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Thermal, structural and magnetic properties of icosahedral $Al_{86}Cr_8Fe_6$ alloy

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ABSTRACT

Icosahedral alloy $Al_{86}Cr_8Fe_6$ and its crystallization products have been studied with X-ray diffraction, differential scanning calorimetry, ^{57}Fe Mössbauer spectroscopy, and magnetic susceptibility methods. The presence of a multiplicity of Fe sites is demonstrated, and this is interpreted as evidence of intrinsic disorder characteristic of icosahedral alloys. The analysis of the Mössbauer spectra of icosahedral alloys in terms of two doublets is shown to be methodologically incorrect, and consequently the basis of the so-called two-site model is unfounded. The crystallization products of the studied icosahedral alloy are $Al_{13}Fe_4$ and $Al_{13}Cr_{2-x}Fe_x$. A small magnetic moment is present both in the icosahedral sample and in its crystallization products. The origin of the magnetic moment in icosahedral alloys is discussed in view of recent theoretical and experimental advances in the understanding of the electronic structure of these alloys.

1. INTRODUCTION

The first icosahedral (*i*) alloy was discovered in the rapidly quenched binary system $Al_{100-x}Mn_x$ with $x = 10–14$ (Shechtman, Blech, Gratias and Cahn 1984). The search for *i* alloys in Al-rich binary alloys $Al_{100-x}TM_x$ with other transition-metal (TM) elements showed that such alloys exist for TM = V, Cr, Mo, W, Re, and Ru (Bancel and Heiney 1986a, b). Although it was reported that the rapidly quenched $Al_{100-x}TM_x$ alloys with TM = Fe (Dunlap and Dini 1985, Dunlap 1985, Schurer, Koopmans, Van Der Woude and Bronsveld 1986, Liu, Cheng and Shang 1987, Van Der Woude and Schurer 1987, Schurer, Koopmans and Van Der Woude 1988, Lawther, Dunlap, Lloyd and McHenry 1989a, Lawther, Dunlap and Srinivas 1989b) and TM = Co and Ni (Dunlap and Dini 1986) also form an *i* phase, thorough X-ray and electron diffraction investigations failed to find evidence for the existence of the *i* phase in these systems (Bancel and Heiney 1986a, b, Fung *et al.* 1986, Zou, Fung and Kuo 1987, Dong, Li and Kuo 1987, Li and Kuo 1988, Kim and Cantor 1994).

X-ray diffraction (XRD) spectra of the *i* $Al_{100-x}TM_x$ alloys show the presence of very broad *i* Bragg peaks, which indicates the existence of a significant structural disorder in these alloys, accompanied by the peaks due to impurity phases. It was soon discovered that rapidly quenched samples of a much better quality can be obtained in the Al-rich ternary and/or quaternary alloys (Bancel and Heiney 1986a, b, Chen and Chen 1986, Yamane, Kimura, Shibuya and Takeuchi 1987). This is also true for thermodynamically stable 'perfect' *i* alloys in the Al–Cu–M (M = Fe, Ru and Os)

(Inoue, Tsai and Masumoto 1990) or Al–Pd–Mn (Tsai, Yokoyama, Inoue and Masumoto 1991a) systems.

Although no *i* phase is formed in the binary Al–Fe system, it is formed in the ternary Al–($Cr_{1-z}Fe_z$) system. The studied compositions of the ternary system include $Al_{83{\cdot}4}Cr_{8{\cdot}3}Fe_{8{\cdot}3}$ (Janot, Pannetier, Dubois and Fruchart 1986), $Al_{96-y}Cr_yFe_4$ ($y = 1, 3, 5, 7$), $Al_{80}Cr_{20-y}Fe_y$ ($y = 8, 11$), and $Al_{83}Cr_{11}Fe_6$ (Manaila, Florescu, Jianu and Badescu 1988, Manaila, Florescu, Jianu and Radulescu 1989), $Al_{85{\cdot}7}Cr_{10}Fe_{4{\cdot}3}$ (Van Netten, Schurer and Niesen 1988), $Al_{86-x}Cr_{14-x}Fe_x$ ($x = 3, 6, 9, 12$) (Lawther *et al.* 1989a, b), $Al_{82}Si_1Cr_{8{\cdot}5}Fe_{8{\cdot}5}$ (Sadoc and Dubois 1989), and $Al_{86}Cr_{14-x}Fe_x$ ($x = 2{\cdot}8, 5{\cdot}6, 7, 8{\cdot}4, 11{\cdot}2$) (Manaila, Jianu, Popescu and Devenyi 1994). A systematic study of the influence of composition on the degree of the *i* order in these ternary alloys (Manaila *et al.* 1988, 1989, 1994) showed that the optimal composition in the ternary Al–($Cr_{1-z}Fe_z$) system for the formation of the *i* phase occurs for $z = 0{\cdot}40$–$0{\cdot}45$. The composition of the *i* alloy $Al_{86}Cr_8Fe_6$ studied here was therefore chosen to correspond to $z = 0{\cdot}43$.

The purpose of this paper is to present the results of thermal, structural, and magnetic properties of *i* $Al_{86}Cr_8Fe_6$ studied with differential scanning calorimetry (DSC), XRD, Mössbauer spectroscopy (MS), and magnetic susceptibility techniques. The relation between the structural and magnetic properties is discussed in connection with recent advances in our understanding of the magnetism and the electronic structure of *i* alloys. Some problems in the analysis and interpretation of the Mössbauer spectra of *i* alloys are also discussed. The preliminary results of this work were reported in the conference proceedings (Stadnik, Müller, Goldberg, Rosenberg and Stroink 1993a).

§ 2. EXPERIMENT

An ingot of composition $Al_{86}Cr_8Fe_6$ was prepared by arc-melting high-purity elemental constituents in an argon atmosphere. The ingot was melt-spun by ejecting molten alloy through a 0·8 mm orifice in a quartz tube and using a 70 kPa overpressure of argon. The molten alloy impinged upon a circumferential surface of a copper wheel rotating with a tangential velocity of 50 m/s in a helium atmosphere. The resulting ribbons were about 2 cm long and 2 mm wide.

A DSC measurement was conducted using a DuPont 9900 model apparatus at a heating rate of $20\,K\,min^{-1}$. XRD experiments of the as-quenched sample and its crystallization products obtained by annealing the sample for five minutes at 858 K (sample A1) and 908 K (sample A2) were done on a Siemens D500 and a Philips X'Pert scanning diffractometers using Cu $K\alpha$ radiation. The ribbons were gently pulverized for the XRD measurements. The $K\alpha_2$ contribution was subtracted from the measured XRD spectra.

^{57}Fe MS measurements were carried out at room temperature using a Wissel MSII spectrometer operating in the triangular mode. The spectrometer was calibrated with a 6·35 μm natural-iron foil, and the spectra were folded. The surface densities of the as-quenched, A1, and A2 samples were, respectively, 9·1, 11·4, and $11{\cdot}6\,mg\,cm^{-2}$.

