

# Magnetic measurements of point defect elimination in quenched CoGa and FeAl intermetallic compounds

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## Abstract

The elimination of antistructure atoms via vacancies in CoGa and FeAl ordered with the B2 (CsCl-type) structure has been investigated using magnetic measurements. During an annealing out of quenched-in antistructure atoms, the magnetic susceptibility must decrease. This behaviour is observed in CoGa alloys, whereas in the case of FeAl alloys the annealing out of quenched-in defects starts by a slight increase followed by a strong decrease in susceptibility. These different behaviours are attributed to the different concentrations existing for the two kinds of vacancies which are present in both compounds. These concentrations are calculated in the Bragg–Williams approximation.

## 1. Introduction

The intermetallic compounds AB with B2 (CsCl-type) structure are composed of two interpenetrating simple cubic  $\alpha$  and  $\beta$  sublattices.

The ordered compounds AB, where A is the transition metal occupying the sublattice  $\alpha$ , such as FeAl, CoAl, NiAl and CoGa are reported to be paramagnetic, at high temperatures, in a large range of concentrations around the equiatomic composition. Several experimental studies have shown that for concentrations of transition atoms beyond 0.5, the transition metal atoms in excess occupy the antisite positions  $\beta$  on the aluminium or gallium sublattice and form magnetic clusters with their neighbours [1–4], while for understoichiometric compounds vacancies  $V_\alpha$  are formed.

In the case of CoGa and FeAl compounds, it was shown [2–4] that the magnetic susceptibility can be described by a Curie–Weiss term, proportional to the number of antistructure atoms plus a term depending on temperature.

In a previous paper concerning CoGa [5] we showed that the application of measured magnetic susceptibility changes *vs.* time, during annealing treatments after a quenching process, allows us to investigate the mobility of atomic defects. In the following, we compare the results of isothermal annealing experiments on the CoGa and FeAl intermetallic compounds.

In order to clarify the defect elimination kinetics in FeAl alloys, we evaluated in this compound the different vacancy concentrations  $C_{V_\alpha}$  and  $C_{V_\beta}$  in the Bragg–Williams approximation model.

## 2. Experimental procedure

The CoGa and the FeAl alloys were prepared from weighed amounts of cobalt, iron, gallium and aluminium metals with a high frequency induction furnace. A high purity argon (N60) atmosphere was used to avoid oxidation. After cooling to room temperature, small cylinders of approximately 4 mm diameter and approximately 8 mm thickness, suitable for the magnetic measurements, were cut by spark erosion. The heat treatments, in a quench apparatus under a protective atmosphere of argon, were carried out as follows. First, the two compounds spent 1 h each at 1000 °C for CoGa and at 1050 °C for FeAl. This was immediately followed by annealing which lasted 4 h at 900 °C for CoGa and 1000 °C for FeAl. The samples were then quenched in iced water by gravity.

The magnetic susceptibility measurements *vs.* time, during isothermal annealing at temperatures where defects are mobile, were performed with a microbalance by the Faraday method.

### 3. Experimental results

The magnetic susceptibility is connected with the antistructure atom concentration in the following way: if  $\chi(t)$  is the susceptibility at the annealing time  $t$ , and  $\chi_0$  and  $\chi_\infty$  are the initial and final values corresponding to isothermal annealing, in our previous paper [5] we showed that the expression

$$F(t) = \frac{\chi(t) - \chi_\infty}{\chi_0 - \chi_\infty}$$

is directly proportional to the atomic fraction of antistructure atoms. In these compounds it has been shown [2] that a relationship exists between the vacancy and antistructure atom concentrations; therefore  $F(t)$  is proportional to the vacancy concentration. Thus the mobility of vacancies can be determined if the migration process of antistructure atoms is realized via a vacancy mechanism as has been argued by several researchers [6, 7].

#### 3.1. Co-Ga

As an example, the behaviour of the normalized function  $F$  vs. time at 570 °C in a  $\text{Co}_{50}\text{Ga}_{50}$  specimen is shown in Fig. 1. The observed decrease reflects the elimination of the excess antistructure atoms frozen by the quenching process.

#### 3.2. Fe-Al

In the case of FeAl, the shape of the isothermal curves  $F(t)$  is different from that previously observed for CoGa (Figs. 2 and 3). The curves exhibit two parts. In the first part  $F(t)$  increases and the height of this variation becomes larger with iron content. In the second part  $F(t)$  decreases.

### 4. Discussion

We have seen that the essential difference in the isothermal curves between CoGa and FeAl is the

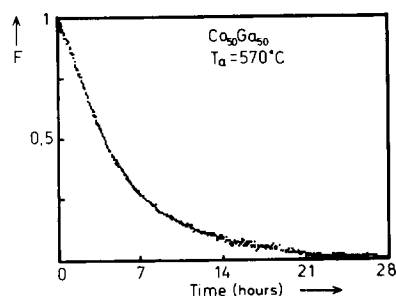


Fig. 1. Isothermal annealing curve  $F(t)$  for  $\text{Co}_{50}\text{Ga}_{50}$  at  $T_a = 570$  °C.

