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Ordering effects in the Fe-Al system

R. Kuentzler
Laboratoire de Magnétisme et de Structure Electronique des Solides (*)
Institut de Physique, 67084 Strasbourg, France

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Résumé. — Un ensemble de mesures de chaleurs spécifiques à basse température a été effectué sur des alliages désordonnés Fe$_{1-c}$Al$_c$ dans le domaine de concentration $0.10 \leq c \leq 0.50$. On observe une différence radicale entre la chaleur spécifique « électronique » d’échantillons désordonnés et celle d’échantillons ordonnés. Cette constatation, jointe aux connaissances récentes sur le diagramme de phase, conduit à reconsidérer l’interprétation des propriétés physiques des alliages de FeAl.

Une analyse qualitative des propriétés physiques, limitées à la chaleur spécifique, la susceptibilité magnétique et l’aimantation montre que ces propriétés dépendent fortement de l’état du système à une concentration donnée. Nous avons considéré l’état recuit (ordonné), trempé (partiellement ordonné) et écroui (désordonné) pour déterminer l’effet d’ordre sur les propriétés physiques.

Abstract. — Low temperature specific heat measurements have been performed on disordered Fe$_{1-c}$Al$_c$ samples in the concentration range $0.10 \leq c \leq 0.50$. A drastic difference between the « electronic » specific heat of the disordered and ordered samples is observed. This observation joined to the recent knowledge on the particularly complex phase diagram led to reconsider the results obtained about the physical properties of the FeAl alloys.

A qualitative review of some physical properties, namely the specific heat, magnetic susceptibility and magnetization, show that these properties depend strongly upon the state of the system at a given concentration. The annealed (ordered), quenched (partially ordered) and cold-worked (disordered) states of samples are used to investigate the ordering effects.

1. Introduction.

The phase diagram of the Fe-Al system has long been controversial [1-23]; however there is now a qualitative agreement between different studies on the nature of the phases and on the order-disorder transitions in the Fe rich regions of the diagram [17-31]. In fact this diagram is very complex and shows some very unusual features in metallurgical systems [15-17]. For instance Allen and Cahn [24] have shown that both the incoherent stable equilibrium and the coherent metastable phase diagrams are important and that either diagram by itself is not sufficient to understand the behaviour of the Fe-Al system. Each of these diagrams shows a tricritical point and has two lines of second order transitions: one between the disordered phase and the ordered FeAl phase which ends at a miscibility gap between the same phases and another between the FeAl and the Fe$_3$Al phases.

These features imply that several different mechanisms of phase transformations may exist: for example Allen and Cahn have shown that a disordered alloy held within the miscibility gap may first transform to a completely ordered state before the phase separation occurs; this is a consequence of the metastable continuous ordering reaction that occurs in this system [24-26]. Therefore the understanding of the physical properties as a function of temperature of the Fe$_{1-c}$Al$_c$ alloys, may become very difficult especially in the concentration range $0.21 \leq c \leq 0.26$ Al where an initially single ordered structure Fe$_3$Al may show phase separation (see sect. 2). Moreover magnetic ordering makes the situation even more complicated. According to the magnetic studies [40, 41], the magnetic phase diagram for $0 \leq c \leq 0.5$ shows paramagnetic, ferromagnetic and spin-glass regimes; the corresponding transition lines meet at a multicritical point near $c = 0.30$ [40]. The magnetic behaviour depends strongly upon the phase state and upon the atomic arrangement i.e. ordered, partially ordered or disordered structures [2, 32, 33, 36, 38, 39, 42, 49, 19].

(*) L.A. 306 du C.N.R.S.
Our aim in this paper is twofold: i) to present new specific heat data in the disordered phase which, in comparison with the previously known results, show strong ordering effects; ii) to reconsider some of the magnetic and calorimetric properties in order to show that both properties depend strongly upon the sample preparation i.e. upon the state of the sample (ordered, disordered, two phases...). In view of the controversies which exist, at the present stage, in the literature, an exhaustive and detailed discussion of all properties of the Fe-Al is of course outside the scope of this paper.

The specific heat has been reported by Beck et al. [48, 49] for the stoichiometric ordered Fe₃Al and FeAl samples and for the quenched samples for 0 ≤ c ≤ 0.5. However quenched samples are only partially disordered; almost completely disordered states can only be obtained by cold-working [2, 19] or by splat cooling. We have therefore investigated the low temperature specific heat of cold-worked samples in the concentration range 0.10 ≤ c ≤ 0.50. We have also measured splat-quenched samples for c = 0.25 and c = 0.48. The outline of the paper is as follows: in section 2 we recall the main features of the phase diagram; in section 3 we briefly discuss some striking features which emerged from the magnetic study in relation with the phase diagram; in section 4 we describe the sample preparation method and the experimental procedure used; in section 5 we report our specific heat results and discuss all specific heat data which are available on this system. Finally in section 6 we briefly discuss some physical properties in the different states of atomic order.

2. Phase diagram.

The phase diagram of the Fe-Al system in the Al concentration range 0 ≤ c ≤ 0.30 has recently been studied by means of several complementary experimental techniques [16-25, 27, 28]; there is now qualitative agreement between the diagrams resulting from the previous investigations except for some systematic shift in concentration. The equilibrium diagram obtained by Köster et al. [23] is shown in figure 2. For a detailed discussion, about the nature of the transitions and the different possible mechanisms of the phase transformations, the reader is referred to the paper by Allen and Cahn [24, 27]. Let us now briefly summarize the main features (see also sect. 1).

