

### Evaluation of point defect concentrations in B2-FeAl intermetallic compound

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Thermal defects are studied for three compositions (49, 50 and 52 at.%Fe) of the intermetallic compound FeAl with B2 structure. Magnetic measurements are used to determine the thermal defect concentrations. These concentrations are determined from fitting the experimental curves of magnetic susceptibility, obtained during an isochronal annealing after a quench. Next we have evaluated theoretically the concentrations of different point defects that exist in this compound. The used model is based in the Bragg-Williams approximation assuming the nearest-neighbour interaction. The calculated concentrations describe well the experimental values.

## I. INTRODUCTION

Intermetallic compounds or ordered alloys have recently attracted much attention as structural materials for high temperature applications. A knowledge of thermal defect formation and of their diffusion behaviour, which is closely linked to the thermal defects, is necessary for the use of these materials in technological applications.

Vacancy formation in alloys has been studied experimentally and theoretically over the last fifty years. While the vacancy concentration in metals at melting points is of order 0.05%, in alloys it can range up to about 10% [1]. It has been found that in some ordered AB alloys vacancies form mainly on one sublattice, and that the other sublattice contains antistructure atoms [1-3].

In the literature, various models and theories have been advanced to determine defect concentrations. In the present study, isochronal magnetic susceptibility measurements  $\chi(T)$  have been carried out to investigate thermal vacancy and antistructure atoms concentrations in the B2 FeAl. We have also evaluated these concentrations with a model based on the Bragg-Williams approximation assuming the nearest neighbour band interaction. The experimental and theoretical results for different compositions were compared.

## II. EXPERIMENTAL EVALUATION OF POINT DEFECT CONCENTRATIONS FROM MAGNETIC MEASUREMENTS

### A. RELATION BETWEEN THE DEFECT CONCENTRATIONS AND MAGNETIC SUSCEPTIBILITY

The ordered compounds FeAl, with B2 (CsCl-type) structure, are composed of two interpenetrating simple cubic with iron and aluminium sublattices. In this

intermetallic compound FeAl various types of defects exist. It was shown [4,5] that, on the iron rich side of

stoichiometry, iron substitutes as antistructure atoms on the aluminium lattice. Whereas, in aluminium-rich compounds, structural vacancies are formed on the iron lattice. In the following,  $\text{Fe}_{\text{Al}}$  and  $\text{V}_{\text{Fe}}$  represent iron antistructure atoms and vacancies on the iron sublattices, respectively. These defects can be retained in the sample by quenching from high temperatures. It was argued that the predominant thermal defects are  $\text{Fe}_{\text{Al}}$  and  $\text{V}_{\text{Fe}}$  [6]; the aluminium antistructures  $\text{Al}_{\text{Fe}}$  and aluminium vacancies  $\text{V}_{\text{Al}}$  also exist, but in a small amount [7-10].

The intermetallic compounds FeAl are reported to be paramagnetic, at high temperatures, in a large range of compositions around the equiatomic composition. Magnetic susceptibility measurements have revealed a Curie-Weiss law behaviour [11], so the total magnetic susceptibility versus temperature  $T$  can be written as:

$$\chi(T) = \chi^0 [1 + \delta T^2] + \frac{C}{T - \theta} \quad (1)$$

where  $\chi^0$  is the expression of Pauli paramagnetism, and  $\delta$  is related to the detailed shape of the density of states. The Curie temperature  $\theta$  reflects the interaction of the magnetic moments with their surrounding and depends on the iron antistructure atoms concentration  $[\text{Fe}_{\text{Al}}]$ . The measured Curie constant  $C$  is correlated with  $[\text{Fe}_{\text{Al}}]$ :

$$C = \frac{N[\text{Fe}_{\text{Al}}] \mu_{\text{eff}}^2}{3k_B} \quad (2)$$

$N$  and  $k_B$  are the Avogadro number and the Boltzmann constant, respectively. The effective magnetic moment  $\mu_{\text{eff}}$ , associated to each  $\text{Fe}_{\text{Al}}$  has been experimentally determined as about  $7.8 \mu_B$  by Caskey et al. [11].

