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Influence of Thermal Treatment and Crystal Growth on the Final Composition and Magnetic Properties of the YFe_xAl_{12-x} ($4 \leq x \leq 4.2$) Intermetallics

J. C. Waerenborgh,*[,†] P. Salamakha,[†] O. Sologub,[†] A. P. Gonçalves,[†] C. Cardoso,[‡]
S. Sério,[‡] M. Godinho,[‡] and M. Almeida[†]

Departamento de Química, Instituto Tecnológico e Nuclear, P-2686-953 Sacavém, Portugal, and Departamento de Física, Faculdade de Ciências da Universidade de Lisboa, P-1749-016 Lisboa, Portugal

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A study by powder X-ray diffraction (using the Rietveld method of structure refinement), ^{57}Fe Mössbauer spectroscopy, and magnetization measurements have shown that YFe_4Al_8, although a stable phase at 1070 K (space group $I4/mmm$, $a = 8.7604(7)$ Å, $c = 5.0504(5)$ Å), does not melt congruently. Large single crystals obtained by the Czochralski method from bulk charges containing Y, Fe, and Al in the atomic ratios 1/4/8 have final compositions $YFe_{4.2(2)}Al_{7.8(2)}$ (space group $I4/mmm$, $a = 8.7303(3)$ Å, $c = 5.0486(2)$ Å). $YFe_{4.2}Al_{7.8}$ shows an antiferromagnetic-like transition at $T_{ord} = 100$ K, in contrast with YFe_4Al_8 ($T_{ord} = 180$ K). In $YFe_{4.2}Al_{7.8}$ a distribution of the moduli of the Fe magnetic moments (μ_{Fe}) is observed between 100 K and ~50 K. Below 45 K the Fe atoms on the 8f site have two different values of μ_{Fe} and on the 8j sites only one is observed. The relative values of the μ_{Fe} may be understood on the basis of the Fe−Fe intersite exchange interactions.

Introduction

Intermetallic systems containing an f element and Fe, crystallizing in the $ThMn_{12}$-type structure, are potential candidates for permanent magnets with the lowest f-element content.[1] In this tetragonal body-centered structure (space group $I4/mmm$), the f element is located on the origin of the unit cell, equiposition 2a, and the other atoms occupy the 8f, 8j, and 8i sites (Figure 1). Besides the potential economical impact, these materials have been extensively studied for the elucidation of the fundamental principles of magnetism and the understanding of their transport properties on the basis of their electronic structure.[1,2] The study of AFe_4Al_8 (A = lanthanide or U) compounds, where the sublattices of Fe (magnetic) and Al (nonmagnetic) are clearly separated, is an important contribution to the understanding of the coupling between the magnetic (f and d) sublattices. The case of nonmagnetic A (= Y, Lu), where there is only one kind of atom carrying a magnetic moment, can be used as a good starting point.

YFe_4Al_8 has been extensively studied. Published results suggest rather complex magnetic properties but are not always consistent. Early ^{57}Fe Mössbauer data of RFe_4Al_8 (R = rare earth) published by Van der Kraan and Buschow[3,4] indicated that well below the magnetic ordering temperature, $T_{ord} \approx 185$ K, the spectra consisted of a single magnetic splitting. However no details of the temperature dependence of the magnetic hyperfine fields (B_{hf}) were given. Certainly due to differences in the synthesis, distinct spectra were later reported for YFe_4Al_8 by different authors.[5] Recent studies made by powder neutron diffraction and ^{57}Fe-Mössbauer spectroscopy have confirmed $T_{ord} \approx 185$ K and have shown that the Fe magnetic moments, μ_{Fe}, give rise to a complex antiferromagnetic (AF) ordering.[6]

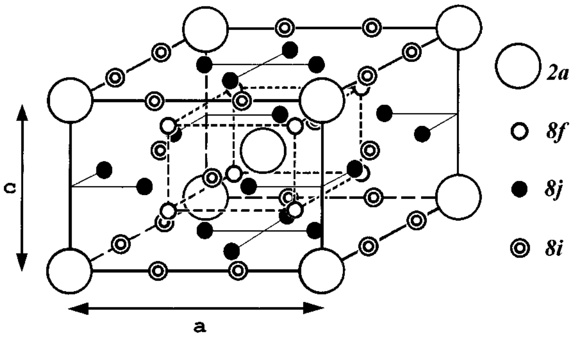

Figure 1. Crystallographic unit cell of the $ThMn_{12}$-type structure. The f-element atoms are located at the origin and body-centered positions (2a sites). The other atoms occupy the 8f, 8j, and 8i sites.

Single-crystal neutron diffraction is a powerful tool for the determination of magnetic structures. Particu-

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* Corresponding author. E-mail: jcarlos@itn1.itn.pt. Fax +351-21-994-14-55. Phone +351-21-994-60-00.

[†] Instituto Tecnológico e Nuclear.

[‡] Universidade de Lisboa.