1. Below 20 at % Al, there is a continuous solid solution α.
2. The lines of transition between the disordered phase α and the ordered FeAl phase and between the ordered Fe₃Al and FeAl structure are lines of second order transition.
3. The first line ends at a tricritical point i.e. below this point the transitions between the same phases are first order. The second line ends at two-phase regions.
4. In the vicinity of c = 0.25, the diagram is quite complex there are two phase regions α + FeAl and α + Fe₃Al in addition to the single phases of disordered α, ordered FeAl and ordered Fe₃Al.
5. There are two bcc based superstructures namely FeAl (B₂ type, a = 2.907 4 Å) and Fe₃Al (DO₃ type, a = 2.896 2 Å). The basic bcc lattice may be viewed as composed of two interpenetrating simple cubic lattices called I and II respectively. FeAl has a CsCl type structure. For the stoichiometric Fe₃Al alloy, sublattice I is occupied by Fe and Al atoms in a NaCl type structure. In off-stoichiometric alloys in the range 0.2 ≤ c ≤ 0.5 the Al atoms occupy preferentially sublattice II while sublattice I is mainly occupied by Fe atoms [2, 29, 33].
6. In the concentration range 0.3 ≤ c ≤ 0.5 the alloys form the ordered B2 or CsCl structure [17]. Recently it has been shown [23] that this homogeneous region can be divided into four fields, in which the dependence upon concentration and temperature of a physical property has a specific form.

7. At high temperature the disordered state which exists below 20 at % Al is expected up to 52 at % Al [2, 33, 38]. Many authors [2, 23, 46] consider that the critical temperature for the order-disorder transition occurs at about 1200 °C which is very close to the melting point.

There have been several attempts to compute the phase diagram of the Fe-Al system [65, 66] as noticed in the introduction, but a qualitative agreement with the experimental diagram is obtained only when the magnetic interactions are included [67, 68]. The competition between chemical and magnetic interactions which takes place in this system has also been shown in other systems like Mn-Pt, Cr-Pt [56, 57].

3. Magnetic properties.

The magnetic properties of the iron rich region of the Fe-Al system have been studied in detail [2, 28, 32-42, 19]. It has been recognized that they depend very strongly upon the phase state which is single or double phase, and upon the arrangement of atoms in the ordered structures [28, 40]. We shall now briefly discuss the essential features.

3.1 CONCENTRATION RANGE 0 ≤ c ≤ 0.20: SOLID SOLUTION. — The alloys are all ferromagnetic in the concentration range 0 ≤ c < 0.20 and the magnetization decreases with increasing Al contents in a way approximately given by the dilution law \( M = M_F (1 - c) \) where \( M_F \) is iron magnetic moment and \( c \) is the impurity concentration. The magnetic moment per iron atom is approximately independent of Al-content. We reproduce on figure 3 the variation of the saturation magnetization (\( M_s \)) as a function of Al concentration.

Fig. 3. — Concentration dependence of the spontaneous magnetization of annealed (broken line) and cold-worked (solid line) Fe-Al alloys (after Ref. 36).

3.2 CONCENTRATION RANGE 0.20 ≤ c ≤ 0.50: ANNEALED SAMPLES (ORDERED). — The variation of the saturation magnetization as a function of Al concentration of annealed samples no longer follows a dilution law in this concentration range (Fig. 3) and the high field susceptibility presents a drastic change (Fig. 4). It is also important to notice that annealed or high temperature quenched samples present the same magnetic behaviour [2]. The recent studies on the Fe-Al alloys in the ordered phases have shown that the magnetic properties are in fact more complex than expected from the earlier studies.

The influence of the atomic arrangement on the magnetic properties has clearly been shown in particular by the investigations of Oki et al. [28]. Moreover it has been shown [28] that the so-called double Curie point phenomena arise in fact from the coexistence of \( \alpha + B_2 \) and \( \alpha + DO_3 \) phases in the constitution diagram.

Above \( c = 0.27 \) anomalous magnetic properties have been registered since 1959 by Arrott and Sato [32] and reconsidered later in particular by Shull et al. [40]. In this concentration range the alloys can have the \( \alpha \), \( B_2 \) or \( DO_3 \) structure depending on the temperature range considered, \( DO_3 \) corresponding to the low temperature phase. Shull et al. [40] studied alloys which have been quenched from 1200 °C and then annealed at the appropriate temperature in order to obtain the \( B_2 \) or \( DO_3 \) structure. The alloy \( Fe_{0.73}Al_{0.27} \) \( DO_3 \) is a pure micromagnet (see [62] for a review on micromagnetism). Alloys in the composition range from \( Fe_{0.73}Al_{0.27} \) to \( Fe_{0.705}Al_{0.295} \) [40], when heat treated to \( DO_3 \)-type atomic order present three magnetic states. Paramagnetic, ferromagnetic and micromagnets...
Magnetic states are observed successively on cooling. Moreover the magnetization curve and unidirectional remanence are displaced. The behaviour of alloy Fe$_{0.70}$Al$_{0.30}$ is unique in that, after becoming ferromagnetic at about 400 K on cooling from the paramagnetic state, it undergoes the reverse transition and becomes superparamagnetic again on further cooling, at 170 K, before finally becoming mictomagnetic at 92 K [40] (Figs. 5 and 6).