Magnetic susceptibility measurements were conducted using a vibrating-sample magnetometer operating with a Mössbauer-type drive in a continuous-flow cryostat in the temperature range 4·2–200 K and in a magnetic field of 1·75 T. The magnetization signal was recorded during warm-up at a rate of about $1\,K\,min^{-1}$ below 15 K and up to $5\,K\,min^{-1}$ at higher temperatures. Magnetization measurements at room temperature in the fields up to 1·75 T were performed to detect magnetic ordering of the samples caused by the possible presence of magnetic impurities. The values of the magnetic susceptibility were obtained by subtracting from the raw data the susceptibility of the sample holder and of the paraffin film and paraffin in which the pulverized ribbons were embedded. The errors of various magnetic parameters given below were obtained from the fit, and they correspond to one standard deviation. However, in reality the relative errors of these parameters are about 10% because of the limited sensitivity of the apparatus resulting from the noise of its mechanical parts.

§ 3. RESULTS AND DISCUSSION

3.1. *X-ray diffraction and differential scanning calorimetry*

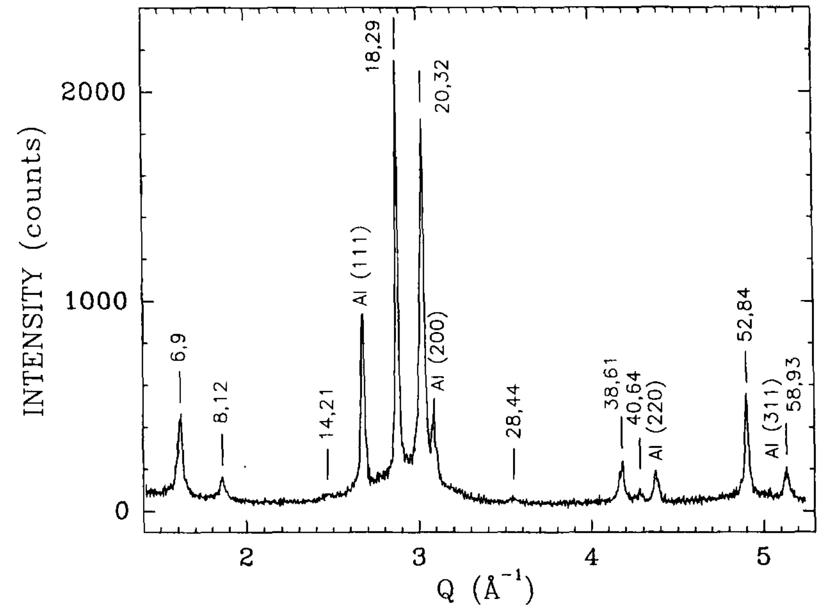
The XRD pattern corresponding to Cu Kα_1 radiation ($\lambda = 1{\cdot}54056$ Å) of the as-quenched $Al_{86}Cr_8Fe_6$ alloy exhibits Bragg peaks owing to the *i* phase and Al (fig. 1). The positions of all detected *i* peaks, Q_{exp} ($Q = 4\pi \sin \Theta/\lambda$), their full widths at half maximum Γ_Q, and their relative intensities above the background were obtained from the fit assuming a Voigt peak-shape and are given in table 1. Table 1 contains also the theoretical positions Q_{cal} which were calculated by taking the position of the most intense and narrowest peak as the reference. Since there are several schemes employed to index the *i* peaks, we present in table 1 the indices that correspond to the most frequently used schemes (Bancel, Heiney, Stephens, Goldman and Horn 1985, Elser 1986, Cahn, Shechtman and Gratias 1986) to enable the reader to make a convenient identification of the *i* peaks.

There is a relatively good agreement between the observed Q_{exp} and theoretical Q_{cal} positions of the *i* Bragg peaks (fig. 1 and table 1). The lack of Bragg peaks that corresponds to half-integer indices confirms that *i* $Al_{86}Cr_8Fe_6$ has a simple icosahedral (SI) six-dimensional Bravais lattice characteristic for *i* alloys that cannot be produced as thermodynamically stable. The value of the six-dimensional hypercubic lattice constant $a_{6D} = 6{\cdot}542(2)$ Å calculated from the value Q_{exp} that corresponds to the (18, 29) *i* peak (table 1) is in good agreement with the literature value for the same composition (Lawther *et al.* 1989b). The width 0·017 Å^{-1} of the sharpest *i* peak (18, 29) (table 1) is narrower than the literature values 0·020–0·024 Å^{-1} for the same composition (Lawther *et al.* 1989a, b). However, it is larger than the instrumental resolution (about 0·010 Å^{-1}) of the XRD spectrometers. This broadening, as well as the shift of Q_{exp} from their ideal positions Q_{cal}, indicate the presence of some structural disorder in the as-quenched *i* $Al_{86}Cr_8Fe_6$ alloy.

It should be noted that although only *i* and Al impurity peaks are seen in the XRD spectrum of $Al_{86}Cr_8Fe_6$, the two strongest *i* peaks are superimposed on a weak and wide maximum. This maximum may be due to the presence of overlapping lines of small amounts of other crystalline and/or amorphous second phases which, as is shown below, can be detected by other techniques. We thus conclude that the as-quenched $Al_{86}Cr_8Fe_6$ alloy consists predominantly of the SI-type *i* phase. The presence of some pure Al does not influence significantly the results obtained from other techniques used in this paper.

The DSC curve of *i* $Al_{86}Cr_8Fe_6$ (fig. 2) exhibits a broad exothermic peak at 663·5 K and two exothermic peaks at 830·4 and 885·5 K. The sample starts to melt above the third exothermic peak. The heats of transformation that correspond to the three exothermic peaks are, respectively, 415, 703, and 344 J mol^{-1}. The first broad peak is probably due to the transformation of a small fraction of the amorphous second phase mentioned above to a crystalline phase/phases. The other two peaks are due to the transformation of the *i* phase into crystalline phases. The values of the heats of transformation are similar to those observed for other as-quenched Al-based *i* alloys (Inoue, Kimura and Masumoto 1987, Tsai, Inoue, Bizen and Masumoto 1989).

Fig. 1

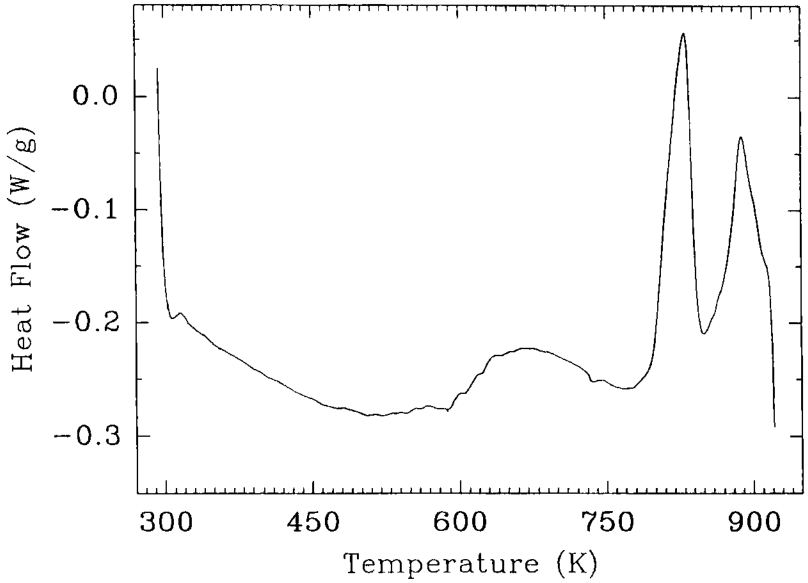


X-ray diffraction spectrum of as-quenched $Al_{86}Cr_8Fe_6$ alloy corresponding Cu Kα_1 radiation. The vertical lines above the icosahedral peaks, which are labelled using the indexing scheme of Cahn *et al.* (1986), correspond to the calculated positions. The relevant parameters of all detected icosahedral peaks are given in table 1. The four peaks due to Al metal are also indicated.