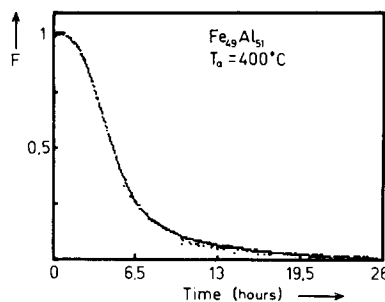


Fig. 2. Isothermal annealing curve  $F(t)$  for FeAl (49 at.% Fe) at  $T_a = 400$  °C.

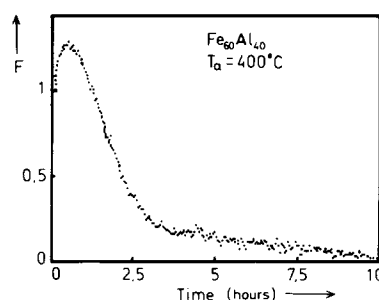


Fig. 3. Isothermal annealing curve  $F(t)$  for FeAl (60 at.% Fe) at  $T_a = 400$  °C.

increase in the magnetic susceptibility in the beginning of the annealing process in the case of FeAl compounds.

To discuss this point in terms of vacancies responsible for iron atom transport to antisites, we present the calculated vacancy concentrations on both sublattices of FeAl evaluated by a model based on the Bragg-Williams approximation with nearest-neighbour interaction between atoms and also between an atom and a vacancy.

We calculated the concentration values in the same way as for CoGa [8, 9].

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

$$\begin{aligned} \mathcal{F} = & -n_{AA}H_{AA} - n_{BB}H_{BB} - n_{AB}H_{AB} - n_{AV}H_{AV} \\ & - n_{BV}H_{BV} - kT \ln W \end{aligned}$$

where  $n_{IJ}$  is the number of pairs of  $I$  and  $J$  atoms (or atom-vacancy),  $H_{IJ}$  is the corresponding bond energy and  $k \ln W$  the configurational entropy.

The various defect concentrations are defined as  $X_{PQ} = N_{PQ}/2N_S$ , where  $N_{PQ}$  is the number of species  $P$  (A, B or V) on site  $Q$  ( $\alpha$  or  $\beta$ ) and  $2N_S$  is the total number of lattice sites. We then have

$$n_{AA} = ZN_S X_{A\alpha} X_{A\beta}, \quad n_{BB} = ZN_S X_{B\alpha} X_{B\beta}$$

$$n_{AB} = ZN_S (X_{A\alpha} X_{B\beta} + X_{A\beta} X_{B\alpha})$$

$$n_{AV} = ZN_S(X_{A\alpha}X_{V\beta} + X_{A\beta}X_{V\alpha})$$

$$n_{BV} = ZN_S(X_{B\alpha}X_{V\beta} + X_{B\beta}X_{V\alpha})$$

where  $Z$  is the coordination number.

The defect concentrations can be obtained by minimizing the free energy of the system. The bond energies  $H_{AA}$  and  $H_{BB}$  were estimated from the cohesive energy of pure metals [10]. The value of  $H_{AB}$  is determined from the experimental heat of formation of the alloy [11]. The energies  $H_{AV}$  and  $H_{BV}$  are determined by fitting the calculated concentration of vacancies with experimental data obtained from density [12] and dilatometric [13] measurements.

So we obtain for FeAl ( $A \equiv \text{Fe}$ ,  $B \equiv \text{Al}$ )  $H_{AA} = 0.78$  eV,  $H_{BB} = 0.54$  eV,  $H_{AB} = 0.722$  eV,  $H_{AV} = 0.34$  eV and  $H_{BV} = 0.27$  eV.

The temperature dependence of  $V_\alpha$  and  $V_\beta$  concentrations is shown, as a function of composition, for FeAl in Fig. 4(a) and for CoGa in Fig. 4(b) (with  $H_{AA} = 0.70$  eV,  $H_{BB} = 0.40$  eV,  $H_{AB} = 0.62$  eV,  $H_{AV} = 0.30$  eV and  $H_{BV} = 0.22$  eV ( $A \equiv \text{Co}$ ,  $B \equiv \text{Ga}$ ) [8, 9]).

It may be noticed that, for a given temperature, when the iron or cobalt content increases, the vacancy concentration  $C_{V_\alpha}$  decreases whereas  $C_{V_\beta}$  increases.