Alloys with higher aluminium contents, from $c = 0.304$ to at least $c = 0.45$, do not become ferromagnetic according to Shull et al. [40]. Other authors have concluded to ferromagnetism up to $c = 0.35$ [36, 41]. Above $c = 0.32$ ($c = 0.35$ following [23]) the low temperature phase is no longer DO$_3$ and B$_2$ is the only existing ordered structure. The transition from paramagnetism directly to mictomagnetism is accompanied by the usual susceptibility cusp, the temperature of which decreases monotonically with increasing Al contents. The maximum of magnetization observed by Gengnagel et al. [76] when the temperature is increased in a fixed magnetic field ($H > 1600$ Oe) for Fe$_{0.49}$Al$_{0.51}$, may correspond to the appearance of mictomagnetism.

The main characteristics of the experimental magnetic phase diagram are represented in figure 7. The actual data which are for DO$_3$ structure, when $c \leq 0.32$ and for B$_2$ structure when $c > 0.32$ are taken from various references [17, 40]. A calculated magnetic phase diagram for ordered Fe-Al alloys has been performed [44] and is in good agreement with the experimental results. The main feature of these diagrams is the existence of a low temperature mictomagnetic phase for $0.27 < c < 0.50$.

### 3.3 Concentration Range 0.20 ≤ c ≤ 0.50: Cold-Worked Samples (Disordered)

The magnetic behaviour of the disordered alloys appears, from the experimental investigations, drastically different from that of the ordered ones (Figs. 3 and 4). In the concentration range up to 30 at % Al, the magnetization of the cold-worked samples decreases with increasing Al contents according to a dilution law [2, 36, 38]. This
behaviour is the extension of the one described in section 3.1 for the concentration 0 < c < 0.20.

Above 30 at % Al, the magnetization decreases stronger than according to a dilution law and vanishes at a concentration higher than 50 at % Al. No anomalous temperature dependence of the magnetization taken in fields of several kOe has been observed [2, 36, 38] but the magnetic behaviour is of a typical ferromagnetic type over the whole concentration range in these experimental conditions.


4.1 Sample preparation. — As mentioned in section 1, quenching in water does not achieve complete disorder [2, 33, 36] but presents partial $B_2$ ordering [28]. Alloys which have been obtained by cold work present effectively a disordered bcc structure [2, 42, 19]. It is well known that cold working of an alloy produces crystal fragmentation and inhomogeneous lattice strain [58-61]. These effects lead to an appreciable degree of broadening of the diffraction lines in the Debye-Scherrer patterns of the cold-worked materials. Cold working in alloys not only produces line broadening, but destroys, in addition, all traces of superlattice lines, i.e. cold working achieves what water quenching fails to do, namely it leads to destruction of all traces of long-range order. The change we have observed in the specific heat after cold working treatment of the samples will therefore be attributed to disordering effect. This supposes that the lattice imperfections introduced by cold working have a negligible effect on the specific heat compared to the disordering effect. This assumption is based on the cold working effect observed on a certain number of elements. Bevk [69] has shown that a cold working treatment leads to an increase of the linear term of the specific heat of 2% for Cu. We have observed an increase of the linear term of the specific heat of 1% for Ni, 2% for V and 3% for Pd. The Debye temperature modification is of the same order of amplitude for V, Ni and Pd.

The splat quenching method can also be used to prevent ordering for certain alloys and we have compared these two methods for two concentrations of Fe-Al, namely $c = 0.25$ and $c = 0.48$.

The alloys we studied were prepared from 99.95% iron and 99.99% aluminium melted under pure argon atmosphere in a high frequency induction furnace using high-purity sintered alumina crucibles. Chemical analysis have shown a loss of aluminium of less than 0.5% ($c = 0.25$ nominal is $c = 0.246$ for example). To obtain disordered Fe$_{0.77}$Al$_{0.23}$, Fe$_{0.75}$Al$_{0.25}$, Fe$_{0.68}$Al$_{0.32}$, Fe$_{0.65}$Al$_{0.35}$, Fe$_{0.59}$Al$_{0.41}$ and Fe$_{0.52}$Al$_{0.48}$ the ingots have been cold-worked by crushing to powder in a ball-mill. A Fe$_{0.90}$Al$_{0.10}$ has been submitted to the same treatment. We submit also two ingots of Fe$_{0.75}$Al$_{0.25}$ and Fe$_{0.52}$Al$_{0.48}$ to splat quenching. In both cases X-ray analysis does not show any superstructure lines. The powder is then pressed together in order to measure the specific heat.

Ordered single crystals have been prepared by P. Lesbats and heat treated by M. Dirand for a study which is under progress. We present here the result for Fe$_{0.50}$Al$_{0.50}$ which concentration is in fact $c = 0.488$ from the microprobe analysis. The sample has been submitted to the following heat treatment: 72 hours at 760 °C, 3 hours at 720 °C, 3 hours at 620 °C, 3 hours at 540 °C, 3 hours at 480 °C, 15 hours at 414 °C, 3 hours at 355 °C, 21 hours at 338 °C, 5 hours at 270 °C and 20 hours at 170 °C.