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larly in the case of $ThMn_{12}$-type phases this technique has recently allowed the determination of the magnetic structure of UFe_4Al_8.[7] Magnetization and susceptibility measurements performed on single crystals grown from a bulk charge containing Y, Fe, and Al in the atomic ratio 1:4:8 have shown an AF transition at ~100 K and another anomaly at ~60 K.[8] These single crystals were also examined by neutrons. Symmetric pairs of satellites appearing at 100 K around the nuclear Bragg peaks correlate with the large AF-like anomaly observed in the susceptibility measurements. However, these results are not consistent with those obtained by powder neutron diffraction,[6] namely the T_{ord} reported which are significantly different (185 K in ref 8 and 100 K in ref 6).

To explain these inconsistencies, and within the frame of a systematic study of the Y−Fe−Al ternary system,[9] a detailed investigation of the relation between magnetic and structural properties of the YFe_xAl_{12-x} ($4 \leq x \leq 4.2$) intermetallics prepared in different conditions, by powder and single-crystal X-ray diffraction (XRD), ^{57}Fe-Mössbauer spectroscopy and magnetization measurements is presented in this work.

Experimental Section

The starting materials, Y, Fe, and Al metal, for the preparation of the ternary alloys were used in the form of ingots with purity higher than 99.9%. Six bulk charges were prepared: three hereafter referred to as 1Y/4Fe/8Al, containing Y, Fe and Al in the atomic ratios 1/4/8, respectively, and another three, 1Y/4.2Fe/7.8Al, containing the same elements in the atomic ratios 1/4.2/7.8. For each composition two of the bulk charges weighted 2 g and the third one ~12 g. All of them were arc melted under high-purity argon on a water-cooled copper crucible. To ensure homogeneity the obtained buttons were turned around and melted at least twice. The weight losses during melting were less than 1%. All the samples were examined by X-ray powder diffraction as explained below. The first bulk charge from each composition was annealed under vacuum at 870 K for 80 days and the second at 1070 K for 30 days.

Large single crystals were grown from the third bulk charges of each of the above compositions in an induction furnace with a levitation cold crucible, by the Czochralski method, using a tungsten needle as a seed. A pulling rate of 2 cm/h and a rotation rate of 15 rpm were employed as described earlier.[10] Part of these pulled materials were ground and used as polycrystalline samples for powder XRD, magnetization, and for ^{57}Fe-Mössbauer effect measurements.

Finely ground powders of each sample prepared was back pressed into standard aluminum holders for powder X-ray diffraction (XRD). Diffracted X-ray intensities were collected on a Philips automated diffractometer system PW1710. A PW1820 Bragg Brentano goniometer, fitted with a PW1752 curved graphite crystal monochromator, incident and diffracted beam Soller slits, one divergence and antiscatter slits, and a 0.2 mm receiving slit, was used. The intensity measurements were made with a normal focus Cu tube operated at 40 kV and 30 mA and using a takeoff angle of 5°. The data were recorded with a 2θ-step size of 0.02° in a 2θ range of 18.00−100.00° and a counting time of 13 s at each step.

All the diffraction peaks which did not correspond to a $ThMn_{12}$-type phase could be assigned to the strongest peaks of the Y−Al and the Fe−Al binary alloys referred below, by comparing the experimental data with the PDF database.[11] To confirm the presence of these additional phases it was checked that all the strongest peaks of the identified binary alloys were either present or overlapping the peaks of the $ThMn_{12}$-type phase.

The least-squares structure refinements of the $ThMn_{12}$-type phases in the samples containing less than 1% impurity phases, were undertaken with the Rietveld powder profile program[12] assuming space group $I4/mmm$. An experimentally determined Kα1/Kα2 intensities ratio of 0.5, a factor $\cos\theta = 0.7998$ for the monochromator polarization correction, the scattering factors for neutral atoms (as defined in ref 12) and a pseudo-Voigt profile shape function were used. The background was refined with a polynomial function.

Site occupation factors assuming the 8f site occupied by Fe and the 8j and 8i sites occupied by Al were allowed to vary. For the 8j sites of three of the samples the estimated values of these parameters have refined to significantly higher values than 100% occupation by Al. In those cases, Fe and Al are assumed to share the 8j site and the fraction of this site occupied by each kind of atom was refined assuming full-site occupancy.

Magnetization measurements were performed on powder samples of the 1Y/4Fe/8Al material annealed at 1070 K, the 1Y/4Fe/8Al pulled material, and the 1Y/4.2Fe/7.8Al material annealed at 870 K using a SQUID magnetometer (MPMS Quantum Design). For all the samples the magnetization was measured as a function of temperature in the range 5−300 K, under low applied fields (<50 mT) after both zero-field-cooling (ZFC) and field-cooling (FC) procedures (M vs T curves). Magnetization was also obtained as a function of applied field for fields up to 5.5 T for different constant temperature values (M vs B curves).

