskal Herriko Unibertsitatea 644 P.K., 48080 Bilbo

This work presents ab-initio self-consistent calculations performed with the TB-LMTO code to study the different phases of the Fe-Al phase diagram, corresponding to the ordered structures B2, DO3 and B32 and for Fe₅₀Al₅₀ and Fe₃Al compositions. Both, unpolarized and spin-polarized calculations have been performed to deduce the energetic difference between the paramagnetic and ferromagnetic state of the corresponding structure. Calculations for the disordered structures have also been performed for the previously mentioned compositions. These results show that by disordering the alloy magnetism is enhanced and that the equilibrium lattice parameter increases.

Keywords: Fe-Al alloys, TB-LMTO code, magnetic transformations, order-disorder.

Propiedades electrónicas y magnéticas de las aleaciones Fe-Al

En este trabajo se presentan cálculos autoconsistentes ab-initio realizados con el método TB-LMTO (Tight Binding Linear Muffin Tin Orbital) con el fin de estudiar las diferentes estructuras que se presentan en el diagrama de fases de las aleaciones Fe-Al. Se han estudiado las estructuras ordenadas B2, DO3 y B32 para las siguientes concentraciones: Fe₅₀Al₅₀ y Fe₃Al. Asimismo, se han realizado cálculos teniendo y sin tener en cuenta la polarización de spin con el fin de poder deducir la diferencia energética entre los estados ferromagnéticos y paramagnéticos de la misma estructura. Por otra parte se han realizado estos mismos cálculos para estructuras desordenadas y las mismas concentraciones. Los resultados muestran que mediante el desorden aumenta el magnetismo de estas aleaciones y crece el parámetro de red.

Palabras clave: Aleaciones Fe-Al, código TB-LMTO, transformaciones magnéticas, orden-desorden.

1. INTRODUCTION

Intermetallic alloys show great potential for structural applications requiring good wear and environmental resistance. In particular iron aluminides have been of interest since the 1930s when their excellent oxidation resistance was first noted (1). They offer a relatively low material cost, conservation of strategic elements and a lower density than stainless steel. These properties tend to occur in restricted composition ranges with crystal structures that may differ from those of their constituent elements.

Iron and aluminium show a complex binary phase diagram (2) with several intermetallic compounds. In the Fe rich side of the phase diagram the Fe-Al system is characterized by a range of disordered body centered cubic (BCC) solution up to 22 at % Al at room temperature, on increasing the Al content the phase diagram shows a variety of intermetallic phases such as Fe₃Al, FeAl, Fe₁₃Al₃ ... Fe₃Al has the DO3 cubic structure, exists between 25 and 33 at % Al, and is ferromagnetic at room temperature. The other compound stable over a wide composition range is FeAl, which is also cubic with B2 structure (CsCl). The B2 Fe₅₀Al₅₀ is non-magnetic, but B2 phase is ferromagnetic at room temperature around 35 at. % Al. For B2 (Fe₅₀Al₅₀) there is only one possible lattice position for the iron while for the DO3 (Fe₃Al) structure there are two.

Recently, Fultz and Gao (3) suggested the existence of a metastable B32 phase. For a single crystal specimen of 20 at % Al content, which was slowly cooled (from 740°C down to

room temperature), B32 long range order was observed by Becker and Schweike in neutron scattering experiments (4). Calculations of model alloys show that the B32 phase has a tendency to exist at even larger deviations from stoichiometry than the B2 phase.

It has been shown that these alloys are of the ferromagnetic disordered type (BCC, A2) for Al concentrations up to 23 at % Al independent of heat treatment (5). In alloys with Al content ranging from 0 to 30 at % the iron atoms carry their normal magnetic moment of 2.2 μ_B when they have at least five or more iron atoms as nearest neighbours (6). The 30 at % Al composition is critical for these systems were the average magnetic moment per Fe atom decreases rapidly from 2.0 to 0.7 μ_B ; coupled with this there is a large fall in the lattice parameter associated with a fall in the atomic radii as the disorder to order transition occurs (20 to 30 at % Al).

By disordering the alloy paramagnetic-ferromagnetic transitions can be induced and these transitions could be related to the changes in volume and not only to nearest neighbour effects as is commonly assumed. As an example we can mention that x-ray diffraction of ball milled alloy of composition Fe₆₀Al₄₀ shows an increase of the lattice parameter with milling time (7). This lattice parameter increase has been assumed to produce a variation of the density of states at the Fermi level that would cause the magnetic transition (8).

In this work we use the TBLMTO (Tight Binding Linear

Muffin Tin Orbital) method to study different phases of the Fe-Al phase diagram, corresponding to different concentrations, and performed the calculations for the ordered and disordered structures. For all these cases spin-polarized and unpolarized calculations for different lattice parameters have been made so that we could compare the energy difference between both states, obtain the equilibrium state and be able to calculate the equilibrium lattice parameter.