4.2 Experimental procedure. — Our measurements have been performed in an isoperibolic calorimeter described elsewhere [47] and the temperature has been evaluated from a germanium resistor produced by Cryocal. Important improvements have been accomplished in order to measure small heat capacities and in particular a careful fit of the new sample holder has been reached with these improvements. We were able to measure samples whose weight was less than 1 g with electronic specific heats as low as $\gamma = 1.15 \text{ mJ g}^{-1} \text{K}^{-2}$ (for TaPd$_3$) or $\gamma = 1.03 \text{ mJ g}^{-1} \text{K}^{-2}$ (for YPd$_3$; 23.5/76.5), experimental situation which is not atypical in our study of the binary transition metal compounds.

5. Specific heat properties.

In this section we present new results in the disordered state and then we discuss all specific heat results available on Fe-Al system.

5.1 Low temperature specific heat in the disordered state. — We have used the standard specific heat relation in order to analyse the experimental results:

$$C = \gamma T + \beta T^3$$

where $\gamma T$ is the electronic specific heat and $\beta T^3$ the lattice contribution. The coefficient $\gamma$ is related to the electronic density of states per spin direction at the Fermi level $n(E_F) : \gamma = \frac{\pi^2}{3} k_B^2 n(E_F)$ when the electron-phonon interaction $\lambda$ is neglected.

The variation of $C/T$ against $T^2$ is shown in figure 8 for the cold worked samples of concentrations $c = 0.25$; 0.32; 0.35; 0.41; 0.48; the variation is essentially linear in our case. The corresponding values of $\gamma$ are summarized in table I.

We have performed preliminary measurements on splat-cooled samples of concentration $c = 0.25$ and $c = 0.48$ which results are shown on figures 9 and 10.

We show also preliminary results of a study of ordered single crystals. The concentration considered here is $c = 0.50$ (Fig. 11).

All values of $\gamma$ which are available both in the disordered and in the ordered FeAl alloys are given in figure 12.
Table I. — Specific heat of cold-worked samples of Fe$_{1-x}$Al$_x$ (our work).

<table>
<thead>
<tr>
<th>$c$</th>
<th>0.10</th>
<th>0.23</th>
<th>0.25</th>
<th>0.32</th>
<th>0.35</th>
<th>0.41</th>
<th>0.48</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (mJ mole$^{-1}$ K$^{-2}$)</td>
<td>5.16</td>
<td>5.10</td>
<td>5.24</td>
<td>6.70</td>
<td>10.0</td>
<td>11.0</td>
<td>13.2</td>
</tr>
<tr>
<td>$\beta$ (mJ mole$^{-1}$ K$^{-2}$)</td>
<td>0.440</td>
<td>0.090</td>
<td>0.066</td>
<td>0.073</td>
<td>0.072</td>
<td>0.050</td>
<td>0.210</td>
</tr>
<tr>
<td>$\theta_0$ (K)</td>
<td>360</td>
<td>278</td>
<td>308</td>
<td>298</td>
<td>300</td>
<td>338</td>
<td>212</td>
</tr>
</tbody>
</table>

Fig. 8. — Specific heat of cold-worked Fe-Al alloys in the $C/T$ versus $T^2$ representation.

Fig. 9. — Specific heat of Fe$_3$Al in the annealed (at 480 °C), water-quenched (from 1200 °C), splat-cooled and cold-worked states, in the $C/T$ versus $T^2$ representation.

Fig. 10. — Specific heat of FeAl in the annealed (at 450 °C), water-quenched (from 1200 °C), splat-cooled and cold-worked states, in the $C/T$ versus $T^2$ representation.

The magnetic specific heat anomaly $\Delta C = C - (\gamma T + \beta T^2)$ is reported in the inset.
5.2 SPECIFIC HEAT AS A FUNCTION OF CONCENTRATION.

5.2.1 Concentration range $x < 0.20$: solid solution. — Cheng et al. have studied in 1964 [48] the heat capacity behaviour in this concentration range. For comparison, we have measured a cold-worked sample of concentration $c = 0.10$. The electronic specific heat coefficient $\gamma$ variation is of 10% as the Al-content increases up to about 20 at% Al.

5.2.2 Concentration range $0.20 < x \leq 0.50$: quenched alloys (ordered). — As mentioned in section 4 the quenched samples of Cheng et al. [48] may become more and more B$_2$ type ordered as the concentration of Al increases. A considerable increase in $\gamma$ at Al-contents between 0.20 and 0.30 has been found by Cheng et al. [48]. The $\gamma$ values stay very high up to 50 at% Al and for stoichiometric concentration the data show a marked "upturn" anomaly in the plot $C/T$ vs. $T^2$ (see Fig. 10).

In order to check whether the large increase in $\gamma$ between $x = 0.20$ and $x = 0.30$ comes from a magnetic contribution, Cheng et al. [48] have measured the Fe$_{0.75}$Al$_{0.25}$ alloy specimen submitted to different heat treatment. The sample heat treated to have the Fe$_3$Al type structure (ferromagnetic) presents a much lower $\gamma$ value than for the FeAl type structure (non magnetic order). It should be noted that Fe$_{0.75}$Al$_{0.25}$ in the FeAl-type of order deviates greatly from FeAl stoichiometry and consequently has a considerable degree of atomic disorder with a complex magnetic structure. The effect of various heat treatments, to obtain various atomic states (and various magnetic states), on the low temperature specific heat has been reconsidered by Okamoto and Beck in 1972 [49] for $x = 0.25$ and $x = 0.51$. They observed an important decrease of $\gamma$ when the heat treatment increases the long range order parameter in the Fe$_3$Al state for $x = 0.25$ (= 9.2; 8.4; 7.9; 7.7; 7.3 mJ mole$^{-1}$ K$^{-2}$).

