

Physical properties of icosahedral $\text{Al}_{86}\text{Cr}_8\text{Fe}_6$

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X-ray diffraction, ⁵⁷Fe Mössbauer effect, differential scanning calorimetry, and magnetic susceptibility measurements have been performed on the icosahedral $\text{Al}_{86}\text{Cr}_8\text{Fe}_6$ alloy. It is found that Fe atoms are distributed among a multiplicity of sites, which is interpreted as evidence of intrinsic disorder present in metastable icosahedral alloys. It is shown that the crystallization products of the alloy under study are $\text{Al}_{13}\text{Fe}_4$ and $\text{Al}_{13}\text{Cr}(\text{Fe})_2$. It is found that the transition metal atoms in both the icosahedral alloy and its crystallization products possess a localized magnetic moment.

1. Introduction

Soon after remarkable discovery by Shechtman et al. [1] of an icosahedral (i)-phase in the $\text{Al}_{86}\text{Mn}_{14}$ alloy, attempts to find other binary Al–TM (TM = transition metal) i alloys were made. It was soon established that such alloys can be also produced with other TM atoms (Cr, V, Mo, Ru, W, Re). There was some controversy concerning the formation of Al–TM i alloys with other TM elements. For example, it was claimed that an i-phase also exists in Al–TM alloys with TM = Fe [2–8], Co and Ni [9]. However, careful diffraction studies either failed to find evidence for the existence of the i-phase in these systems [10] or showed that decagonal- rather than i-phase is formed for TM = Fe [11], and Co and Ni [12].

It was soon realized that a much wider choice of i systems can be obtained in Al-based ternary alloys which, at the same time, are of better quality than the binary ones (purely single phase, less defective or with no defects, and possibly thermally stable). For example, adding Si or Ru

to i-Al–TM alloys significantly improves their quality [10,13]. Similarly, ternary alloys with TM = $\text{Cr}_{1-x}\text{Fe}_x$ [7,8,14] exhibit a much higher degree of i order than the corresponding binary alloys.

The influence of composition on the degree of the i order in Al-($\text{Cr}_{1-x}\text{Fe}_x$) system was systematically studied by Manaila et al. [15]. These authors found that the optimal composition for the formation of an i-phase occurs for x between 0.40 and 0.45. This result was later confirmed by Lawther et al. [3]. We therefore chose the alloy $\text{Al}_{86}\text{Cr}_8\text{Fe}_6$ ($x = 0.43$) for studies of its physical properties.

2. Experimental procedure

An ingot of $\text{Al}_{86}\text{Cr}_8\text{Fe}_6$ was prepared by arc-melting high-purity elemental constituents in an argon atmosphere. After having been melted by induction heating in a quartz tube, the ingot was rapidly solidified by ejecting the melt through a 0.8 mm orifice with 70 kPa overpressure of argon. The molten alloy impinged upon a circumferential surface of the copper wheel rotating with a tangential velocity of 50 m/s in a helium atmosphere. The ribbons produced were about 2 mm wide and 2 cm long.

Room-temperature X-ray diffraction (XRD) measurements of the as-quenched sample and its

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crystalline products obtained by annealing the sample for a few minutes at 858 (sample A1) and 908 K (sample A2) were performed on a Siemens D500 and a Philips X'Pert scanning diffractometers using $Cu K\alpha$ radiation. For the XRD measurements, the ribbons were gently pulverized and in the analysis the $Cu K\alpha_2$ contribution to the spectra was subtracted. A differential scanning calorimetry (DSC) measurement was done using DuPont 9900 model apparatus at the heating rate of 20 K/min.

^{57}Fe Mössbauer effect (ME) measurements were performed at room temperature using a standard Mössbauer spectrometer operating in the triangular mode. The spectrometer was calibrated with a $6.35 \mu m$ Fe foil, and the spectra were folded. The surface densities of the as-quenched, A1, and A2 samples were respectively 9.1, 11.4, and 11.6 mg/cm^2 . Magnetic susceptibility measurements were conducted using a vibrating sample magnetometer in the temperature range 4.2–210 K and in the magnetic field of 17.5 kOe.