Table 1. Parameters corresponding to the icosahedral peaks in the X-ray diffraction spectrum of as-quenched $Al_{86}Cr_8Fe_6$ (fig. 1). I_1, I_2 and I_3 are the indices based on the indexing schemes of, respectively, Bancel *et al.* (1985), Elser (1986) and Cahn *et al.* (1986). Q_{exp} and Γ_Q are, respectively, the position corresponding to Cu Kα_1 radiation and the full width at half maximum of all icosahedral peaks in fig. 1 determined from the fit of the peaks to a Voigt peaks profile. Q_{cal} is the calculated Q value by taking the position of the strongest icosahedral peak as the reference.

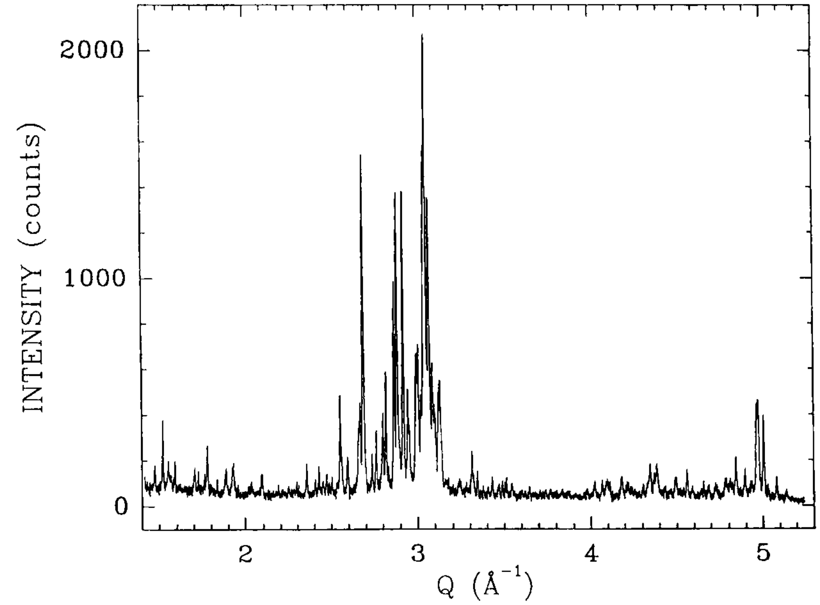
Index						
I_1	I_2	I_3	Q_{exp} (Å^{-1})	Q_{cal} (Å^{-1})	Γ_Q (10^{-3}Å^{-1})	Intensity
110001	111000	6,9	1·614 (1)	1·619	31 (3)	19·1
$1110\bar{1}0$	111100	8,12	1·861 (2)	1·868	37 (4)	5·0
$21\bar{1}001$	211100	14,21	2·467 (8)	2·473	47 (25)	0·8
100000	211111	18,29	2·877 (1)	2·877	17 (1)	100·0
110000	221001	20,32	3·026 (1)	3·025	31 (3)	81·8
210001	311111	28,44	3·549 (4)	3·557	53 (12)	0·9
111000	322101	38,61	4·180 (1)	4·175	39 (3)	8·3
111100	322111	40,64	4·282 (3)	4·279	42 (5)	2·0
101000	332002	52,84	4·903 (1)	4·895	24 (2)	25·5
210000	333101	58,93	5·145 (3)	5·156	38 (4)	5·8

Fig. 2



Differential scanning calorimetry curve of as-quenched $Al_{86}Cr_8Fe_6$ alloy.

Fig. 3



X-ray diffraction spectrum of as-quenched $Al_{86}Cr_8Fe_6$ sample annealed at 908 K for 5 min, corresponding to Cu $K\alpha_1$ radiation.

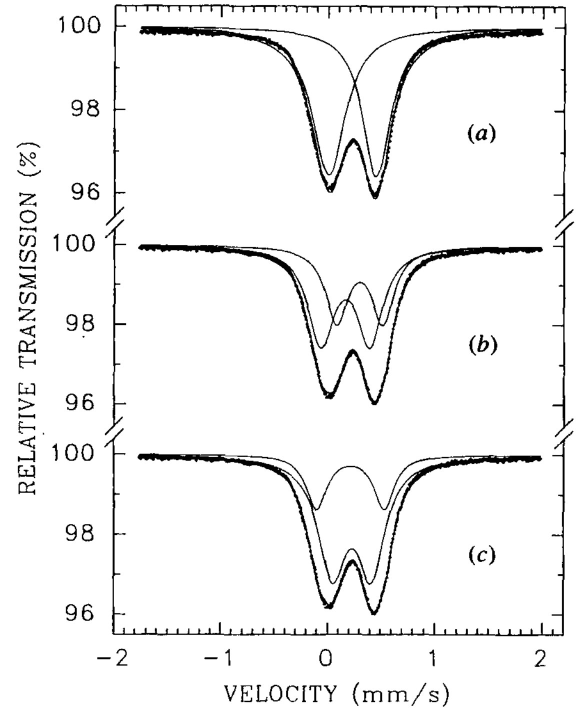
To identify the crystallization products of the metastable *i* $Al_{86}Cr_8Fe_6$, the as-quenched sample was annealed at 858 K (between the second and third exothermic peaks in fig. 2) and at 908 K (above the third exothermic peak) for five minutes, and the XRD spectra of the resulting samples A1 and A2 were measured. As an example, the XRD spectrum of sample A2 is shown in fig. 3. All the Bragg peaks could be accounted for as being due to Al, and crystalline alloys $Al_{13}Fe_4$ (Black 1955 and JCPDS file 29-42) and $Al_{13}Cr_2$ (Cooper 1960 and JCPDS file 29-14). The composition of the latter alloy is in reality $Al_{13}Cr_{2-x}Fe_x$ and evidence for this based on the MS results is presented below. Since the atomic radii of Cr and Fe are similar, the shift of the XRD peaks of $Al_{13}Cr_{2-x}Fe_x$ with respect to the peaks of $Al_{13}Cr_2$ is expected to be very small. This explains the good match of the peaks in fig. 3 to the positions expected for $Al_{13}Cr_2$.

3.2. *Mössbauer spectroscopy*

A Mössbauer spectrum of *i* $Al_{86}Cr_8Fe_6$ (fig. 4) consists of two broad and structureless lines, and is very similar to the Mössbauer spectra of other non-magnetic *i* alloys and metallic glasses (for a recent review of the MS studies of quasicrystals, see Stadnik (1994)). Such a spectrum can be analysed at two levels of sophistication.