For the concentration $x = 0.51$, the specific heat measured by Okamoto and Beck [48] behaves as a linear function of temperature $C = A + \gamma' T$. The coefficient $A$, which is a magnetic contribution to the specific heat, decreases drastically when the heat treatment increases the long range order parameter of FeAl and the coefficient $\gamma'$ decreases as well ($\gamma' = 11.7; 11.4; 10.8; 10.6$ mJ mole$^{-1}$ K$^{-2}$). The $\gamma$ values obtained for annealed samples leading to the best ordered atomic structure for $x = 0.25$ and $x = 0.51$ are reported on figure 12.

The ordered single crystal FeAl we have studied is shown in figure 11. A drastic upturn at low temperature is registered, similar to Okamoto and Beck result's for the quenched sample. We have extrapolated the high temperature normal behaviour in order to extract $\gamma$ and $\beta$ coefficients, $\gamma = 9.19$ mJ g$^{-1}$ K$^{-2}$ and $\beta = 0.028$ 7 mJ g$^{-1}$ K$^{-4}$. In the figure 11 is also represented the deviation of $C$ from the linear behaviour.

5.2.3 Concentration range $0.20 < x < 0.50$: cold-worked alloys (disordered). — We have seen that the value of the linear coefficient of the specific heat is closely related to the degree of atomic order in the Fe-Al alloys. As mentioned in section 4 we measured the specific heat of Fe-Al alloys which have been cold-worked to reach the atomically disordered state. It is to be noticed that Fe$_{0.52}$Al$_{0.48}$ has a perfectly linear behaviour in the plot $C/T$ vs. $T^2$ contrary to the very large upturn observed by Okamoto and Beck for the incompletely disordered sample obtained by quenching (which we also observed for the splat-cooled sample).

From figure 12 it appears clearly that when $c$ increases $\gamma$ decreases down to at least $c = 0.25$ in the disordered state. The value of $\gamma$ for $c = 0.32$ stays also relatively low. This behaviour is quite different from the one registered for quenched samples. Above $c = 0.32$ we have registered a drastic increase of $\gamma$. 

Fig. 12. — Coefficient of low-temperature specific heat term linear in temperature, $\gamma$, as a function of Al-content for Fe-Al alloys in the quenched (from 1100°C in oil) and cold-worked states.

Fig. 13. — Debye temperature as a function of Al-content for Fe-Al alloys in the quenched (from 1100°C in oil) and cold-worked states.
up to $\gamma = 13.2 \text{ mJ mole}^{-1} \text{K}^{-2}$ for $c = 0.48$; a value which is nearly equal to the value of the water quenched sample but with a very different $C/T$ vs. $T^2$ behaviour.

The main features of figure 12 can be summarized by:

- A relatively constant value of $\gamma$ from 0 to $c = 0.20$.
- A drastic increase of $\gamma$ around $c = 0.25$ with a maximum of $\gamma$ reached for $c = 0.27$ followed by a constant $\gamma$ value up to $c = 0.50$ for the water quenched samples (nearly ordered state).
- A drastic increase of $\gamma$ around $c = 0.35$ with a maximum of $\gamma$ reached for $c = 0.48$ for the cold-worked samples (disordered state).

Table 1 also includes the variation of the Debye temperature $\theta_0$ as a function of aluminium concentration. A relatively regular curve can be drawn through our experimental $\theta_0$ values except for $c = 0.48$. Following Tsang et al. [70] we attribute essentially the deviations from the mean curve $\theta_0(c)$ to short-range order effects. The $\theta_0(c)$ variation will not be discussed further in the absence of an appropriated theoretical model.

6. Discussion.

The discussion of the physical properties of the Fe-Al alloys needs a critical study of each experimental result in the light of the recent phase diagrams discussed in section 2. However, we shall restrict ourselves to the discussion of the main features of magnetic and specific heat properties; a complete study is out of the scope of the present paper.

6.1 Concentration $0 \leq c < 0.20$. In this concentration the Fe-Al system presents the disordered $\alpha$ structure according to the various authors and the magnetic properties are the same for any heat treatment. The magnetization decreases following the dilution law and the iron magnetic moment is approximately independent of the Al-content. The coefficient $\gamma$ does not vary very much with the Al content. An increase of less than 10 per cent is followed by a decrease down to a value corresponding to that of pure iron for $c = 0.15$. These results have been tentatively interpreted in a rigid band model [52, 53] but it appears that a complete calculation should be done using a more realistic model. Progress have been registered in the dilution concentration range by Terakura [63]. In the high concentration range Jo and Akai [43] have performed a KKR-CPA calculation. They show, for example, that Fe$_{0.80}$Al$_{0.20}$ presents a band structure very similar to that of iron. Unfortunately no evaluation of $\gamma$ has been reported in order to check the model with the experimental results.