3. Results

3.1. X-ray diffraction

The XRD pattern of the as-quenched $Al_{86}Cr_8Fe_6$ alloy exhibits peaks due to the *i*-phase and unreacted Al (fig. 1). We use here the indexing scheme of Bancel et al. [16]. The positions of the six strongest *i* peaks, (110001), (1110 $\bar{1}$ 0), (100000), (110000), (111000), and (101000), were used to fit the experimental Q values ($Q = 4\pi \sin \Theta/\lambda$), Q_{expt} , to the straight line mQ_{\parallel} , where Q_{\parallel} is the length of the general Bragg vector calculated for a given $(n_1 n_2 n_3 n_4 n_5 n_6)$ peak [16], and m is a scale factor related to the interatomic distance in a given *i* alloy. Such a fit is shown in fig. 2. The value of $m = 1.514(1) \text{ \AA}$ obtained from this fit was used to calculate the positions of the expected low-intensity *i* peaks. As can be seen in fig. 1, the low-intensity *i* peaks (21 $\bar{1}$ 001), (210001), (111100), and (210000) show up at the calculated positions. All XRD peaks in fig. 1 can be accounted for, and it is thus con-

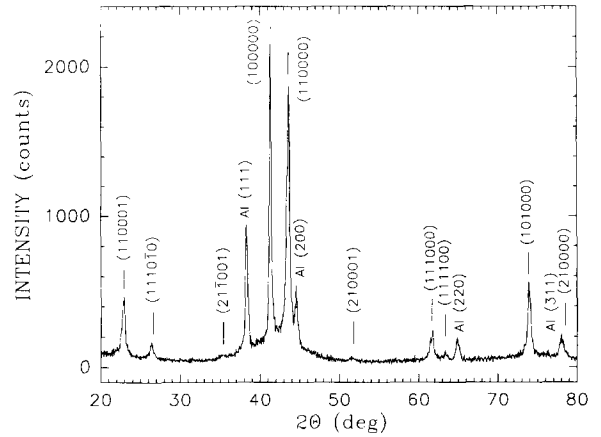


Fig. 1. X-ray diffraction pattern of as-quenched $Al_{86}Cr_8Fe_6$ alloy. The vertical lines above the *i* peaks correspond to the positions calculated on the basis of the fit shown in fig. 2.

cluded that the as-quenched $Al_{86}Cr_8Fe_6$ alloy consists of only *i*-phase and some unreacted elemental Al. Using the m value from the fit, one can calculate the 'quasilattice constant', a_R (the edge length of the rhombic dodecahedron cells that make up the three-dimensional Penrose tiling [17]), which for the studied alloy is $4.621(4) \text{ \AA}$. The full width at half maximum of the (100000) peak is 0.018 \AA^{-1} and is larger than the experimental resolution of the diffractometer (0.005 \AA^{-1}). This line broadening mainly reflects the

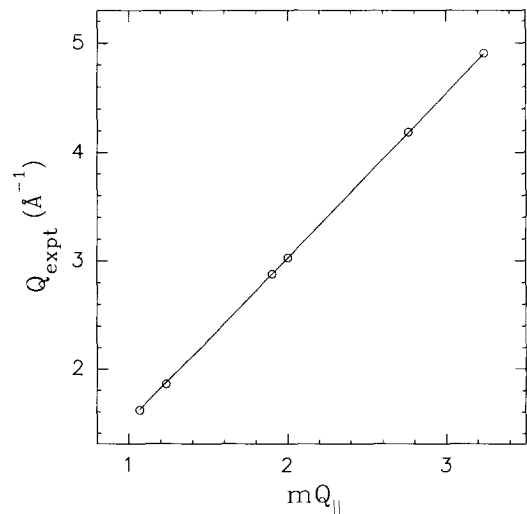


Fig. 2. Experimental values of the wavevectors determined from the selected peak positions in fig. 1 fitted to the straight line mQ_{\parallel} , as described in the text.