Following a successful analysis of many non-magnetic crystalline materials with Fe atoms at one or more crystallographic sites in terms of a finite number of doublets (Greenwood and Gibb 1971, Long and Grandjean 1989), it was assumed that the Mössbauer spectra of *i* alloys can be analysed in a similar way (Swartzendruber, Shechtman, Bendersky and Cahn 1985, Dunlap, Lawther and Lloyd 1988). An example of such an analysis is presented in fig. 4, and the relevant parameters obtained from the fits are given in table 2. The one-site fit (fig. 4(*a*) and model *a* in table 2) is clearly unsatisfactory, which is also reflected in a high value of χ^2 (table 2) and unphysically broad lines as compared with the linewidth of 0·245(5) mm/s obtained from the fit of the inner two lines of the Fe calibration Zeeman sextet. A better fit can be obtained with two component doublets. It can be done in two ways: either with two different values of δ and two similar values of Δ (fig. 4 (*b*) and model *b* in table 2, Dunlap *et al.* (1988)) or with two similar values of δ and two different values of Δ (fig. 4 (*c*) and model *c* in table 2, Swartzendruber *et al.* (1985)). The very fact that the two-doublet fit can be done in two ways, providing completely different sets of fitted parameters (table 2), already indicates the non-uniqueness, and possibly the incorrectness, of such an analysis. The only common thing for models *b* and *c* is the similar average values $\bar{\delta}$ and $\bar{\Delta}$ (table 2). A physical meaning was ascribed to the two doublets (model *b*) by Dunlap *et al.* (1988) who associated them with 'the existence of two distinct transition-metal sites' in *i* $Al_{86}Cr_{14-x}Fe_x$ alloys. The two-doublet fit and the two-site model associated with it were criticized on both methodological and physical grounds (Stadnik and Stroink 1988, Stadnik 1994), and were shown to be incompatible with the in-field Mössbauer experiments (Le Caër, Brand and Dubois 1987, 1988, Brand, Le Caër and Dubois 1990a, b). From a methodological point of view, the main flaw of the two-doublet fits is the fact that the value of Γ of one of the component doublets is unphysically large (table 1), which is the consequence of the broad and structureless experimental Mössbauer spectrum characteristic for most non-magnetic *i* alloys as well as for non-magnetic amorphous alloys. One can even fit the Mössbauer spectra of non-magnetic amorphous alloys with two broad doublets (Stadnik 1994). It would, however, be false to argue that these doublets represent the two distinct sites in an amorphous alloy. The concept of a distinct crystallographic site is also at variance with the notion of a quasicrystal, which by its very nature has an infinite number of such sites

Fig. 4



^{57}Fe Mössbauer spectrum of as-quenched $Al_{86}Cr_8Fe_6$. The solid line is a least-squares fit to: (*a*) an asymmetric doublet, and (*b*), (*c*) to two symmetric doublets. Parameters obtained from the fit are given in table 2. The velocity scale is relative to α-Fe.

Table 2. Parameters determined from the fits of *i* $Al_{86}Cr_8Fe_6$ with the models *a*, *b* and *c* which correspond, respectively, to figs 4 (*a*), 4 (*b*) and 4 (*c*). The isomer shift δ_i (relative to α-Fe), the quadrupole splitting Δ_i, and the full width at half-maximum Γ_i ($i = 1,2$), $\bar{\delta}$ and $\bar{\Delta}$ are all given in $mm\,s^{-1}$. A_i ($i = 1,2$) is the relative area in per cent of the *i*th line for the one-site model *a*, and the relative area of the *i*th doublet for the two-site models *b* and *c*. χ^2 is defined in a usual way (Stadnik and Stroink 1988).

Model	δ_1	δ_2	Δ_1	Δ_2	Γ_1	Γ_2	A_1	$\bar{\delta}$	$\bar{\Delta}$	χ^2
c	0·230(1)		0·450(1)		0·376(1)	0·329(3)	53·1			9·79
b	0·167(1)	0·302(1)	0·461(1)	0·438(1)	0·296(1)	0·253(2)	59·6	0·221	0·452	3·31
c	0·229(1)	0·216(1)	0·370(3)	0·637(3)	0·315(2)	0·225(4)	74·6	0·226	0·437	3·14

(Janot and Dubois 1988). Thus, the only physically meaningful parameters obtained from the two-doublet analysis are the averages $\bar{\delta}$ and $\bar{\Delta}$ (table 2). However, if only these averages are of interest, then they can be determined even more precisely from a perfect fit ($\chi^2 \approx 1$) of the Mössbauer spectrum which can always be obtained by fitting the spectrum to a sufficient number of Voigt lines, to which no physical meaning has to be ascribed. Such a fit of the experimental spectrum in fig. 4 to four Voigt lines gives $\bar{\delta} = 0{\cdot}229\,mm\,s^{-1}$, $\bar{\Delta} = 0{\cdot}452\,mm\,s^{-1}$, and $\chi^2 = 1{\cdot}01$.

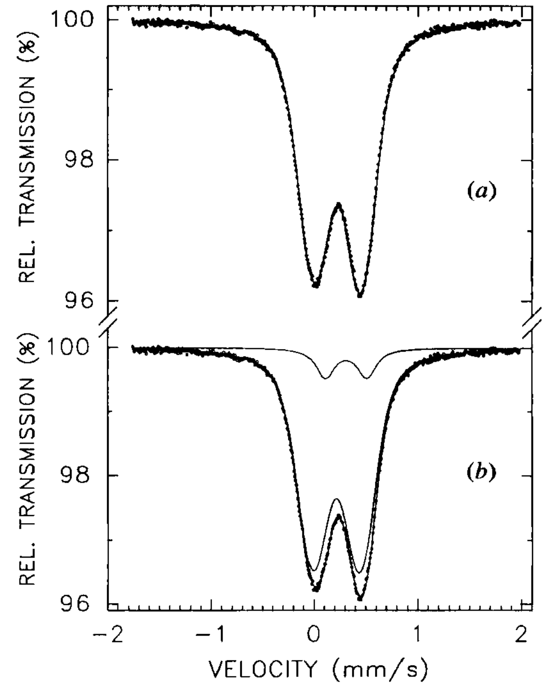
A rather limited insight into the structural properties of *i* alloys is obtained by analysing only the averages values $\bar{\delta}$ and $\bar{\Delta}$. This is due to the fact that $\bar{\delta}$ and $\bar{\Delta}$ do not change significantly in metallic systems of different structures (Greenwood and Gibb 1971, Long and Grandjean 1989). For example, the $\bar{\Delta}$ values for amorphous, *i* and crystalline forms of the $Al_{65}Cu_{20}Fe_{15}$ alloy are, respectively, 0·50(1), 0·38(1), and 0·41(1) mm s^{-1} (Chen and Lu 1992). The corresponding $\bar{\delta}$ values (relative to α–Fe) are 0·26(1), 0·24(1), and 0·23(1) mm s^{-1} (Chen and Lu 1992). The large line broadening observed in the Mössbauer spectrum of *i* $Al_{86}Cr_8Fe_6$ (fig. 4 and table 2), which is characteristic for the Mössbauer spectra of all non-magnetic *i* and decagonal alloys (Stadnik 1994), reflects the presence of a multiplicity of sites in quasicrystals (Eibschutz, Chen and Hauser 1986, Stadnik and Stroink 1988). This multiplicity of sites gives rise to a distribution of the quadrupole splittings, $P(\Delta)$. It is the knowledge of this distribution which is of great physical importance as it reflects the complex local atomic structure of *i* alloys. A reliable determination of this distribution requires an analysis of the Mössbauer spectra at another level of sophistication.