6.2 Concentrations $0.20 \leq c \leq 0.24$ and $c = 0.25$.

In the concentration range $0.20 \leq c \leq 0.24$ the phase diagram is very complex. Depending on the temperature, various structures appear ($\alpha + \text{DO}_3$); ($\alpha + \text{B}_2$); $\text{B}_2$ and $\alpha$. No detailed magnetic and specific heat study has been performed as a function of the various phases. Oki et al. [28] has shown that the apparent double Curie point phenomenon is due in fact to the atomic phase transformation. The $\alpha$ ferromagnetic phase dominates largely the magnetic properties of the alloys between $c = 0.20$ and $c = 0.24$.

The stoichiometric concentration $c = 0.25$ has been the object of more systematic studies. Physical properties corresponding to the various states (atomically disordered, partially ordered...), obtained by adequate heat treatment, have been investigated.

The annealing treatment (below 450 °C) leads to the appearance of a pure $\text{DO}_3$ phase. This ordered $\text{DO}_3$ phase is ferromagnetic with $T_s$ above 500 °C and $M_s = 1.8 \mu_B$ per Fe atom and with a value of $\gamma$ of 7.3 mJ mol$^{-1}$ K$^{-2}$ regarding Okamoto and Beck [40, 49]. The magnetic behaviour is consistent with the observation of Gengnagel et al. [36] (who have cooled very slowly their sample from 1 000 °C to room temperature) and with the observation of Wakiyama [35] who obtained a saturation magnetic moment per Fe atom of 1.87 $\mu_B$.

The annealing treatment at 640 °C followed by water quenching should lead to the $\text{B}_2$ structure. (It is to be noticed that in this case the concentration is very far from the stoichiometry corresponding to the $\text{B}_2$ structure.) Shull et al. [40] observed a magnetic behaviour, not very different of that of the $\text{DO}_3$ phase, which is in disagreement with Oki et al. [28] who consider the $\text{B}_2$ phase as non magnetic. The $\gamma$ value is 9.3 mJ mol$^{-1}$ K$^{-2}$ [49].

A quenching treatment into water from 1 200 °C should lead to a partial $\text{B}_2$ ordered structure according to the phase diagram [23] and to the investigations of Shull et al. [40]. Cheng et al. [48] have registered a value of $\gamma$ of 9.7 mJ mol$^{-1}$ K$^{-2}$.

We have performed a preliminary heat capacity measurement on a splat-cooled sample which should approach the disordered state. The $\gamma$ value is of 6.8 mJ mol$^{-1}$ K$^{-2}$. A magnetic measurement is under progress.

Finally, by a cold-work treatment, we have been able to reach the disordered $\alpha$ phase which is ferromagnetic with a saturation magnetic moment per Fe atom of 2.15 $\mu_B$ [38] for $c = 0.248$. The $\gamma$ value we have obtained is 5.24 mJ mol$^{-1}$ K$^{-2}$.

This sequence of heat treatments and the corresponding specific heat and magnetic properties is an example, on the particular case $c = 0.25$, of the complexity of ordering effects on physical properties.

In the concentration range just considered, $0.20 \leq c \leq 0.25$, it can be concluded that the samples presenting an ordered or partially ordered structure are ferromagnetic with a variation of magnetization versus concentration which deviate from a dilution law. The disordered samples (submitted to a cold-work treatment) are also ferromagnetic but moreover they follow the dilution law. The variation of the electronic specific heat coefficient $\gamma$, as a function of $c$, is positive.
in the ordered state and negative in the disordered one. It appears therefore that the magnetic and specific heat results are modified by ordering effects in the considered concentration range.

6.3 $0.25 < c \leq 0.35$. — In this concentration range, the phase diagram is simpler: D0$_3$ at low temperature and B$_2$ above with a possibility of reaching the disordered phase $\alpha$ at the highest temperatures. The interpretation of the electronic properties should therefore in principle be unambiguous.

In the low temperature phase D0$_3$ (annealing at 440 °C during 23 to 30 days), when 27 at % Al concentration is reached, the ordered samples are micromagnetic at low temperature which increased the $\gamma$ value due to a magnetic contribution. The high field susceptibility measured by Wakiyama [35] (samples slowly cooled from 600 °C to 150 °C) increases also drastically in agreement with the appearance of the micromagnetic state. At room temperature, the samples are ferromagnetic up to 30 at % Al in the D0$_3$ state, and above no magnetic order can be noticed.

Samples submitted to the heat treatment producing the B$_2$ structure present a magnetic behaviour which is comparable with the one presented by the samples in the D0$_3$ state [40]. This is in disagreement with Oki et al. [28] who assert that the B$_2$ phase is non magnetic. No $\gamma$ values have yet been reported on annealed samples. The $\gamma$ values (similar to our preliminary results) observed on samples quenched from 1 200 °C which are certainly strongly B$_2$ ordered [40] are increasing up to 30 at % Al and then stay constant. A study on single crystals is under progress.

From the present results, it appears that $\gamma$ increases drastically with the decrease of the magnetization and correspond to the appearance of the micromagnetic regime.

The cold worked samples ($\alpha$ structure) are ferromagnetic [2, 38] with a magnetization (measured in fields of several kOe) which decreases faster than with a dilution law when c increases. The corresponding $\gamma$ values increase up to 50 at % Al, whereas the susceptibility follows a quite similar increase with Al concentration.