The previous energy difference between the magnetic and non-magnetic states gives information about how easy the paramagnetic-ferromagnetic transition might occur. The dependence of this energy difference on the lattice parameter and the structure has been calculated to determine the influence on the paramagnetic-ferromagnetic transition.

2. THEORETICAL CALCULATIONS.

The conventional LMTO-ASA method (9) as well as its transformation to a localized representation TB-LMTO are well described in the literature (10). By ASA it is meant Atomic Sphere Approximation where the individual Weigner-Seitz atomic polyhedra are taken to be spheres around each atom. On the other hand TB means Tight Binding indicating that the electronic levels of the free atoms are taken in order to describe the electronic levels of the metal.

Here we give only the relevant computational details. From calculations with this method we can obtain the equilibrium lattice constant, the total energy, the density of states at the Fermi level, the total magnetic moment and the magnetic moment for each of the non-equivalent iron atoms and some other interesting data. We have also calculated the equation of states by fitting the obtained results with the Murnaghan equation of states, in this way we could calculate the theoretical bulk modulus for each structure.

As mentioned in the introduction we have made the calculations for some structures in the Fe-rich part of the phase diagram corresponding to 50 and 25 at % Al concentrations. To perform the calculations we used the following structures: ordered B2 or CsCl, B32 and D03 (see fig. 1), because they are the structures that appear in the Fe rich side of the phase diagram [2, 11]. In order to define them we took into account the description made by F. S. Schmidt and K. Binder (12) which is shown in figure 1.

At the same time calculations for the disordered A2 structure have also been made for each of the mentioned concentrations.

The 16 atom cell can be divided into four sublattices and depending on the arrangements of the atoms in each one we will have a different kind of structure:

a) *B2 structure*: the composition of the b and d sublattices are the same, but differ from the composition of the a and c sublattices, which again are the same. Corresponding to this structure we chose the alloy $\text{Fe}_{50}\text{Al}_{50}$ so that we could compare the obtained results with previous calculations in this alloy [13].

b) *D03 structure*: the compositions of the a and c sublattices are still the same, while the composition on the sublattice b differs from the composition in the sublattice d. In this case we made the calculations for 25 at % Al, that is to say, for Fe_3Al . We chose this composition because it is the stoichiometric composition for this structure. We constructed a 16 atom unit cell to perform the calculations.

c) *B32 phase*: the compositions on sublattices a and b are the same but differ from the compositions on the c and d sublattices.

TABLE I. CALCULATED ELECTRONIC PROPERTIES IN DIFFERENT STRUCTURES. **NSPIN** INDICATES THAT THE CALCULATIONS WERE DONE (2) WITH OR (1) WITHOUT TAKING INTO ACCOUNT THE SPIN POLARIZATION, **A** IS THE LATTICE PARAMETER IN ATOMIC UNITS ($1 \text{ a.u.} = 0.529177 \text{ \AA} = 0.529177 \times 10^{-10} \text{ m}$), **B** IS THE BULK MODULUS (INVERSE OF THE COMPRESSIBILITY) AND $\mu(\text{Fe})$ IS THE MAGNETIC MOMENT PER IRON ATOM. **E_{min}** IS THE TOTAL ENERGY PER VALENCE ELECTRON AT THE EQUILIBRIUM VOLUME ($1 \text{ Ry} = 13.6058 \text{ eV} = 2.1769 \times 10^{-18} \text{ J}$) AND **E_{dif}** IS THE TOTAL ENERGY DIFFERENCE BETWEEN THE UNPOLARIZED AND SPIN-POLARIZED STATES AT THE EQUILIBRIUM VOLUME.

Structure	NSPIN	Fe at %	a (a.u.)	B(Ry/(au) ³)	$\mu(\text{Fe})$ (μ_B)	E _{min} (Ry)	E _{dif} (Ry)
B2*	1	50	10.773	0.015		-275.1254	$7.19 \cdot 10^{-5}$
	2		10.733	0.014	0.64	-275.1255	
A2	1	50	10.824	0.013		-275.1209	$1.27 \cdot 10^{-3}$
	2		10.936	0.012	1.71	-275.1222	
B32	1	50	10.914	0.003		-275.1212	$1.82 \cdot 10^{-3}$
	2		10.825	0.003	1.70	-275.1231	
D03	1	75	10.513	0.017		-300.3843	$1.13 \cdot 10^{-3}$
	2		10.653	0.012	1.80	-300.3854	
A2	1	75	10.532	0.017		-300.3827	$1.5 \cdot 10^{-3}$
	2		10.709	0.013	1.90	-300.3842	

* The lattice parameter for this phase has been doubled so that it could be compared to the other phases.