^{57}Fe-Mössbauer effect measurements were performed both on samples prepared as polycrystalline material and on samples obtained from crushing the material pulled from their melts. Powdered samples were pressed together with Lucite powder into Perspex holders, to obtain homogeneous and isotropic Mössbauer absorbers containing ~5 mg/cm^2 of natural iron. The ^{57}Fe-Mössbauer spectroscopy results were obtained in the transmission mode using a constant-acceleration spectrometer and a 25 mCi ^{57}Co source in Rh matrix. The velocity scale was calibrated using an α-Fe foil at room temperature. Spectra were collected at several temperatures between 300 and 5 K. Low-temperature spectra were obtained using a flow cryostat with temperature stability of ± 0.5 K. The spectra were fitted to Lorentzian lines using a modified version of the nonlinear least-squares computer method of Stone.[13] The fitting procedure was the same used in the case of the UFe_xAl_{12-x} intermetallics and is described in detail elsewhere.[14]

Results

Polycrystalline Material Prepared from 1Y/4Fe/8Al Bulk Charges. Powder XRD of the 1Y/4Fe/8Al as-cast bulk charge shows diffraction peaks corresponding to the strongest peaks of YAl_3 (low-temperature polymorph crystallizing in space group $R\bar{3}m$), Fe_2Al_5 and $FeAl_3$ (Figure 2a). Peaks corresponding to interatomic distances 2.03 and 1.18 Å are also detected suggesting

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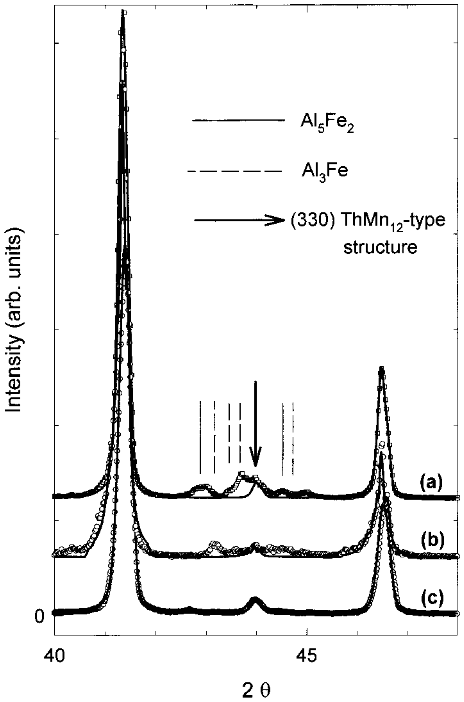

Figure 2. Details of the powder X-ray diffractograms of 1Y/4Fe/8Al bulk charges, as cast (a), annealed at 870 K (b), and annealed at 1070 K (c), showing the 2θ range where the strongest peaks of the Fe_2Al_5 and $FeAl_3$ impurity phases and the (330) peak of YFe_4Al_8 are detected.

the presence of Fe_3Al (Al dissolved in α-Fe), which would indicate that the obtained material is far from equilibrium.

Fe_2Al_5 and $FeAl_3$ are the compositions found in the PDF database.[11] More accurately, the most frequently occurring equilibrium intermetallics in Al base alloys are the θ ($FeAl_3$ or Fe_4Al_{13}) and the η (Fe_2Al_5) phases which have a temperature-dependent composition. Their lattice parameters depend on the exact composition.[15] Therefore, on nonequilibrated samples broad diffraction peaks should be expected, as well as slight deviations of their positions relative to those of standard phases equilibrated at well-defined temperatures such as those reported in ref 11.

After annealing for 2 months at 870 K, although with relative diffracted intensities lower than in the as-cast sample, the Fe_2Al_5 and $FeAl_3$ are still present (Figure 2b). It should be noticed that with powder diffractograms obtained with lower quantities of sample or with faster 2θ-scan speeds such a low content of these impurity phases might have been overlooked. The strongest peaks of Fe_2Al_5 and $FeAl_3$ are very close to the (330) reflection of the $ThMn_{12}$-type phase and may be easily mistaken by this reflection if their relative intensities are very low. However, the presence of both these phases, which are still paramagnetic at 6 K,[15] was confirmed by the Mössbauer spectrum taken at this temperature (Figure 3). As in the spectrum reported for YFe_4Al_8 in ref 5, the relative intensities of the central peaks observed in the spectrum shown in Figure 3 are much larger than those expected for a single magnetic splitting, as reported for YFe_4Al_8 annealed at 1070 K in ref 3.

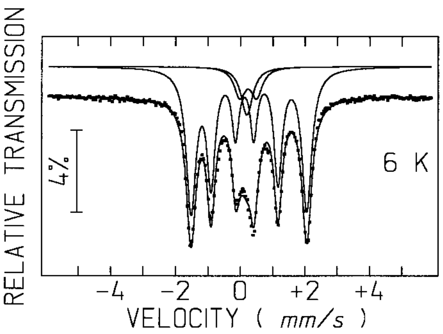

Figure 3. Mössbauer spectrum, at 6 K, of the YFe_4Al_8 sample prepared as polycrystalline material and annealed at 870 K. Quadrupole doublets are due to the presence of paramagnetic $FeAl_3$ (unresolved doublet) and Fe_2Al_5.

In the powder XRD diffractogram of our sample annealed for 30 days at 1070 K, the relative intensity of the strongest peak corresponding to an impurity phase is less than 0.5% of the strongest peak of the $ThMn_{12}$-type phase (Figure 2c). The Rietveld analysis of the powder XRD data is consistent with YFe_4Al_8 composition and indicates that Fe is only present on the 8f site, in agreement with published results.[6] Other relevant parameters are summarized in Table 1.