In this intermetallic compound, a widely used model assumes triple defects as the dominant thermal defect type. So from structure symmetry, it follows that each iron antistructure atoms formed on aluminium sublattice must be accompanied by two iron vacancies on the iron

sublattice. Then the thermal concentration  $[V_{Fe}]$  and  $[Fe_{Al}]$  may be calculated from:

$$[V_{Fe}] = 2[Fe_{Al}] = \frac{6Ck_B}{N\mu_{eff}^2} \quad (3)$$

## B. EXPERIMENTAL TECHNIQUES

The FeAl alloys were prepared by melting aluminium of 99.999% purity and iron of 99.995% purity in a high frequency induction furnace under ultra pure argon atmosphere (N60). For magnetic measurements, small cylindrical specimens of 4 mm in diameter and about 9 mm in thickness were cut by spark erosion. To produce non-equilibrium point defects, the sample was first heated at 1323K for one hour then annealed during four hours at 1273K, thereafter it was quenched into iced water. These thermal treatments were performed in an inert atmosphere (purified argon) to avoid the oxidation of the sample as much as possible. The reproducibility of results was found to be quite good after the first heat treatment at 1050°C used in these experiments.

## C. RESULTS

The temperature dependence of the susceptibility for two heating runs, of the same sample  $Fe_{50}Al_{50}$ , are presented in figure 1.

The first one was performed up to 923K after a quench. Then just after slowly cooling the sample in situ to room temperature, the second heating run was done in the same conditions.

At low annealing temperatures a pronounced difference between the two curves  $\chi(T)$  is observed, because the susceptibility is significantly higher after the quench. Above about 773°C both curves are identical. The decrease of  $\chi(T)$  demonstrates that the concentration of the thermal iron antistructure atoms at the beginning of the first heating run, after quenching, is larger than that obtained at the end. Since the  $Fe_{Al}$  atoms is sensitively detected by magnetic susceptibility, the step appearing at 683K probably reflects the annealing-out of iron antistructure atoms frozen by the quenching process. Below this value the temperature dependence of magnetic susceptibility is determined by  $\frac{1}{T}$  behaviour of the Curie

term. Therefore, it is possible to extract the value of Curie constant  $C$  from fitting the experimental data of figure 1 by equation (1). So the concentration of eliminated

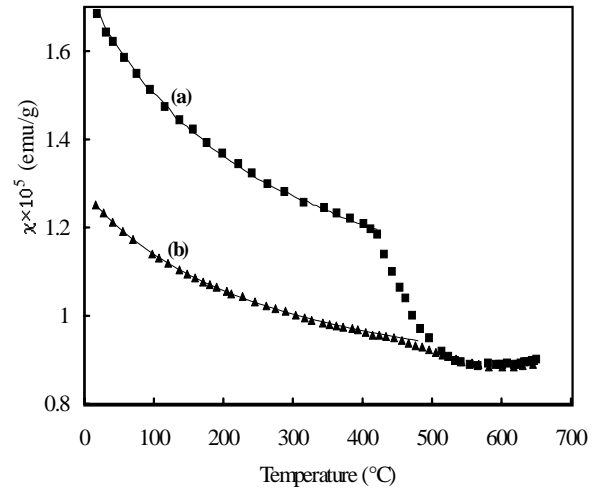
antistructure atoms  $[Fe_{Al}]$  and vacancies  $[V_{Fe}]$  can be determined by the following formula:

$$[V_{Fe}] = 2[Fe_{Al}] = \frac{6k_B(C_1 - C_2)}{N\mu_{eff}^2} \quad (4)$$

where  $C_1$  and  $C_2$  are the Curie constants corresponding to the first and the second heating run, respectively. Thus, the obtained values of  $[Fe_{Al}]$  and  $[V_{Fe}]$  are listed in table 1.