TABLE II. MAGNETIC MOMENT AND ENVIRONMENT OF THE TWO IRON SITES IN ORDERED Fe_3Al .

	μ (μ_B) experimental ⁽¹³⁾	μ (μ_B) TB-LMTO	Nearest neighbours	Next nearest neighbours
Fe_1 (Fe_2Al)	1.46	1.63	4 Al, 4 Fe	6 Fe
Fe_2 (Fe_2Al)	2.14	2.22	8 Fe	6 Al

Figure 1: Description of B2, D03 and B32 structures that appear in the Fe-rich side of the Fe-Al system.

tices which are equal. The calculations were done for the 50 at % Al alloy and a 4 atom cell was chosen.

d) *Disordered A2 structure*: the average composition of Fe and Al atoms is identical in all four sublattices, the calculations were performed taking this condition into account for all the above mentioned concentrations ($\text{Fe}_{50}\text{Al}_{50}$, Fe_3Al , $\text{Fe}_{13}\text{Al}_3$), in order to compare the energy and magnetic differences between the ordered and disordered alloys.

3. RESULTS AND DISCUSSION

3.1. Ordered structures.

The calculations performed for B2 structure and concentration $\text{Fe}_{50}\text{Al}_{50}$ showed that the spin-polarization lowers the energy and we took this into account in order to calculate the electronic properties of these alloys. The results obtained are in very good agreement with previous calculations [13], for example we deduce the total energy per valence electron difference for the equilibrium volume is $7.19 \cdot 10^{-5}$ Ry and the lattice parameter at the same point is 5.366 a.u. consistent with the experimental results that give a lattice constant of 5.409 a.u., so that the computed values for the equilibrium lattice constant are underestimated by about 1 %. In addition the spin polarized calculation gives a magnetic moment of $0.63 \mu_B$ which is in good agreement with the results obtained in references (13) and (14).

It is worth noting that although we found a magnetic moment of $0.63 \mu_B$ there is no experimental evidence of magnetic moment in ordered $\text{Fe}_{50}\text{Al}_{50}$ alloy. Bogner et al. (14) recently showed that it is due to the high density of defects present in this equiatomic alloy. Anyway, we are mainly interested in showing the general trends of the ordered alloys and the effect of the disorder on them, so we will not take this effect into account. It can, however, be added that the observed behaviour is in good agreement with the effect of the disorder we found in this work.

In the DO3 structure (concentration 25 at %Al) the difference between spin polarized and unpolarized calculations is more obvious than in B2 structure and once again the energy is lower for the spin-polarized case (see table I).

As far as the magnetic moment is concerned we observe that the values we get for the two non-equivalent positions of the iron atoms (see fig.1) are quite close to the experimental ones (see table II).

In the B32 phase we have not found any experimental result that describe the main features of this structure. Once again the spin polarized calculations lower the energy and the energy difference is larger than for the B2 structure and of the same order as in the DO3 structure (see table I).

The magnetic moment per Fe atom at the equilibrium volume is $1.67 \mu_B$, and as we can see it has an intermediate value between the values we obtain for B2 and DO3 structures.

3.2. Disordered structure.

In order to model the disordered structure we built two different unit cells that fulfil the conditions of the A2 phase (12) and took 75 and 50 at % Fe concentrations. In all of them the spin polarized calculations lower the energy (see table I) with respect to the unpolarized calculations. This result is a clear indication that in the studied alloys the disordering of the structure favours the magnetism which

Figure 2: Electronic energy per valence electron versus lattice parameter for spin-polarized calculations in ordered (B2, B32, DO3) and disordered (A2) structure for the following compositions: a) $\text{Fe}_{50}\text{Al}_{50}$, b) Fe_3Al .

is especially pronounced in the case of FeAl (B2), where the magnetic moment increases by more than $1\mu_B$ after disordering (see table I). These theoretical calculation results are in agreement with the experimentally observed increase of the magnetism in deformed or ball-milled alloys [16].

Figure 2 shows the variation of the electronic energy per valence electron with the lattice parameter for spin-polarized calculations in $\text{Fe}_{50}\text{Al}_{50}$ and Fe_3Al and it can be seen that the calculated energy minimum in the disordered structures is above the ones corresponding to the ordered phases (see figure 2) in agreement with the fact that in the calculated range of concentrations the stable structures are the ordered ones. Moreover the energy curve of the B32 structure in the $\text{Fe}_{50}\text{Al}_{50}$ concentration is above the B2 and even above the disordered one, indicating that even if this phase has been recently found at larger amounts of Fe at the equiatomic concentration, this structure is even more metastable than the disordered one.

In addition to the increase of the magnetic moment per iron atom on disordering, figure 2 clearly shows that the lattice parameter for the equilibrium volume is larger for the disordered structure. This result is in agreement with the increase in the lattice parameter with milling time reported in $\text{Fe}_{40}\text{Al}_{60}$ (5).