The extraction of the meaningful distribution $P(\Delta)$ from a measured Mössbauer spectrum is a very complex task. There are generally two main approaches used to derive $P(\Delta)$: either a specific shape of $P(\Delta)$ is assumed and the parameters that characterize this shape are obtained from the fit; or no *a priori* assumption about the shape of $P(\Delta)$ is made (for a review of various approaches, see Rancourt and Ping (1991), Le Caër and Brand (1992)). The main drawback of the first approach is that it presupposes the shape of $P(\Delta)$ which may differ considerably from the real $P(\Delta)$. The main disadvantage of the second model-independent approach is the instability of its algorithms resulting in large and unphysical oscillations in $P(\Delta)$. This instability is the consequence of the fact that, from a mathematical point of view, derivation of $P(\Delta)$ from an experimental spectrum, which has unavoidable spectral noise, belongs to the class of the so-called ill-defined mathematical problems (Le Caër and Brand 1992). Recently, a new approach to derive $P(\Delta)$ has been suggested (Rancourt and Ping 1991) which avoids the problems associated with the two approaches. It assumes that the true $P(\Delta)$ can be expressed as a sum of Gaussian distributions with different widths, positions and relative areas. It is important to underline that in this approach only the derived distribution $P(\Delta)$ is uniquely related to the measured Mössbauer spectrum, not the Gaussian components that are intermediate mathematical entities with no physical meaning (Rancourt 1994). As in the above two approaches, the asymmetry of the experimental spectra are taken into account by assuming a linear relation between the isomer shift δ and the quadrupole splitting Δ of the elemental doublets, $\delta = \delta_0 + a\Delta$, where δ_0 and a are fitted parameters (Stadnik 1994). This new approach turns out to be very stable and efficient in deriving $P(\Delta)$ in various disordered systems (Stadnik, Stroink, Lamarche and Inoue 1991, Ping, Rancourt and Stadnik 1991, Stadnik 1994, Rancourt 1994), and has also been used in this paper.

The best fit of the Mössbauer spectrum of *i* $Al_{86}Cr_8Fe_6$ (fig. 5 (*a*)) could be obtained for $P(\Delta)$ (solid curve in fig. 6) which is the sum of two Gaussian component distributions. Increasing the number of Gaussian components did not result in an improvement of the fit. The value of χ^2 for this fit is 1·89, and $\bar{\delta}$ and $\bar{\Delta}$ are equal, respectively, to 0·226 and 0·453 mm s^{-1}. The elemental doublet parameters obtained from the fit are $\delta_0 = 0{\cdot}235(1)$ mm s^{-1}, $a = -0{\cdot}021(1)$, and $\Gamma = 0{\cdot}211(2)$ mm s^{-1}.

The fit in fig. 5 (*a*) is still unsatisfactory in the middle of the experimental spectrum. This is also reflected in the value of $\chi^2 = 1{\cdot}89$, which is expected to be close to 1·0 for an ideal fit. To have confidence in the derived $P(\Delta)$, one should be able to account for the occurrence of even such a small misfit. The analysis of the XRD data in § 3.1 indicated the possibility of the presence of a small amount of a second phase in the

Fig. 5



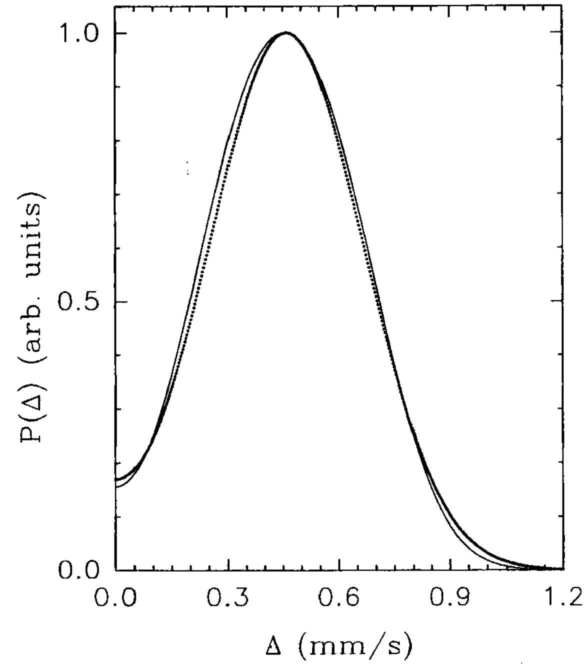
^{57}Fe Mössbauer spectrum of as-quenched $Al_{86}Cr_8Fe_6$ fitted assuming: (*a*) one distribution $P(\Delta)$ (solid curve in fig. 6), and (*b*) two independent distributions due to the icosahedral phase (dotted curve in fig. 6) and the impurity phase. The component spectra resulting from the icosahedral and impurity phases are indicated in (*b*) by solid lines. The velocity scale is relative to α-Fe.

studied *i* $Al_{86}Cr_8Fe_6$. This possibility has been taken into account in the next fitting attempt based on two separate distributions corresponding, respectively, to the *i* and the second-phase fractions in the studied alloy. The new fit, for which $\chi^2 = 1{\cdot}18$, is shown in fig. 5 (*b*), and the distribution $P(\Delta)$ associated with the *i* fraction is indicated by dotted curve in fig. 6. As in the fit in fig. 5 (*a*), $P(\Delta)$ corresponding to the *i* phase is the sum of two Gaussian distributions, and it results in $\bar{\delta} = 0{\cdot}214\,\mathrm{mm\,s^{-1}}$ and $\bar{\Delta} = 0{\cdot}459\,\mathrm{mm\,s^{-1}}$. The elemental doublet parameters corresponding to the *i* phase are $\delta_0 = 0{\cdot}217(1)\,\mathrm{mm\,s^{-1}}$, $a = -0{\cdot}006(1)$ and $\Gamma = 0{\cdot}204(1)\,\mathrm{mm\,s^{-1}}$. The distribution $P(\Delta)$ associated with the second phase is in the form of one Gaussian component and the corresponding parameters obtained from the fit are $\bar{\delta} = 0{\cdot}309\,\mathrm{mm\,s^{-1}}$, $\bar{\Delta} = 0{\cdot}400\,\mathrm{mm\,s^{-1}}$, $\delta_0 = 0{\cdot}299(1)\,\mathrm{mm\,s^{-1}}$, $a = 0{\cdot}024(3)$ and $\Gamma = 0{\cdot}204(1)\,\mathrm{mm\,s^{-1}}$. The relative area of the subspectrum that corresponds to the impurity phase (fig. 5 (*b*)) is 8·8(2)%.

It is important to note that the fit with the distribution of the quadrupole splittings gives a value for the linewidth of the elemental doublets which is only slightly larger than Γ_{nat}. This is expected as the sample used in this study is thin (Greenwood and Gibb 1971). This also confirms that the analysis of the Mössbauer spectra of *i* alloys in terms of $P(\Delta)$ are methodologically correct (Stadnik 1994).