The obtained concentrations  $[Fe_{Al}]$  atoms are much smaller than those found by Haberkern [12]. This difference comes essentially from two factors: first, in our result the contribution of structural defects is subtracted and, second, it may be due essentially to the value of the effective magnetic moment used in equation (4). On the other hand, Vogl and Sepiol [13,14] estimated a Fe antisite atoms concentration of 1.5% at  $T=1338K$  in  $Fe_{50.5}Al_{49.5}$  from the Broadening of Mössbauer lines.

Paris et al. [7] determined the vacancy concentration of FeAl alloys, quenched from 1273K, by a dilatometric technique. They obtained a value of  $1,85 \times 10^{-2}$  for  $Fe_{50.5}Al_{49.5}$  and  $2.3 \times 10^{-2}$  for  $Fe_{49}Al_{51}$ . Except for the later value these data are comparable to our results.



**FIG 1:** Magnetic susceptibility vs. temperature for first (a) and second (b) heating with  $\beta=2^\circ C/mn$ ; the curves ( $\blacksquare, \blacktriangle$ ) are fitted in the low temperature region by Curie law (equation 1)

at.%Fe	$(C_1 - C_2) \times 10^3 (\text{emu K mole}^{-1})$	$[Fe_{Al}] \times 10^2$	$[V_{Fe}] \times 10^2$
49	65.79	0.86	1.72
50	67.09	0.88	1.76
52	70.39	0.92	1.85

**Table 1.** Concentrations of eliminated iron antistructure atoms  $Fe_{Al}$  and vacancies  $V_{Fe}$  in FeAl for 49, 50 and 52at.%Fe.

### III. THEORETICAL EVALUATION OF POINT DEFECT CONCENTRATIONS

To explain our experimental results, we tried to evaluate theoretically the concentration of different defect types on both sublattices by means of a simple model based on the Bragg-Williams approximation.

#### A. BRAGG-WILLIAMS MODEL.

If a random distribution of point defects over the crystal lattice sites is assumed, simple statistical models of the Bragg-Williams type [8-15], the ab-initio statistical type [10] or the Wagner-Scottky type [9] can be applied to calculate the equilibrium concentrations of the defects for all compositions within the homogeneity range.

The Bragg-Williams approximation resides in the following assumptions. First, only the nearest neighbour pairwise interactions contribute to the binding energy. Secondly, the bond energies of identical atoms are supposed to be those for the pure constituents and are independent of the alloy composition and the vacancy concentration. Thirdly, the configurational entropy for a random solid solution is used instead of the entropy for the ordering alloy and the defect formation entropies are omitted.

Since the AB alloy is assumed to consist of  $\alpha$  and  $\beta$  sites occupied by  $N_A$  and  $N_B$  atoms, as well as the vacancies  $V$ , free energy of system can be expressed by:

$$F = -n_{AA}E_{AA} - n_{BB}E_{BB} - n_{AB}E_{AB} - n_{AV}E_{AV} - n_{BV}E_{BV} - k_B T \ln W$$

Where  $n_{IJ}$  is the number of pairs of I and J atoms (or atom-vacancy),  $H_{IJ}$  is the corresponding bond energy and  $k_B T \ln W$  is the configurational entropy. This entropy can be written as:

$$S = k_B \ln \frac{N_S!}{N_{V\alpha}! N_{A\alpha}! N_{B\alpha}!} \times \frac{N_S!}{N_{V\beta}! N_{A\beta}! N_{B\beta}!}$$

where  $2N_S$  is the total number of lattice sites and  $N_{PQ}$  is the number of species P (A, B or V) on site Q ( $\alpha$  or  $\beta$ ). The various defects concentrations are defined as  $[P_Q] = \frac{N_{PQ}}{2N_S}$ .