Hernando et al. (8) have found that an important contribution of these materials comes from changes in the lattice parameter induced in the order-disorder transitions. This contribution is linked to the modifications in the electronic band structure induced by volume changes. However, our results indicate that the disorder has also a large contribution that, depending on the structure, can be even larger than the lattice contribution.

4. CONCLUSIONS.

- The calculations indicate that the disorder enhances the magnetism of the alloy in comparison to the ordered structures. This increase is particularly large in the case of $\text{Fe}_{50}\text{Al}_{50}$ where the magnetic moment per iron atom increases more than $1\mu_B$.

- The calculations indicate that the equilibrium lattice parameter increases with disorder in all the studied compositions.

ACKNOWLEDGEMENTS

This work was undertaken with the aid of a grant from DGES (Project No. PB98-0780-C02-02).

The authors are very much indebted to O. K. Andersen and O. Jepsen for supplying the TB-LMTO code.

REFERENCES

1. H. Reuther, "Structure, properties and applications of thin Fe-Al layers", *Hyp. Int.* 111, 135-140, 1998, see also: W. Justusson, V. F. Zackay, E. R. Morgan, *Trans. ASM* 49, 905, (1957).
2. O. Kubaschewski, *Iron Binary Phase Diagrams*, Springer, Berlin (1986).
3. B. Fultz and Z. Q. Gao, "A Mössbauer spectrometry of hyperfine magnetic fields and ordering in Fe_3Al ", *Phil. Mag.* 67B, 787, (1993).
4. M. Becker and W. Schweike, "B32 order in iron rich Fe-Al alloys", *Scripta Materialia*, 35, 11, 1259-1264, (1996).
5. E. Jartych, J. Zurawicz, D. Oleszak, M. Pekala, J. Sarzynski, Mieczyslan, M. Budzynski. "Magnetic properties and structure of nanocrystalline $\text{Fe}_{70}\text{Al}_{30}$ alloy prepared by mechanosynthesis", *J. Magn. And Mag. Materials* 186, 299-305, 1998 see also: P. R. Swann, W. R. Duff, R. M. Fisher. *Metall. Trans.* 3, 905, (1972).
6. M. J. Besnus, A. Herr, A. J. P. Meyer, "Magnetization of disordered cold-worked Fe-Al alloys up to 51 at % Al", *J. Physics F: Metal Phys.* 5, 2138-2147, (1975).
7. X. Amils, J. Nogués, S. Surinach, M. D. Baró, J. S. Muñoz, "Magnetic properties of Ball-Milled Fe-40Al at. % alloys" *IEE Trans. Magn.*, 34 (4) Part 1, 1129-1131, (1997).
8. A. Hernando, J. M. Rojo, J. C. Gomez-Sal and J. M. Novo, "On the conduction band polarization in metallic systems with a periodic array of localized magnetic moments", *J. App. Physics*, 79, 4815, (1996).
9. H.L.Skriver, *The LMTO Method*, Springer-Verlag, Berlin Heidelberg (1984).
10. O. K. Andersen, O. Jepsen and M. Sob, *Electronic Band Structure and its Applications* (Springer Lecture Notes in Physics 283) ed. M. Yussouff (Berlin: Springer), p. 1
11. A. Taylor and R.M. Jones, "Constitution and magnetic properties of iron-rich iron-aluminium alloys" *J. Phys. Chem, Solids*, 6, 16-37, (1958).
12. F. Schmid and K. Binder, "Modelling order-disorder and magnetic transitions in iron-aluminium alloys", *J. Phys.: Condens. Matter* 4, 3569-3588, (1992).
13. V. Sundararajan, B. R. Sahu, D. G. Kanhere, P. V. Panat and G. P. Das, "Cohesive, electronic and magnetic properties of the transition metal aluminides FeAl, CoAl and NiAl", *J. Phys.: Condens. Matter* 7, 6019-6034, (1995).
14. J. Bogner, W. Steiner, M. Rissner, P. Mohn, P. Blaha, K. Schwarz, R. Krachler, H. Ipser, B. Sepiol, "Magnetic order and defect structure of $\text{Fe}_x\text{Al}_{1-x}$ alloys around $x = 0.5$: An experimental and theoretical study", *Phys. Rev. B*, 58, 22, 14922-14933, (1998).
15. R. Nathans, H. T. Pigott and C. G.Shull, "The magnetic structure of Fe_3Al ", *J. Phys. Solids*, 6, 38-42, (1958).
16. K. Oki, M. Hasaka, T. Eguchi, "Process of Order-Disorder Transformations in Iron-Aluminum Alloys", *Jap. J. Appl. Phys.*, 12, 10, (1973).