The derived $P(\Delta)$ (fig. 6) has no structure which could be associated with more than one class of Fe sites in *i* $Al_{86}Cr_8Fe_6$. Here the concept of a class of Fe sites, as opposed

Fig. 6



Distributions $P(\varDelta)$ in the icosahedral $Al_{86}Cr_8Fe_6$ phase, corresponding to the fits in fig. 5 (*a*) (solid curve), and fig. 5 (*b*) (dotted curve).

to the concept of a single crystallographic Fe site in crystalline materials with long-range translational order, refers to a multiple of crystallographically different Fe sites which may be part of a 'building block' which, when connected with some 'glue' atoms (Eibschütz *et al.* 1987), could fill up the three-dimensional space. The lack of structure in $P(\varDelta)$ additionally confirms (Stadnik 1994) that the two-site model (Dunlap *et al.* 1988) is an artefact that results from an erroneous analysis of the Mössbauer spectra.

The derived $P(\varDelta)$ is similar, both in its shape and width, to the distributions in amorphous alloys (Maurer, Friedt and Sanchez 1985). This implies the presence of a considerable disorder in *i* $Al_{86}Cr_8Fe_6$. This disorder has at least four major sources. The first is related to the sample production process (rapid solidification) which inherently introduces a random inhomogeneous strain. It is termed phonon strain (Horn, Malzfeldt, DiVincenzo, Toner and Gambino 1986) and it also occurs in ordinary commensurate materials. This type of disorder is clearly reflected in the broadening of the XRD lines (fig. 1 and table 1). The second type of disorder, which is specific to incommensurate solids, is called the phason disorder. Both these types of disorder are present in the metastable SI alloys, but they were shown to disappear in the stable face-centred icosahedral (FCI) alloys (Tsai, Chen, Inoue and Masumoto 1991b). However, the distribution $P(\varDelta)$ is also present in thermodynamically stable FCI alloys (Stadnik 1994) for which the width of the XRD peaks is similar to that found in the best periodic metallic systems. This shows that other types of disorder must be considered. If one envisages that the structure of stable quasicrystals, which are all ternary alloys, consists of an sp-type sublattice associated with Al, Ga or Mg and a d-type sublattice associated with TM elements, then one clearly expects the presence of chemical disorder in these sublattices. Such a disorder must be also present in the studied alloy, and thus it contributes to the observed $P(\Delta)$. As mentioned earlier in this section, the concept of quasiperiodicity implies that no two crystallographic positions of a given atom are exactly the same, which can be regarded as a fourth type of disorder of a topological character. It must also contribute to $P(\Delta)$. It can be concluded that different types of disorder present in the *i* structure contribute significantly to $P(\Delta)$ observed for all *i* alloys (Stadnik 1994).

The XRD analysis of the crystallization products of *i* $Al_{86}Cr_8Fe_6$ (§ 3.1) suggested that they are in the form of crystalline alloys $Al_{13}Fe_4$ and $Al_{13}Cr_{2-x}Fe_x$. To verify this, ^{57}Fe spectra of samples A1 and A2 were recorded. As an example, the spectrum of sample A2 is shown in fig. 7. The spectrum in fig. 7 should result from two subspectra due to $Al_{13}Fe_4$ and $Al_{13}Cr_{2-x}Fe_x$ crystalline alloys. The Mössbauer spectrum of $Al_{13}Fe_4$ is well known (Müller, Rosenberg, Liu and Köster 1991), so its hyperfine parameters were fixed in the fit to the values given in the literature (Müller *et al.* 1991). The crystal structure of $Al_{13}Cr_2$ (Cooper 1960) implies that the second subspectrum due to $Al_{13}Cr_{2-x}Fe_x$ has to be in the form of a quadrupole doublet. As can be seen in fig. 7, a satisfactory fit could be obtained with these two subspectra. The parameters associated with the quadrupole doublet due to $Al_{13}Cr_{2-x}Fe_x$ are $\delta = 0{\cdot}286(4)\,\mathrm{mm\,s^{-1}}$ and $\Delta = 0{\cdot}380(2)\,\mathrm{mm\,s^{-1}}$. It should be noted that they are close to the $\bar{\delta}$ and $\bar{\Delta}$ values that characterize the impurity phase (fig. 5(*b*)) present in *i* $Al_{86}Cr_8Fe_6$. This suggests that a significant fraction of the impurity phase in *i* $Al_{86}Cr_8Fe_6$ consists of $Al_{13}Cr_{2-x}Fe_x$.

3.3. *Magnetic susceptibility*

The temperature dependence of the magnetic susceptibility χ of the *i* $Al_{86}Cr_8Fe_6$ alloy and its crystallization products is shown in fig. 8. It follows the Curie–Weiss law. To allow for the possible presence in the samples of a small amount of a ferromagnetic impurity with the saturation magnetization M_0, the $\chi(T)$ dependence was represented by the equation containing an additional $T^{3/2}$ term associated with the Bloch spin-waves law (Müller *et al.* 1991)

$$\chi = \chi_0 + \frac{C}{T-\Theta} + \frac{M_0}{H}(1 - a_{3/2}T^{3/2}), \tag{1}$$

where χ_0 is the temperature-independent Pauli susceptibility, C is the Curie constant and Θ is the paramagnetic Curie temperature. It should be noted that if M_0/H cannot be neglected, then χ_0 cannot be directly associated with the Pauli susceptiblity. The $\chi(T)$ dependence in fig. 8 was thus fitted to the equation

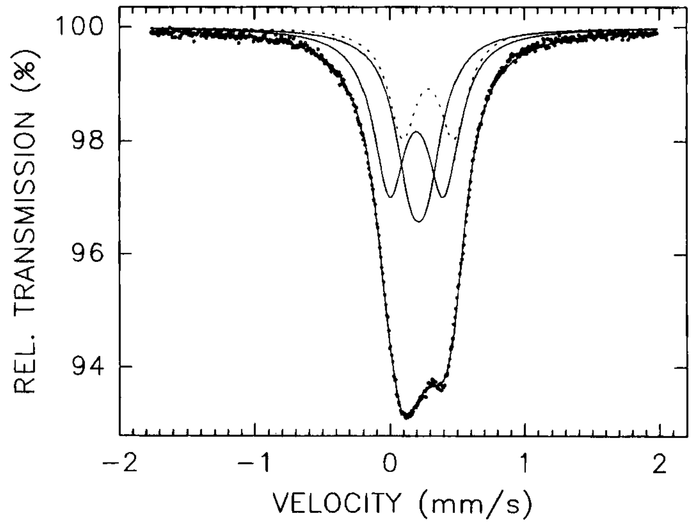
$$\chi = a_0 + \frac{C}{T-\Theta} + a_3T^{3/2}, \tag{2}$$

where $a_0 = \chi_0 + M_0/M$ and $a_3 = -a_{3/2}M_0/H$. The results of the fit are listed in table 3.

The room-temperature magnetization measurement showed that only sample A1 contains a ferromagentic impurity (the magnetization M extrapolated to $H = 0$ was $4{\cdot}8 \times 10^{-3}\,\mathrm{emu\,g^{-1}}$), which resulted in the non-zero value (table 3) of the fitted parameter a_3 (see (2)). The value of M_0 was estimated from the Bloch $T^{3/2}$ law using the values of a_3 from table 3 and M. This $M_0 = 9{\cdot}0 \times 10^{-3}\,\mathrm{emu\,g^{-1}}$ was then used to calculate $\chi_0 = a_0 - M_0/H$, which is given is table 3, from the value $a_0 = 1{\cdot}234 \times 10^{-6}\,\mathrm{cm^3\,g^{-1}}$ obtained from the fit of the $\chi(T)$ dependence (fig. 8(*a*)) to (2).