At room temperature the Mössbauer spectrum (Figure 4) consists of a symmetrical doublet: line widths and relative areas of each peak are equal within experimental error. This is consistent with each kind of atom being present on only one crystallographic site. The Mössbauer spectra taken below ~50 K show a single sextet and are very similar to those reported in ref 3. At 6 and 41 K, the estimated B_{hf} are 10.7 T (Table 2) and 10.5 T, respectively, in agreement with the single value of μ_{Fe} reported by Papamantellos et al.[6] At 55 K and above, although only six lines are observed, their relative intensities and widths are physically unreasonable. Particularly those of the inner pair of peaks are very large and increase with temperature. If more than one sextet is considered (Figure 4) the ratio of the relative areas $I_{1,6}/I_{2,5}/I_{3,4}$ may be kept equal to 3:2:1 for each sextet and the line widths of each line pair increase only slightly from the inner to the outer lines of each sextet, typically $\Gamma_{1,6}/\Gamma_{2,5}/\Gamma_{3,4} \approx 1.2/1.1/1.0$. Furthermore, the quality of the fit is significantly improved by considering more than one sextet.

At 100 K, paramagnetic Fe is already present in the sample. The fraction of paramagnetic Fe increases gradually with increasing temperature up to 185 K where all the Fe is paramagnetic (Figure 4) in agreement with magnetization measurements which show a broad maximum in both M vs T curves, obtained after FC and ZFC, at ~180 K (Figure 5). Other features of these magnetization curves may be understood on the basis of the Mössbauer results. Below ~180 K a fraction of the Fe atoms becomes magnetically ordered; this fraction increases as temperature decreases until at ~100 K, where a change in the slope of the M vs T curves is observed, all the Fe atoms become magnetically ordered. It is noteworthy that the same correlation between Mössbauer results and similar anomalies on magnetization data was already reported for other $ThMn_{12}$-type intermetallics: $RFe_{9.5}Mo_{2.5}$ (R = Y, Nd, Dy, and Er).[16] Finally at 5 K, the observed increase of the

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Table 1. Crystallographic Data Including Estimated Atomic Positions (*x,y,z*), Site Occupations (in atoms/fu) and Equivalent Isotropic Temperature Factors (B_{eq}) from the Rietveld Analysis of the Powder XRD Data of the Samples Containing Less than 1% Impurity Phases

sample	1Y/4Fe/8Al 1070 K	1Y/4Fe/8Al pulled material	1Y/4.2Fe/7.8Al pulled material	1Y/4.2Fe/7.8Al 870 K
space group (no.139)	*I*4/*mmm*	*I*4/*mmm*	*I*4/*mmm*	*I*4/*mmm*
lattice parameters (at 300 K), Å				
a	8.7604(7)	8.7365(3)	8.7303(3)	8.7418(6)
c	5.0504(5)	5.0478(3)	5.0486(2)	5.0488(4)
cell volume, Å^3	387.59(5)	385.28(4)	384.72(3)	385.82(5)
radiation	Cu Kα	Cu Kα	Cu Kα	Cu Kα
2θ range, deg	18−100	18−100	18−100	18−100
site occupation Y 2a	0.99(5)	1.00(1)	0.95(7)	1.00(5)
Fe 8f	4.0(1)	4.0(1)	4.0(1)	4.0(1)
Al 8j	3.8(1)	3.7(1)	3.8(1)	3.7(1)
Fe 8j		0.3(1)	0.2(1)	0.3(1)
Al 8i	4.0(1)	3.7(1)	4.0(1)	4.0(1)
B_{eq} (Å^2) Y 2a	0.54	0.50	0.43	0.70
Fe 8f	0.57	0.50	0.58	0.61
Al, Fe 8j	0.44	0.49	0.42	0.53
Al 8i	0.44	1.01	0.43	0.75
Site 8j (x_1, 1/2, 0)	0.2802(4)	0.2719(5)	0.2688(5)	0.2760(5)
Site 8i (x_2, 0, 0)	0.3397(4)	0.3446(7)	0.3445(6)	0.3301(7)
agreement factors R_{Bragg}, R_F (%)	6.17, 5.01	8.09, 7.42	8.08, 6.45	6.42, 5.79
formula obtained from site occupations	$YFe_{4.0(2)}Al_{7.8(2)}$	$YFe_{4.3(2)}Al_{7.4(2)}$	$YFe_{4.2(2)}Al_{7.8(2)}$	$YFe_{4.3(2)}Al_{7.7(2)}$

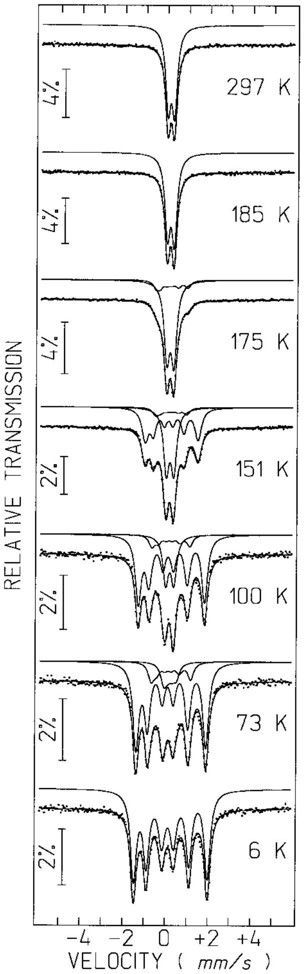

Figure 4. Mössbauer spectra, taken at different temperatures, of the YFe_4Al_8 sample prepared as polycrystalline material and annealed at 1070 K.

magnetization, approximately linear with the applied field (Figure 5), suggests a mainly AF arrangement of the μ_{Fe} in agreement with the general shape of the *M* vs *T* curves.