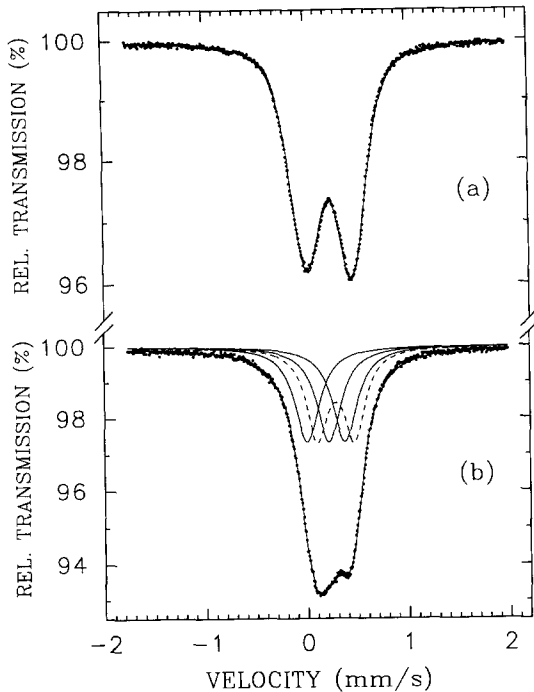


Fig. 3. ^{57}Fe Mössbauer spectrum of (a) $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ fitted (solid line) with the one-Gaussian-component model and of (b) sample A2 fitted with two-component subspectra corresponding to $\text{Al}_{13}\text{Fe}_4$ (three singlets drawn with a solid line) and $\text{Al}_{13}\text{Cr}(\text{Fe})_2$ (a doublet drawn with a dashed line).

presence of structural defects introduced by the melt-spinning process, which may smooth any possible unusual features in the physical properties of the i alloy induced by its quasiperiodicity.

3.2. Mössbauer effect (ME)

The ME spectrum of the i sample (fig. 3(a)) exhibits two broad lines resulting from the electric quadrupole interactions. The full linewidths at half maximum, Γ , obtained from a fit with a single asymmetric Lorentzian doublet are 0.376(1) and 0.329(3) mm/s, respectively, for the low-velocity and high-velocity lines. This should be 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. Since the Mössbauer absorber is very thin (the effective absorber thickness $T_a = 0.576f_a$, where f_a is the absorber Debye–Waller factor [18]), the expected line

broadening due to the absorber thickness is negligibly small. Thus the broad lines indicate the existence of the distribution, $P(\Delta)$, of the quadrupole splittings, Δ [18].

Broad, two-lines quadrupole spectra of i alloys are sometimes fitted with two symmetric doublets [6,7,19–21]. On the basis of such fits, claims were made about the existence of two distinct TM sites [20] (this should not be confused with two classes of TM sites [22,23]) in i alloys. As was discussed in detail earlier [22,24], the two-doublet fits are incorrect for two reasons. First, they are methodologically unjustified since the value of Γ of one of the doublets is either much larger [6,7,19–21] than the expected value for a given Mössbauer absorber or smaller than the natural linewidth 0.194 mm/s (table I in ref. [21]). Second, in-field Mössbauer spectra [25] are at variance with the two-site model.