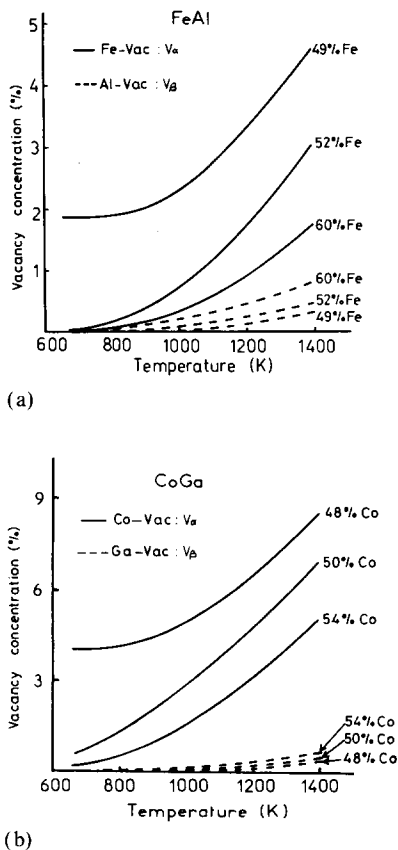


Fig. 4. Temperature dependence of vacancy concentrations for (a) FeAl and (b) CoGa.

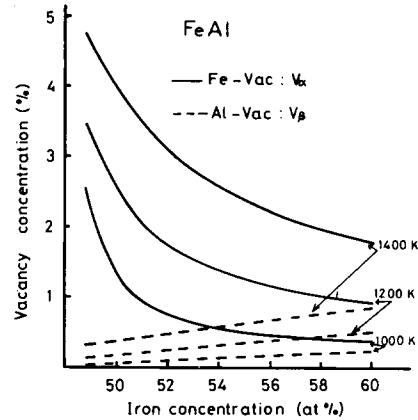


Fig. 5. Composition dependence of vacancy concentration for FeAl.

In our experimental conditions, in the case of CoGa the ratio  $C_{V_\alpha}/C_{V_\beta}$  is equal to 23 at 900 °C. For FeAl (50 at.% Fe) at 1000 °C, this ratio is lower; its value is 13. On the contrary, there is an enormous change in  $C_{V_\alpha}/C_{V_\beta}$  with the composition of FeAl (Fig. 5); this could explain our experimental results. For FeAl (60 at.% Fe) this ratio  $C_{V_\alpha}/C_{V_\beta}$  is about 2 (at 1000 °C) and as the vacancies  $V_\beta$  can also be trapped in the specimen by quenching [14] we can assume that in this case  $C_{V_\beta}$  cannot be neglected with regard to  $C_{V_\alpha}$ .

So we can suppose that  $\text{Fe}_\alpha$  atoms have a non-negligible probability of finding  $V_\beta$  vacancies in the nearest-neighbour region after quenching. Then the following reaction appears during the annealing:



The formation of this kind of antistructure atom  $\text{Fe}_\beta$  leads to the increase in magnetic susceptibility observed at the beginning of the annealing process. This is seen in the first part of the curve  $F(t)$  vs. time in Fig. 3. Moreover, as the iron content increases further, this effect becomes more marked, which is in accordance with our interpretation.

## References

- 1 E. Wachtel, V. Linse and V. Gerold, *J. Phys. Chem. Solids*, **34** (1973) 1461.
- 2 D. Berner, G. Geibel, V. Gerold and E. Wachtel, *J. Phys. Chem. Solids*, **36** (1975) 221.
- 3 M. W. Meisel, W. S. Zhou, J. R. Owers-Bradley, Y. Ochiai, J. O. Brittain and W. P. Halperin, *J. Phys. F*, **12** (1982) 317.
- 4 G. R. Caskey, J. M. Franz and D. J. Sellmyer, *J. Phys. Chem. Solids*, **34** (1973) 1179.
- 5 O. Sassi, J. Aride, G. Moya and A. Berrada, *J. Chem. Phys.*, **88** (1991) 2191.
- 6 H. Bakker, *Mater. Sci. Forum*, **15-18** (1987) 1155.
- 7 N. A. Stolwijk, M. Van Gend and H. Bakker, *Philos. Mag. A*, **42** (1980) 783.

- 8 F. Nakamura and K. Furukawa, *Mater. Sci. Forum*, 15–18 (1987) 1317.
- 9 F. Nakamura and K. Takamura, in J. Takamura, M. Doyama and M. Kiritani (eds.), *Point Defects and Interactions in Metals*, University of Tokyo Press, Tokyo, 1982, p. 627.
- 9 S. Benlemlih, *Thèse 3ème Cycle*, Rabat 1987.
- 10 M. Doyama and J. S. Koehler, *Acta Metall.*, 24 (1976) 871.
- 11 Y. A. Chang and J. P. Neumann, *Prog. Solid State Chem.*, 14 (1982) 221.
- 12 J. P. Rivière, *Mater. Res. Bull.*, 12 (1977) 955.
- 13 K. Ho and R. A. Dodd, *Scr. Metall.*, 12 (1978) 1055.
- 14 D. Paris and P. Lesbats, *J. Nucl. Mater.*, 69–70 (1978) 628.