The Mössbauer data obtained between 180 and 55 K can only be explained if not all the Fe atoms are equivalent. These anomalies may be attributed to the presence of defects close to the limit of detection of the structural characterization techniques used in this work, such as a very small degree of atomic disorder or even vacancies, the content of which is within the experimental error of the estimated site occupation factors. Furthermore, these low concentration of defects do not produce any asymmetry in the sextet or in the doublet peaks observed in the Mössbauer spectra obtained at 6 K or above T_{ord} respectively. It should be noted that the refined site occupation factor of Al on the 8i site suggests the presence of vacancies on this site (Table 1). Because of the large estimated uncertainties the presence of 0.2 vacancies per formula unit on a certain site cannot be ascertained from the Rietveld analysis alone. On the other hand the presence of Fe atoms on the 8j sites should be discarded since they are expected to have a completely different effect on the Mössbauer spectra as will be shown below.

Polycrystalline Material Prepared from 1Y/4.2Fe/7.8Al Bulk Charges. Powder XRD of the as-cast sample shows a content of YAl_3, Fe_2Al_5, and $FeAl_3$ lower than that observed in the 1Y/4Fe/8Al as-cast sample. In the sample annealed at 870 K for 2 months, these additional phases are virtually absent, within the sensitivity of the powder XRD method used. Both the refinement of the diffracted intensities as well as the estimated unit-cell parameters by the Rietveld analysis of the latter sample are consistent with $YFe_{4.2}Al_{7.8}$ composition with the Fe atoms fully occupying the 8f sites and sharing the 8j sites with Al (Table 1).

Mössbauer spectra of the material annealed at 870 K, taken at 6 and 298 K (Figure 6) are very similar to those obtained for $UFe_{4.2}Al_{7.8}$.[14] As in the U analogue, in the $YFe_{4.2(2)}Al_{7.8(2)}$ intermetallic below the correspond-

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Table 2. Estimated Parameters from the Mössbauer Spectra[a] I, Relative Areas, Are Fixed, Consistent with the Calculated Probabilities for the Different Number of Fe NN (*z*) of Fe Atoms on the 8*f* and 8*j* Sites

T	material	site	z	*I* (%)	δ (mm/s)	Δ, ϵ (mm/s)	Γ (mm/s)	B_{hf} (T)
295 K	YFe_4Al_8	8f	2	100	0.18	0.31	0.30	
	annealed 1070 K							
	1Y/4Fe/8Al	8j	≥4	4	0.04	0.64	0.32	
	pulled material	8f	≥3	11	0.13	0.69	0.32	
		8f	2	85	0.17	0.35	0.30	
	1Y/4.2Fe/7.8Al	8j	≥4	5	0.04	0.68	0.32	
	pulled material	8f	≥3	18	0.12	0.74	0.32	-
		8f	2	77	0.17	0.36	0.32	-
	$YFe_{4.2}Al_{7.8}$	8j	≥4	4	0.04	0.68	0.30	-
	annealed 870 K	8f	≥3	11	0.13	0.73	0.30	-
		8f	2	85	0.18	0.37	0.32	-
6 K	YFe_4Al_8	8f	2	100	0.31	0.14	0.38	10.7
	annealed 1070 K							
	1Y/4Fe/8Al	8j	≥4	4	0.18	0.40	0.27	18.6
	pulled material	8f	≥3	11	0.26	0.16	0.25	13.9
		8f	2	85	0.31	0.14	0.30	10.7
	1Y/4.2Fe/7.8Al	8j	≥4	5	0.17	0.47	0.28	18.5
	pulled material	8f	≥3	18	0.26	0.18	0.25	14.1
		8f	2	77	0.31	0.14	0.30	10.7
	$YFe_{4.2}Al_{7.8}$	8j	≥4	4	0.17	0.37	0.28	18.4
	annealed 870 K	8f	≥3	11	0.26	0.17	0.26	14.3
		8f	2	85	0.31	0.14	0.27	11.1

[a] Abbreviations: *I*, relative areas, are fixed, consistent with the calculated probabilities for the different number of Fe NN (*z*) of Fe atoms on the 8f and 8j sites; δ, isomer shift relative to metallic α-Fe at 295 K; Δ, quadrupole splitting (at 295 K); $\epsilon = (e^2V_{ZZ}Q/4)(3\cos^2\theta - 1)$, quadrupole shift (at 5 K) calculated from $(\phi_1 + \phi_6 - \phi_2 - \phi_5)/2$ where ϕ_n is the shift of the *n*th line of the magnetic sextet due to quadrupole coupling; Γ, line widths of the two inner peaks of a sextet; B_{hf}, magnetic hyperfine field. Estimated errors for δ, Δ, and Γ of doublets with $I > 15\%$ are ≤ 0.02 mm/s and of the others ≤ 0.04 mm/s. Estimated errors for the sextets with $I > 11\%$ are ≤ 0.2 T for B_{hf}, ≤ 0.02 mm/s for δ, ϵ, Γ, and for the others ≤ 0.4 *T* for B_{hf}, ≤ 0.03 mm/s for δ, and ≤ 0.04 mm/s for Γ and ϵ.