We then have:

$$n_{AA} = ZN_S[A_\alpha][A_\beta]$$

$$n_{BB} = ZN_S[B_\alpha][B_\beta]$$

$$n_{AB} = ZN_S([A_\alpha][B_\beta] + [A_\beta][B_\alpha])$$

$$n_{AV} = ZN_S([A_\alpha][V_\beta] + [A_\beta][V_\alpha])$$

$$n_{BV} = ZN_S([B_\alpha][V_\beta] + [B_\beta][V_\alpha])$$

where  $Z$  is the coordination number. The defect concentrations can be obtained by minimizing the free

energy of the system by the "Lagrange multiplier" method. If we assume that the defect concentrations are much smaller than  $[A_\alpha]$  and  $[B_\beta]$ , we have:

$$[A_\beta] = \exp\left[\frac{-Z}{K_B T}(E_{AB} - E_{AA}) - \frac{2t}{K_B T}\right]$$

$$[B_\alpha] = \exp\left[\frac{-Z}{K_B T}(E_{AB} - E_{BB}) + \frac{2t}{K_B T}\right]$$

$$[V_\alpha] = \exp\left[\frac{-Z}{K_B T}\left(\frac{E_{AB}}{2} - E_{BV}\right) + \frac{t}{K_B T}\right]$$

$$[V_\beta] = \exp\left[\frac{-Z}{K_B T}\left(\frac{E_{AB}}{2} - E_{AV}\right) - \frac{t}{K_B T}\right]$$

With:

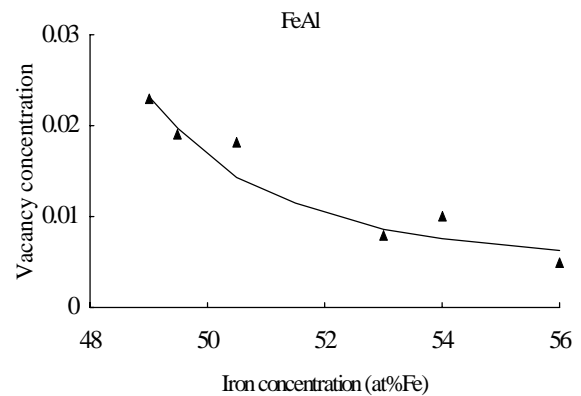
$$2[A_\beta] - 2[B_\alpha] + [V_\beta] - [V_\alpha] = 2s$$

where the parameter  $t$  depends on the Lagrange multipliers and  $s = \frac{N_A - N_B}{N_A + N_B}$  is the deviation from

stoichiometry. These equation can be readily solved by iteration. The value of  $E_{AB}$  is determined from the experimental formation heat of the alloy [6]. The bond energies  $E_{AA}$  and  $E_{BB}$  were estimated from the cohesive energy of pure metals [16]. The energies  $E_{AV}$  and  $E_{BV}$  are determined by fitting the calculated concentrations of vacancies with experimental data.

#### B. APPLICATION TO THE FeAl COMPOUNDS

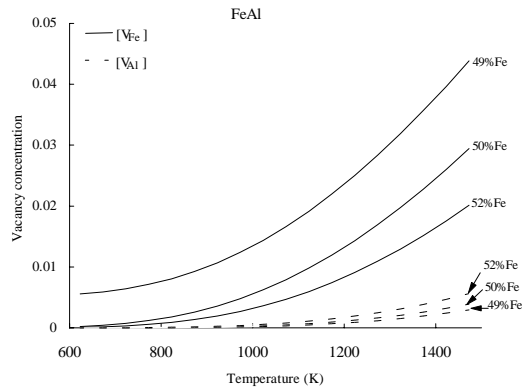
The composition dependence of the vacancy concentration in FeAl at 1273 K determined by means of lattice parameter, length and pycnometric density measurements [7,17] is shown in figure 2(a).