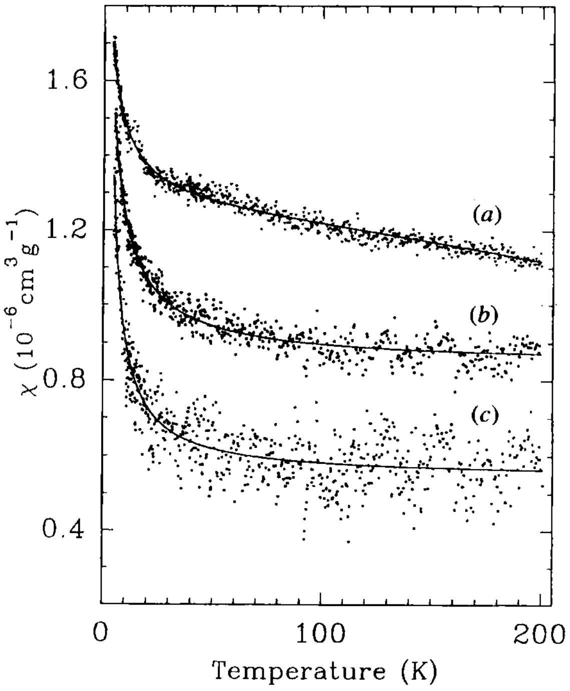
It is reasonable to expect that the ferromagnetic impurity in sample A1 is in the form of a Fe–Cr binary alloy. This can be substantiated as follow. Using the value of M_0

Fig. 7



^{57}Fe Mössbauer spectrum of *i* $Al_{86}Cr_8Fe_6$ annealed at 908 K for 5 min (sample A2) fitted with two subspectra due to $Al_{13}Fe_4$ (solid line) and $Al_{13}Cr_{2-x}Fe_x$ (broken line).

Fig. 8



Temperature dependence of magnetic susceptibility of: (*a*) icosahedral $Al_{86}Cr_8Fe_6$ annealed at 858 K for 5 min (sample A1), (*b*) icosahedral $Al_{86}Cr_8Fe_6$, and (*c*) icosahedral $Al_{86}Cr_8Fe_6$ annealed at 908 K for 5 min (sample A2). The solid lines are the fits.

Table 3. Parameters obtained from the fit of the temperature dependence of the magnetic susceptibility of icosahedral $Al_{86}Cr_8Fe_6$ and its crystallization products (samples A1 and A2). The symbols $\mu_{\mathrm{eff}}^{\mathrm{TM}}$ and $\mu_{\mathrm{eff}}^{\mathrm{Fe}}$ correspond, respectively, to the effective magnetic moments per transitiion-metal (i.e. per Fe and Cr) and per Fe.

Sample	χ_0 (10^{-6} cm^3 g^{-1})	C (10^{-6} cm^3 g^{-1} K)	Θ (K)	a_3 (10^{-11} cm^3 g^{-1} K$^{-3/2}$)	$\mu_{\mathrm{eff}}^{\mathrm{TM}}$ (μ_B)	$\mu_{\mathrm{eff}}^{\mathrm{Fe}}$ (μ_B)
i $Al_{86}Cr_8Fe_6$	0·846 (3)	5·188 (140)	− 3·1 (2)	0·0	0·095 (1)	0·145 (2)
A1	0·719 (32)*	3·315 (116)	− 3·2 (3)	− 4·74 (7)	0·076 (1)	0·116 (2)
A2	0·544 (4)	3·741 (174)	− 0·1 (3)	0·0	0·081 (1)	0·123 (2)

*Calculated from $a_0 - M_0/H$, as explained in the text.

estimated above and the value of a_3 from the fit, one can calculate the coefficient $a_{3/2}$ from the relation $a_{3/2} = -a_3M_0/H$. The value of this coefficient is $9{\cdot}1 \times 10^{-5}\,\mathrm{K}^{-3/2}$. It should be compared with the values of $a_{3/2}$ in the range 3×10^{-5}–$2 \times 10^{-4}\,\mathrm{K}^{-3/2}$ for the binary series $Fe_{1-x}Cr_x$ with $0{\cdot}5 \leqslant x \leqslant 0{\cdot}7$ (Aldred 1976, Stearns 1986).

The values of the Pauli susceptibility χ_0 are similar in the *i* $Al_{86}Cr_8Fe_6$ alloy and in its crystallization products (table 3), and are much the same as the values observed in other Al-based *i* alloys containing Cr and Fe elements (Stadnik, Stroink, Ma and Williams 1989). It can be thus concluded that, from a magnetic point of view, the properties of *i* $Al_{86}Cr_8Fe_6$ are similar to those of corresponding crystalline phases. The negative values of Θ (table 3) indicate the predominantly antiferromagnetic interaction between the TM elements, which was also observed in other Al–TM *i* alloys (Stadnik *et al.* 1989).

The values of the magnetic moments (table 3) are lower than those in other Al–Mn-based *i* alloys (Stadnik *et al.* 1989). This agrees with the experimental fact that Cr atoms do not carry a magnetic moment in the crystalline Al–Cr alloys (Taylor 1961), and thus their presence is expected to decrease the effective magnetic moment in alloys with other TM elements (Fukamichi, Hattori, Nakane and Goto 1993). The non-zero effective magnetic moments in samples A1 and A2 must be mainly due to $Al_{13}Fe_4$ (its $\mu_{\mathrm{eff}}^{\mathrm{Fe}}$ is $0{\cdot}44\,\mu_B$ (Müller *et al.* 1991)) since the magnetic moment of $Al_{13}Cr_{2-x}Fe_x$ is expected to be negligibly small.

The magnetic studies of the *i* series $Al_{73}(Mn_x(Fe_{0{\cdot}5}Cr_{0{\cdot}5})_{1-x})_{21}Si_6$ showed no temperature dependence of the magnetic susceptibility for the composition $x = 0$ (Kandel and Hippert 1992). It was concluded that Fe and Cr bear no magnetic moment in that series. It is argued in the next section that a small magnetic moment observed in the studied *i* $Al_{86}Cr_8Fe_6$ is the consequence of disorder.

It can be thus concluded that *i* symmetry does not produce any magnetic properties in the studied *i* $Al_{86}Cr_8Fe_6$ which are different from those present in similar crystalline systems.

3.4. *Structural disorder and magnetism*

The non-zero value of the effective magnetic moment in *i* $Al_{86}Cr_8Fe_6$ (table 3) raises the question on its origin. This question was first posed after Hauser, Chen and Waszczak (1986a) in an experimental investigation found the presence of a local magnetic moment in *i* $Al_{86}Mn_{14}$ and its absence in the crystalline orthorhombic alloy of the same composition. The widely accepted explanation on the origin of the magnetic moment in *i* alloys has been based on theoretical calculations performed on small Al and Al–Mn clusters (McHenry, Eberhart, O'Handley and Johnson 1986, Bagayoko, Brener, Kanhere and Callaway 1987, McHenry, Vvedensky, Eberhart and O'Handley 1988). These calculations predict that the consequence of the *i* symmetry is the apparent high density of states (DOS) at the Fermi level, DOS (E_F), and the presence of a magnetic moment on Mn atoms. This explanation is at variance with the results of the recent theoretical studies on large clusters (De Coulon, Reuse and Khanna 1993, Liu *et al.* 1993) and on crystalline approximants of *i* alloys (Fujiwara and Yokokawa 1991, Hafner and Krajči 1992), and with the results of the experimental investigations of the electronic structure of *i* alloys (Poon 1992, Belin, Dankhazi and Sadoc 1993, Stadnik and Stroink 1993b). Therefore, it has to be revised.