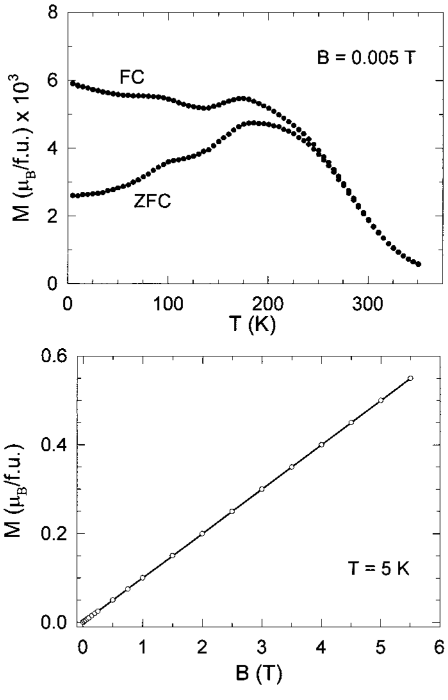

Figure 5. Magnetization vs temperature and vs external field of the YFe_4Al_8 sample prepared as polycrystalline material and annealed at 1070 K.

ing T_{ord}, the B_{hf} of the Fe atoms depend not only on the crystallographic site but also on the number of Fe nearest neighbors (NN). Assuming a statistical occupation of the 8j sites by Fe and Al atoms, three sextets, corresponding to Fe atoms on the 8j sites with four or more Fe NN, on the 8f sites with two Fe NN and on the 8f sites with three or more Fe NN, should be observed. The relative intensities of these sextets, *I*, may be calculated from the fraction of 8j sites occupied by Fe as explained in ref 14. Values of *I* given in Table 2 for $YFe_{4.2}Al_{7.8}$ annealed at 870 K correspond to the actual composition $YFe_{4.15}Al_{7.85}$. The difference in composition between $YFe_{4.3(2)}Al_{7.7(2)}$ (Table 1) and $YFe_{4.15}Al_{7.85}$ is within the error of the XRD data but the set of *I* values

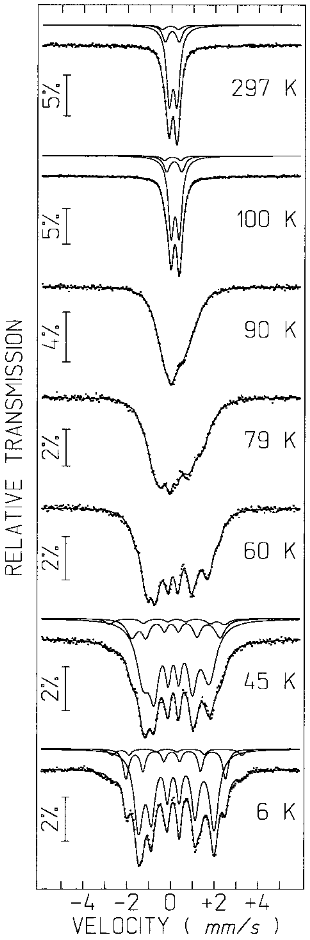

Figure 6. Mössbauer spectra, taken at different temperatures, of the $YFe_{4.2}Al_{7.8}$ sample prepared as polycrystalline material and annealed at 870 K.

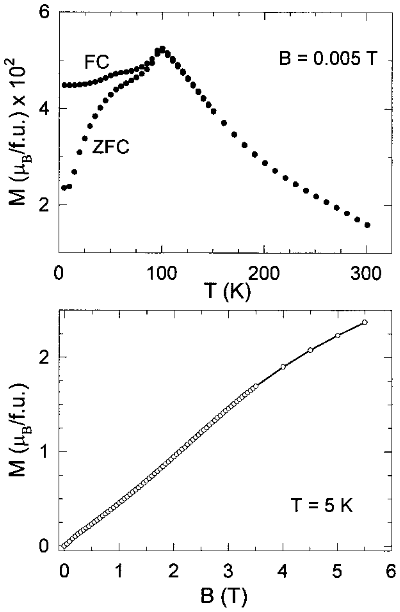

Figure 7. Magnetization vs temperature and vs external field of the $YFe_{4.2}Al_{7.8}$ sample prepared as polycrystalline material and annealed at 870 K.

obtained assuming the latter composition give a significantly better fit to the Mössbauer spectra of the sample studied. The estimated hyperfine parameters are also given in Table 2. The increase of B_{hf} and decrease of δ with the increasing number of Fe NN, may be understood on the basis of the Fe−Fe intersite exchange interactions and of the decrease of the electron density at the Fe nuclei, respectively.[14]