The ME spectrum of the $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ alloy (fig. 3(a)) was fitted using a recently proposed method [26] for obtaining an arbitrary-shape $P(\Delta)$ equal to a sum of Gaussian components. The asymmetry of the spectral lines was taken into account by assuming a linear coupling between the isomer shift (relative to $\alpha\text{-Fe}$) δ and Δ , $\delta = \delta_0 + a\Delta$, where δ_0 and a are fitted parameters. A reasonably good fit (fig. 3(a)) could be obtained with only one Gaussian component. The values of fitted parameters $\bar{\Delta}$, σ_Δ , δ_0 , a , and $\bar{\delta}$ are respectively 0.454(1) mm/s, 0.189(1) mm/s, 0.238(1) mm/s, $-0./025(1)$, and 0.226(1) mm/s. The width, σ_δ , of the Gaussian distribution of δ is equal to $\text{abs}(a\sigma_\Delta) = 0.0048(3)$ mm/s. The value of Γ was set to 0.230 mm/s during the fit; this choice of Γ is substantiated by the thickness of the absorber used and the broadening produced by the spectrometer. The presence of a wide distribution of quadrupole splittings observed for metastable $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ and for other i alloys [22–27], including the thermodynamically stable $i\text{-Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ [24] whose XRD peaks have the widths comparable with the resolution of the diffractometer [24], is direct evidence of the multiplicity of TM sites. This distribution can also be interpreted as the manifestation of topological disorder which must be an intrinsic property of i alloys.

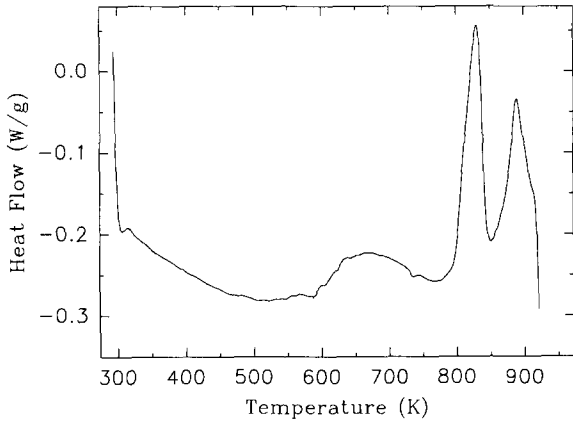


Fig. 4. Differential scanning calorimetry curve of $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$.

3.3 Differential scanning calorimetry

The DSC curve of $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ (fig. 4) exhibits a broad exothermic peak at 663.5 K and two exothermic peaks at 830.4 and 885.5 K. The corresponding heats of transformation are 13.5, 22.9, and 11.2 J/g. To determine the crystallization products, the i sample was heated to 858 K (above the second but before the third peak in fig. 4) and to 908 K (above the third peak), and the XRD spectra of the corresponding samples A1 and A2 were measured. As an example, the XRD spectrum of sample A2 is shown in fig. 5. All the 91 lines can be accounted for as originating from unreacted Al, and the $\text{Al}_{13}\text{Fe}_4$ (PDF 29-42) and

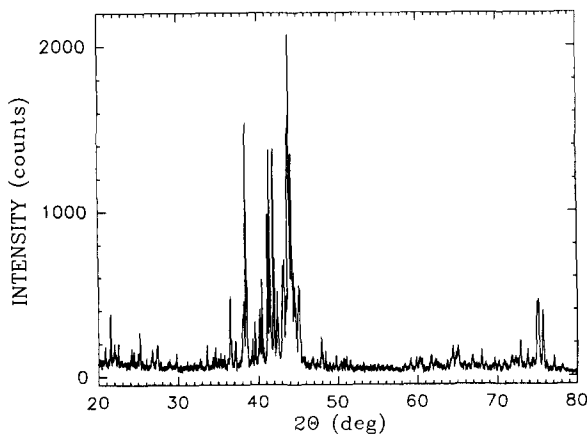


Fig. 5. X-ray diffraction pattern of $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ heated to 908 K.