In the concentration $0.25 < c \leq 0.35$ it appears that the magnetic and specific heat results at low temperature are very different for the samples in the ordered phases and in the $\alpha$ phase with in particular the appearance of micromagnetism at $c = 0.27$ in the ordered state, whereas the disordered phase stays ferromagnetic.

6.4 $0.35 < c \leq 0.50$. — In this concentration range, the phase diagram shows a B$_2$ structure at low temperature (and eventually the $\alpha$ structure at high temperature or directly the liquids depending upon the authors). It is quite difficult to obtain the disordered state by usual methods for high order-disorder temperature transformation and the quenched samples of Cheng et al. [48] have to be considered at least as partially ordered.

6.4.1. — The ordered alloys present a micromagnetic behaviour and no ferromagnetism at any temperature [40]. The freezing temperature decreases down to nearly 0 for $c = 0.50$. The $\gamma$ values (of quenched samples from 1 200 °C which have the B$_2$ structure regarding Shull et al. [40] and the phase diagram), are staying high and pratically constant over all the concentration range $0.35 < c < 0.50$. The $\gamma$ values do not represent the density of states at the Fermi level contribution only but include a micromagnetic contribution $\gamma_m$ which explain at least partially the $\gamma(c)$ behaviour between $0.27 \leq c < 0.50$.

The stoichiometric FeAl is very interesting and has been the subject of many experimental and theoretical investigations Okamoto et al. [49] have studied in detail the magnetic and specific heat properties of Fe$_{0.49}$Al$_{0.51}$ increasing the long-range order parameter by various heat treatment. No micromagnetic behaviour has been detected in the magnetic field and temperature experimental conditions used in reference 49. Nevertheless the sample does not show a pure paramagnetic behaviour. The calorimetric data of Fe$_{0.49}$Al$_{0.51}$ of Okamoto and Beck show for example a marked « upturn » anomaly (see Fig. 10) which they attributed to additional magnetic specific heat contribution. The linear temperature contribution $\gamma'' T = (\gamma' + \gamma_m) T$ is also considered as an overestimated value of the electronic specific heat $\gamma' T$. When the heat treatment increases, the atomic order parameter $\gamma''$ decreases from 11.7 mJ mole$^{-1}$ K$^{-2}$ (sample quenched from 1 200 °C) to 10.6 mJ mole$^{-1}$ K$^{-2}$ (sample annealed at 700 °C and cooled down to 480 °C per 10 °C/day and then quenched) whereas $\gamma''$ for Fe$_{0.50}$Al$_{0.50}$ (sample quenched from 1 200 °C) is equal to 13.2 mJ mole$^{-1}$ K$^{-2}$. The result we have obtained for an ordered single crystal of Fe$_{0.51}$Al$_{0.49}$ shows also a drastic upturn at low temperature in the $C/T versus T^2$ representation (Fig. 11). The $\gamma''$ coefficient, determined in the 12.4-17.3 K temperature range where the upturn no more exists, is 9.19 mJ mole$^{-1}$ K$^{-2}$ whereas the Debye temperature is $\theta_D = 407$ K. The low temperature anomaly $\Delta C = C - (\gamma'' T + \beta T^2)$ is also represented in figure 11.

All the results obtained up to now concerned off-stoichiometric FeAl alloys, including Fe$_{0.50}$Al$_{0.50}$ alloys. In fact, following Caskey et al. [74], even at exact stoichiometry there is an intrinsic degree of disorder which is of 0.25 at % Al or 1 at % Al depending of the estimations. This means that instead of having a perfectly ordered CsCl structure with a non-magnetic behaviour, there is a very low concentration of « anti-structure » iron atoms located on Al sites. Such Fe atoms have 8 Fe nearest neighbours and thus also an atomic moment. Therefore, Okamoto and Beck [49] have assimilated the experimental situation to the magnetically dilute problem envisaged in Marshalls theory [75] yielding to a $\gamma_m$ contribution due to the
location of a sufficient number of spins in a near-zero field, \( \gamma_m \) which is independent of the impurity concentration as it was observed for example in CuMn alloys. Moreover, the upturn at low temperature in \( C/T \) vs. \( T^2 \) plot can be explained by the presence of a certain number of magnetic clusters. It would be useful to perform a magnetic study of FeAl in very small fields in order to check the existence of a micromagnetic phase with a low freezing temperature which can be suspected from previous results \[76\] and which would explain nicely the experimental specific heat results.