The spectra obtained with the sample between 60 and 90 K could only be fitted by a continuous distribution of B_{hf}. Either a true continuous distribution of B_{hf} is observed or a large enough number of different B_{hf} values which cannot be resolved. Assuming that the μ_{Fe} are proportional to the B_{hf} this suggests that, in this temperature range, there is either an incommensurate distribution of the μ_{Fe} values or at least a large number of different μ_{Fe}, in contrast to the presence of only three different μ_{Fe} at 6 K. At 100 K all the Fe atoms become paramagnetic. *M* vs *T* curves (Figure 7) are consistent with Mössbauer data showing an AF-like transition at ~100 K and a shoulder at ~50 K in the temperature range corresponding to the change from a distribution of B_{hf} to a set of three well-defined values of B_{hf}. The maximum at ~100 K is sharper than the maximum at 180 K observed for YFe_4Al_8 (Figure 5). This may be related to the fact that while for $YFe_{4.2}Al_{7.8}$ there are no paramagnetic Fe atoms below $T_{ord} \approx 100$ K in YFe_4Al_8 paramagnetic Fe atoms coexist with magnetically ordered Fe atoms in a broad temperature range below the corresponding $T_{ord} \approx 180$ K. The *M* vs *B* curve agrees with the AF-like behavior suggested by the *M* vs *T* curve (Figure 7).

Pulled Material Prepared from 1Y/4Fe/8Al and 1Y/4.2Fe/7.8Al Bulk Charges. The results of the Rietveld analysis of the powder X-ray diffractogram of a fraction of the ground material pulled from a 1Y/4Fe/8Al bulk charge are given in Table 1. By comparing these results with those obtained for the samples prepared as polycrystalline materials, the estimated unit-cell parameters and site occupation factors are much closer to those obtained for $YFe_{4.2}Al_{7.8}$ than for YFe_4Al_8.

The Mössbauer spectra of the same sample powder taken in the temperature range between 298 and 6 K are virtually identical to those obtained at the same temperatures for $YFe_{4.2}Al_{7.8}$ (Figure 6). Estimated parameters from the analysis of the Mössbauer spectra are also identical for both samples, within experimental error (Table 2). The 6 and 40 K spectra show the three magnetic sextets typical of $AFe_{4.2}Al_{7.8}$ (A = U, Y) intermetallics where the 8j sites are partially occupied by Fe and the 8f sites fully occupied by Fe (Figure 6 and ref 14). Spectra taken between 60 and 91 K (Figure 6) also show a distribution of B_{hf} and finally at 100 K all the Fe is paramagnetic.

As in the case of the Mössbauer spectra the magnetization curves *M* vs *T* and *M* vs *B* of the ground material pulled from a 1Y/4Fe/8Al bulk charge are very similar to those obtained for $YFe_{4.2(2)}Al_{7.8(2)}$ (Figure 7). The maximum at 100 K and the anomaly at ~60 K reported for the magnetization curves of the nominal YFe_4Al_8 single crystal in ref 8 most likely indicate that the Fe content of this crystal is larger than the assumed one.

As expected, powder XRD and Mössbauer spectra of the ground pulled material obtained from the 1Y/4.2Fe/7.8Al bulk charge reproduce the results obtained with the $YFe_{4.2}Al_{7.8}$ sample obtained as polycrystalline material and annealed at 840 K (Tables 1 and 2). For this sample, the set of *I* values (Table 2) which gives a better fit to the spectrum is that obtained assuming the exact composition $YFe_{4.2}Al_{7.8}$.

General Discussion and Conclusion

Powder XRD, magnetization measurements, and ^{57}Fe-Mössbauer spectroscopy have shown that large single crystals obtained by the Czochralski method from a bulk charge containing Y, Fe, and Al in the atomic ratios 1/4/8, contain more than four Fe atoms per formula unit, having a final composition close to $YFe_{4.2}Al_{7.8}$. This explains the results obtained in ref 8 for a single crystal with nominal composition YFe_4Al_8 and most likely with an actual composition close to $YFe_{4.2}Al_{7.8}$. The small difference in composition between $YFe_{4.2}Al_{7.8}$ and YFe_4Al_8 correspond to an error of only 1.1% of the total mass and to a variation of the number of Fe/Al atoms of only ~1.5% relative to the total number of atoms. Such small differences in the final composition are not unlikely to occur in routine procedures used for the preparation of these intermetallics (errors in weighing or, during arc melting or high-temperature annealing, alteration of composition caused by evaporation of Al, the element with the highest vapor pressure). Those differences are also very difficult to detect from the refinement of X-ray diffracted intensities. The typical uncertainties of the standard quantitative chemical analyses performed by scanning electron microscopy techniques are also ~1%. However, by comparing the estimated unit-cell parameters of several samples (cp. values in Table 1 and in ref 9), it is possible to distinguish between YFe_4Al_8 and $YFe_{4.2}Al_{7.8}$. Furthermore, in the AFe_xAl_{12-x} (A = Y and U[14]) intermetallics a small change in composition corresponding to *x* varying from 4 up to 4.2 has a huge effect on the magnetic properties. T_{ord} drops from 180 K in YFe_4Al_8 down to 100 K in $YFe_{4.2}Al_{7.8}$; at 6 K, in YFe_4Al_8 only one value of μ_{Fe} is observed while in $YFe_{4.2}Al_{7.8}$ three values are clearly detected. These effects allow a very easy detection of the small excess of Fe in these samples.