The earlier conclusion about the high DOS (E_F) (McHenry *et al.* 1986, 1988) disagrees with the results of the recent band-structure calculations (Fujiwara and Yokokawa 1991, Hafner and Krajči 1992) predicting a very small DOS (E_F), which has been confirmed experimentally using soft X-ray emission (Berlin *et al.* 1993), photoemission spectroscopy (Stadnik and Stroink 1993b), and other techniques (Poon 1992). The theoretical calculations by De Coulon *et al.* (1993) and Liu *et al.* (1993) show convincingly that the earlier conclusion (McHenry *et al.* 1986, 1988, Bagayoko *et al.* 1987) regarding the finite Mn magnetic moment induced by the *i* symmetry is an artifact resulting from the small clusters used to mimic an *i* alloy, and that Mn atoms in an environment with *i* symmetry should be non-magnetic. If this is the case, then the origin of the non-zero magnetic moments in Al–TM *i* alloys must be associated with other effects.

The first possibility is related to a pair TM–TM magnetic interaction, as first suggested by Hauser *et al.* (1986a) for *i* Al–Mn alloys. It is based on the experimental observation (Hauser *et al.* 1986a, Fukamichi *et al.* 1993) of the increase of the effective magnetic moment with the Mn concentration in Al-based *i* alloys. The second possibility, which was first proposed by Warren, Chen and Espinosa (1986) and Hauser, Chen, Espinosa and Waszczak (1986b), is associated with the presence of disorder in *i* alloys. We suggest below that these two mechanisms are interrelated.

It is well established that magnetic interactions depend crucially upon interatomic distances. It has been demonstrated via modern total-energy band calculations that there is a transition from a non-magnetic state to a magnetic one with increasing volume both in pure TM and in their alloys (Moruzzi and Marcus 1992, 1993). This general result is due to the fact that at low volumes the d bands are spread over wide energy ranges, resulting in a low value of DOS (E_F) which prevents the Stoner criterion for magnetic moment formation to be fulfilled; at large volumes the opposite is true. There is thus a system-dependent critical separation between the TM atoms below which they carry no magnetic moment; this moment appears for separations larger than the critical one. This picture then implies that the presence of structural disorder, which involves different TM–TM separations, in an alloy may be crucial for the formation of a magnetic moment.

There are several experimental facts which clearly demonstrate the presence of disorder in both metastable and stable *i* alloys. The structural disorder is manifested in the metastable *i* alloys as a broadening of the XRD peaks. This is also observed for the studied *i* $Al_{86}Cr_8Fe_6$ (fig. 1 and table 1). The thermodynamically stable *i* alloys, such as Al–Cu–Fe (Ru, Os) or Al–Pd–Mn, are sometimes called 'perfect', since their XRD peaks are as sharp as the peaks of the best periodic alloys. It is less recognized, however, that local probes, such as MS or nuclear magnetic resonance (NMR), provide evidence (Stadnik 1994) for the presence of a structural disorder which is more sensitive than that provided by the XRD technique. As is discussed in § 3.2, the derived distribution $P(\Delta)$ is the measure of disorder and such a distribution is present even in perfect (from an XRD point of view) *i* alloys (Stadnik 1994).

Structural disorder is necessary for the occurrence of spin-glass characteristics in a given compound (Binder and Young 1986). Spin-glass behaviour, which was observed both in metastable (Hauser *et al.* 1986a, Stadnik *et al.* 1989, Berger and Prejean 1990, Fukamichi *et al.* 1993) and stable (Chernikov, Bernasconi, Beeli, Schilling and Ott 1993) *i* alloys, is thus another manifestation of the influence of disorder on the formation of a magnetic moment. Also the experimental fact of the presence of the magnetic moment in the *i* and amorphous alloys, but its absence in the crystalline alloys of similar composition (Hauser *et al.* 1986a, b), as well as the overall similarity of other magnetic properties of *i* and amorphous alloys (Godinho, Berger, Lasjaunias, Hasselbach and Bethoux 1990), are evidence for disorder being a common origin for the moment formation in *i* and amorphous alloys. And finally, the presence of the distribution of the interatomic distances between the TM atoms in the *i* alloys naturally explains the existence of two classes of TM atoms (Eibschütz *et al.* 1987, Stadnik *et al.* 1989, Godinho *et al.* 1990); those TM atoms with TM–TM distances smaller than the critical one would bear no magnetic moment, whereas those for which these distances are larger than the critical distance would carry a magnetic moment.

The origin of the small magnetic moment observed in the studied *i* $Al_{86}Cr_8Fe_6$ (fig. 8 (*b*) and table 3) can be thus associated with the disorder present in the sample rather than its *i* structure. This is consistent with the expected low value of DOS (E_F), which is believed to be an intrinsic property of *i* alloys (Fujiwara and Yokokawa 1991, Hafner and Krajči 1992), and which via the Stoner criterion does not promote the formation of a magnetic moment. Although no experimental electronic structure studies were performed for *i* $Al_{86}Cr_8Fe_6$ to verify the expected low value of DOS (E_F), one can apply the following qualitative argument to indicate that this value must be small. The formation and stability of the *i* alloys appears to be qualitatively explained in terms of the Hume-Rothery rules (Inoue *et al.* 1990). The *i* alloys seem to form for certain well defined values of the electron-per-atom ratios *e*/*a* (Inoue *et al.* 1990). At these critical ratios the Fermi sphere of radius k_F just touches a Brillouin zone plane, i.e. $2k_F = Q$. This corresponds to the opening of an energy gap at the Fermi surface, giving rise to a minimum in DOS (E_F). Following Inoue *et al.* (1990), one can find that $e/a = 2{\cdot}05$ for *i* $Al_{86}Cr_8Fe_6$, from which the value $2k_F = 3{\cdot}176\,\text{Å}^{-1}$ can be calculated. The latter compares well with the Q values corresponding to the two strongest *i* peaks (table 1).

§ 4. CONCLUSIONS

A distribution of the electric quadrupole interaction in the *i* $Al_{86}Cr_8Fe_6$ alloy reflects the presence of a structural disorder, which is an intrinsic property of all *i* alloys. The analysis of the Mössbauer spectra of *i* alloys in terms of two quadrupole doublets is shown to be methodologically incorrect, and the notion of the so-called two-site model is also shown to be unfounded. The formation of a small magnetic moment in the studied alloy is mainly due to this disorder, since the density of electronic states at the Fermi level is expected to be very small. In view of recent theoretical and experimental advances in the understanding of the electronic structure of icosahedral alloys, a close relation between disorder of icosahedral alloys and their magnetic properties is discussed. The crystallization products of the studied alloy are $Al_{13}Fe_4$ and $Al_{13}Cr_{2-x}Fe_x$ and the crystallized samples have a small magnetic moment due the moment of Fe atoms in $Al_{13}Fe_4$.

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