**FIG 2(a):** Composition dependence of vacancy concentration in FeAl

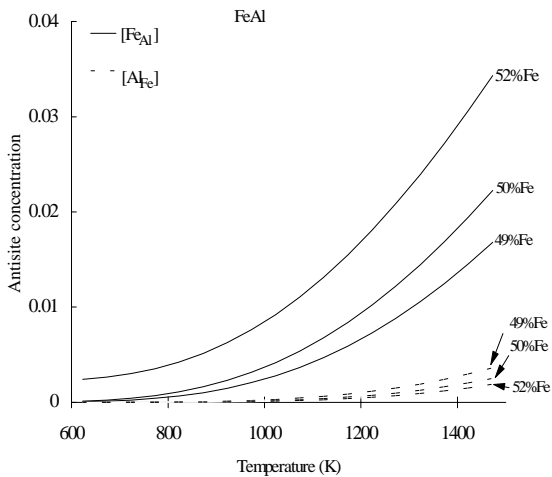
Theoretical concentrations curve were fitted through the experimental data, and the best agreement was obtained

with the energies:  $E_{\text{FeFe}}=0.78\text{eV}$ ,  $E_{\text{AlAl}}=0.54\text{eV}$ ,  
 $E_{\text{FeAl}}=0.722\text{eV}$ ,  $E_{\text{FeV}}=0.34\text{eV}$ ,  $E_{\text{AlV}}=0.27\text{eV}$ .



**FIG 2(b):** Temperature dependence of vacancy concentration in FeAl

In figure 2(b), we have shown the temperature dependence of the iron and aluminium vacancies  $[V_{\text{Fe}}]$  and  $[V_{\text{Al}}]$  respectively, for different compositions. The calculated concentrations  $[V_{\text{Fe}}]$  were found to be important and the concentrations  $[V_{\text{Al}}]$  were not equal to zero.



**FIG 2(c):** Temperature dependence of antisite atoms concentration in FeAl

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In figure 2(c), the theoretical variation of iron and aluminium antisite atoms  $[\text{Fe}_{\text{Al}}]$  and  $[\text{Al}_{\text{Fe}}]$ , respectively, with temperature for different compositions were represented. It may be noticed that, for a given temperature, when the iron content increases,  $[\text{Fe}_{\text{Al}}]$  increases. On the other hand, the  $[\text{Al}_{\text{Fe}}]$  decreases with increasing the iron content.

#### IV. CONCLUSION

In the present paper, isothermal magnetic susceptibility measurements  $\chi(T)$  have been carried out to investigate thermal vacancy and antisite atoms concentrations in the B2-FeAl for 49, 50 and 52 at.%Fe compositions. The observed step in  $\chi(T)$  at about 683K reflects the annealing-out of iron antisite atoms frozen by the quenching process from 1273K. Below 683K, the concentration of the eliminated defect has been determined from fitting the experimental  $\chi(T)$  curves by the Curie Weiss law. The concentrations of vacancies were found to be slightly different than those obtained by usually used techniques (RX, Dilatometric, Density...). So in this latter technics, the presence of complex defects as dislocations, loops and voids can falsify the measurements. But the differential method which we have developed minimize the influence of these parameters.

To explain our experimental results, we have also evaluated the concentrations of these defects with one model based in the Bragg-Williams approximation assuming the nearest neighbour interaction.

For the comparison of theoretical and experimental results, we should take into account the presence of structural defects  $[\text{Fe}_{\text{Al}}]_{\text{S}}$  and  $[V_{\text{Fe}}]_{\text{S}}$ , because our used method allow to determine only the thermal defect concentrations. So, the concentration of these defects are  $[\text{Fe}_{\text{Al}}]_{\text{S}} = 2 \times 10^{-2}$  for 52at.%Fe and  $[V_{\text{Fe}}]_{\text{S}} = 1 \times 10^{-2}$  for 49at.%Fe. If we add these values to those reported in the table 1, our experimental and theoretical results are in good agreement.

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