$\text{Al}_{13}\text{Cr}_2$ (PDF 29-14) alloys. The above analysis suggests that the crystallization products of $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ are $\text{Al}_{13}\text{Fe}_4$ and $\text{Al}_{13}\text{Cr}(\text{Fe})_2$, where in the latter alloy part of Cr is believed to be partially replaced by Fe. To test this conjecture, the ME spectrum of sample A2 (fig. 3(b)) was fitted to two subspectra. The first subspectrum must originate from $\text{Al}_{13}\text{Fe}_4$ and its shape can be well described by three lines of equal width and intensity [28]. In order to obtain a satisfactory fit to the spectrum in fig. 3(b), the second subspectrum had to be in the form of a quadrupole doublet, which is compatible with the crystal structure of $\text{Al}_{13}\text{Cr}_2$ [29]. The positions of the three lines describing the $\text{Al}_{13}\text{Fe}_4$ subspectrum are 0.000(2), 0.215(1), and 0.372(4) mm/s (their linewidth is 0.297(3) mm/s) and are in good agreement with the positions determined in ref. [28]. The parameters of the $\text{Al}_{13}\text{Cr}(\text{Fe})_2$ doublet are $\delta = 0.282(1)$ mm/s, $\Delta = 0.369(2)$ mm/s, and $\Gamma = 0.255(4)$ mm/s.

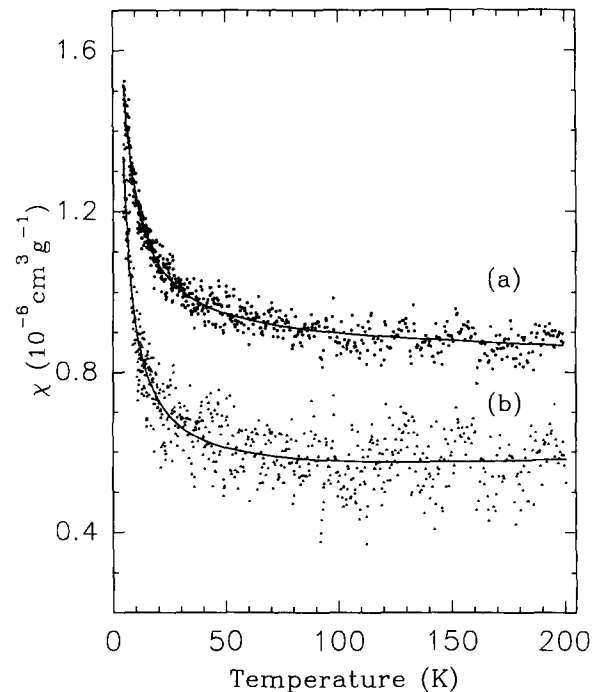


Fig. 6. Temperature dependence of magnetic susceptibility of (a) $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ and (b) $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ heated to 908 K. The solid lines are the fits, as described in the text.

3.4. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility, $\chi(T)$, was fitted assuming the Curie–Weiss law, as described in ref. [30]. The values of the temperature-independent susceptibility, χ_0 , the Curie constant, C , and the paramagnetic Curie temperature, Θ_p , with their errors obtained from the fit, are respectively $0.855(6) \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, $4.914(210) \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ K}$, and $-2.7(3) \text{ K}$ for the i alloy, and $0.522(9) \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, $4.256(277) \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ K}$, and $-0.7(4) \text{ K}$ for sample A2 (fig. 6). The effective magnetic moments per transition metal in these samples are respectively $0.093\mu_B$ (or $0.142\mu_B$ per Fe atom) and $0.086\mu_B$ (or $0.132\mu_B$ per Fe atom). The non-zero effective magnetic moment in sample A2 is mainly due to $Al_{13}Fe_4$ (its effective magnetic moment per Fe is $0.44\mu_B$ [30]) as the effective magnetic moment of $Al_{13}Cr(Fe)_2$ is expected to be negligibly small.

We conclude that the i symmetry does not induce in the Al–Cr–Fe system magnetic properties which are significantly different from the properties of a corresponding crystalline system.

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