The presence of $FeAl_3$ and Fe_2Al_5, detected both by powder XRD data and Mössbauer spectroscopy in YFe_4Al_8 annealed at 870 K, are a possible explanation of the differences in the Mössbauer spectra of this material published in the literature. The as-cast polycrystalline material with nominal composition $YFe_{4.2}Al_{7.8}$ already has a very small content of Y−Al and Fe−Al binary alloys in contrast with the as-cast polycrystalline material with nominal composition YFe_4Al_8. This latter sample has to be annealed at 1070 K before a single-phase material (containing less than 1% impurity phases) is obtained. Therefore, one may conclude that YFe_4Al_8 does not melt congruently, while the $YFe_{4.2}Al_{7.8}$ composition is much easier to obtain. This might explain why the sample obtained from a bulk charge with nominal composition YFe_4Al_8, slowly cooled as it is pulled from a melt during the process of single-crystal growing, becomes enriched in Fe in such a way that the final composition of the pulled material is approximately $YFe_{4.2}Al_{7.8}$. Therefore, large single crystals of YFe_4Al_8, required for neutron diffraction studies have to be grown by a different technique, such as mineralization.

Special care in the preparation and structural characterization of intermetallics which have similar stability with the same structure type but with slightly different compositions (such as AFe_xAl_{12-x}, x variable), should be emphasized. Checking their final composition or the presence of additional phases even in very low content is particularly important. The situation is even more complex in cases such as the Y−Fe−Al system where vacancies are very easily formed. Loss of a small amount of Al is hard to detect by weight loss of the sample or by XRD. Although the presence of ≤ 0.2 vacancies per formula unit is the best explanation found to understand the Mössbauer spectra of YFe_4Al_8 taken at intermediate temperatures, it is virtually impossible to quantify by XRD, even in this case where only one kind of atom is present on each crystallographic site.

Magnetization measurements showed that YFe_4Al_8 and $YFe_{4.2}Al_{7.8}$ intermetallics show an AF-like transition of the Fe sublattice at 180 and 100 K (in agreement with Mössbauer data), respectively. The distribution of the Fe atoms (filling the 8f sites and, in the $YFe_{4.2}Al_{7.8}$ case, the remaining Fe atoms sharing the 8j site with Al atoms) is the same as in the UFe_4Al_8 and $UFe_{4.2}Al_{7.8}$ intermetallics, respectively. Besides the strikingly different magnetic properties of the Y intermetallics already mentioned, considering that similar trends may be expected for the values of B_{hf} and the corresponding μ_{Fe},[14] other information may be deduced from the Mössbauer spectra. In the case of YFe_4Al_8, within a certain temperature range below T_{ord}, 180−100 K, paramagnetic Fe atoms coexist with long-range magnetic order, probably due to the very low content of vacancies referred above. Between 100 and 50 K, although all the Fe atoms are magnetically ordered a fraction of them (decreasing with temperature) have μ_{Fe} lower than the majority of the Fe atoms. Below ~50 K a single value for μ_{Fe} is detected. In $YFe_{4.2}Al_{7.8}$ although all the Fe atoms show long-range magnetic order below the same temperature, $T_{ord} \approx 100$ K, a distribution of a large number of different μ_{Fe} is observed. Only for temperatures below ~50 K the number of different μ_{Fe} becomes reduced to three distinct values: Fe atoms on the 8f sites have two different μ_{Fe} and those on 8j sites present the highest μ_{Fe}. The μ_{Fe} values increase with the number of Fe NN and with the Fe−Fe interatomic distances as explained in ref 14.

For both the Y and U intermetallics the 8f−8f magnetic coupling is AF although in YFe_4Al_8 the magnetic ordering of the μ_{Fe} is described by a complex spiral structure. The larger magnetization values of $YFe_{4.2}Al_{7.8}$ as compared to YFe_4Al_8 obtained for the same applied field values in the M vs B curves (Figures 5 and 7) suggest an easier ferromagnetic alignment of the μ_{Fe} in $YFe_{4.2}Al_{7.8}$. If the presence of Fe atoms on the 8j sites in $YFe_{4.2}Al_{7.8}$ favors a ferromagnetic alignment of the μ_{Fe}, as also observed in the UFe_xAl_{12-x} ($x > 4$) intermetallics,[17] the resulting frustration might explain the decrease in T_{ord} with increasing Fe content in the Y intermetallics. In the U materials, however, T_{ord} increases with x, suggesting that the U−Fe magnetic coupling is significant.

Single-crystal magnetization and XRD of single-crystals selected from the $YFe_{4.2}Al_{7.8}$ pulled material are now in progress. Research on adequate techniques for growing large single crystals of YFe_4Al_8, adequate for single-crystal neutron diffraction, is also being undertaken.

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