The determination of the pure electronic specific heat coefficient \( \gamma' \) has been considered by various authors. Okamoto et al. \[49\] have estimated \( \gamma' \) at 5.5 mJ mole\(^{-1}\) K\(^{-2}\) for Fe\(_{0.49}\)Al\(_{0.51}\). Okuchi \[54\] did an electronic structure calculation of an ordered FeAl alloy and found \( \gamma = 4.60\) mJ mole\(^{-1}\) K\(^{-2}\). More recently Eibler and Neckel \[55\] published a self-consistent APW calculation of the density of states of the ordered stoichiometric FeAl, CoAl and NiAl. The theoretical corrected \( \gamma \) value obtained by Eibler et al. for FeAl is 7.44 mJ mole\(^{-1}\) K\(^{-2}\) whereas a very recent LMTO calculation of Koenig et al. \[77\] gives : 6.95 mJ mole\(^{-1}\) K\(^{-2}\). These theoretical calculations concern an « ideal FeAl alloy » without any intrinsic disorder and cannot be compared quantitatively without precise determination of \( \gamma_m \). In relation with FeAl it is interesting to compare the agreement between theory and experience for another CsCl alloy. The alloy CoAl presents only very few magnetic clusters according to Parthasarathi and Beck’s magnetic results \[39\] and is therefore a good candidate to check the theoretical models which do not take into account magnetic contributions. There experimental \( \gamma \) values are available : Begot et al. \[50\] value is \( \gamma = 1.1\) mJ mole\(^{-1}\) K\(^{-2}\) (for Co\(_{0.50}\)Al\(_{0.49}\)) Waterman et al. \[51\] indicate \( \gamma = 1.6\) mJ mole\(^{-1}\) K\(^{-2}\) and we found \( \gamma (1.8\) mJ mole\(^{-1}\) K\(^{-2}\) (for Co\(_{0.50}\)Al\(_{0.49}\)). This discrepancy in the experimental value is due, in our opinion, to problems of sample preparation which can affect greatly the atomic and magnetic order). The theoretical evaluation \( (\gamma = 1.92\) mJ mole\(^{-1}\) K\(^{-2}\) \) seems quite reliable. This confirms once more that the difference between theoretical and experimental evaluation of \( \gamma \) for FeAl is due essentially to a large experimental magnetic contribution.

6.4.2 In the disordered state (obtained by cold working treatment) the samples are ferromagnetic \[38\] and the magnetization decreases with \( c \) increase. The mean moment of iron atom decreases also and reaches a value of 1 \( \mu_b \) at \( c = 0.50 \) (instead of 2.2 \( \mu_b \). This phenomenon is due to environment problem (2.2 \( \mu_b \) is observed only when Fe is surrounded by more than 8 iron neighbours on nearest neighbours sites). The susceptibility \( \chi \) increases with \( c \) \[33, 38\] and \( \gamma \) presents approximatively the same variation with \( c \) as \( \chi \) (Figs. 4 and 12). It appears that the drastic change of behaviour of \( \gamma(c) \), which takes place above \( c = 0.30, \) is probably correlated with the change in the magnetic properties, but no clear explanation is yet available.

An attractive explanation can be given in relation with possible magnetic properties. It is to be noticed that the magnetic properties of the disordered alloys \[38\] have been studied in magnetic fields of at least a few kOe. It is well known that a relatively small field (100 Oe for example) can be sufficient for changing a spin glass in a ferromagnet \[73\]. Moreover the curve \( M \) versus \( H \) at 4.2 K for FeAl \[38\] is not different from the corresponding curve observed for a well known spin glass as Auo.96Feo.10 \[72, 78\]. It is to be noticed that, in a small field (13 Oe), the magnetization of the Fe\(_{0.66}\)Al\(_{0.34}\) decreases steeply at 137 K, whereas, for a stronger field (300 Oe), the apparent Curie temperature occurs above room temperature. We suggest that a micromagnetic behaviour could take place for \( c > 0.35 \).

In this hypothesis the increases of \( \gamma \) and \( \chi \) in the vicinity of \( c = 0.35 \) would find their origin, at least partially, in the appearance of a micromagnetic state. The proposed hypothesis is coherent with the shift of the curves \( \gamma(c) \) corresponding to the quenched partially B\(_2\) state and the cold worked state. The same shift is also observed for the \( \chi(c) \) curves. There is a tendency to reduce the number of nearest neighbours pairs of Fe-Fe in the DO\(_3\) structure and for the B\(_2\) structure this tendency is even stronger. This could explain why atomic order, which decreases the number of Fe-Fe couplings, reduces the tendency to ferromagnetism whereas in the disordered state the ferromagnetism stays for a higher concentration.

In the concentration 0.35 < \( c \leq 0.50 \) \( \gamma \) stays practically constant in the ordered state whereas \( \gamma \) increases when \( c \) increases in the disordered state. The effect of atomic ordering is also observed in the magnetic properties : the alloys are micromagnetic in the ordered state and ferromagnetic in the disordered state but this point should be reconsidered by appropriated experiments. The appearance of a micromagnetic phase in the disordered state, like in the ordered state but shifted in concentration, is an hypothesis in the appearance of a micromagnetic state. The proposed hypothesis is coherent with the shift of the curve \( \gamma(c) \) corresponding to the quenched partially B\(_2\) state and the cold worked state. The same shift is also observed for the \( \gamma(c) \) curves. There is a tendency to reduce the number of nearest neighbours pairs of Fe-Fe in the DO\(_3\) structure and for the B\(_2\) structure this tendency is even stronger. This could explain why atomic order, which decreases the number of Fe-Fe couplings, reduces the tendency to ferromagnetism whereas in the disordered state the ferromagnetism stays for a higher concentration.

7. Conclusion.

In conclusion, the review of the knowledge of the phase diagram of Fe-Al and the magnetic and specific heat properties we have presented here, illustrate the drastic effect of ordering on physical properties. More generally we have pointed out the importance of precise phase diagrams in order to interpret the physical phenomena observed.

The original specific heat results for disordered alloys we have presented are drastically different from the available quenched samples results. In order to
explain the variation of the linear specific heat coefficient, the magnetic properties should be reconsidered and band structure calculations performed. 

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