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Mössbauer studies of the alloys Fe_3Ga_4 , $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$

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Abstract. The crystal structure of the alloy Fe_3Ga has four inequivalent crystallographic iron sites. Mössbauer spectra recorded at 4.2 K were able to be fitted with four sextets corresponding to these sites. Measurement of the hyperfine fields B_{hf} gave values 271 kG, 191 kG, 152 kG and 195 kG respectively. For the series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ spectra were recorded at 4.2 and 300 K for $x = 0.05$, $x = 0.10$ and $x = 0.15$. These spectra were fitted to five sextets, each associated with a distinct iron site. The magnetic ordering temperature T_C was observed to be essentially unchanged for $0 \leq x \leq 0.15$. Site preference for Ti atoms was observed for $x = 0.10$ and $x = 0.15$ causing a large change in hyperfine field values at a neighbouring site.

Similar Mössbauer studies were made on the series $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ ($0 \leq y \leq 0.20$). Spectra at 4.2 K could be fitted with four sextets but continuous reductions in hyperfine field values and ordering temperature T_C were observed with increasing y . The contrast in the magnetic behaviour of the two series is associated with different patterns of substitutional site preference.

1. Introduction

The magnetic behaviour of binary and ternary transition metal alloys—specifically the magnitudes of transition metal atom moments, the magnetic structure and magnetic phase transitions—has been the subject of a number of studies in recent years [1–3]. A variety of experimental techniques have been used and several theoretical models have been presented to explain the magnetic interactions involved [4, 5]. In the ternary alloys $\text{FeAl}_{1-x}\text{T}_x$ and $(\text{Fe}_{1-x}\text{T}_x)_3\text{Ga}_4$ (T = transition metal) different transition metals T give rise to different degrees of competing ferromagnetic and antiferromagnetic interactions [3, 6, 7] leading to phenomena such as spin glass phases and reentrant ferromagnetism [3]. A general comprehensive theory on the nature, origin and mechanisms of the magnetic interactions in these alloys has not yet been worked out and further experimental results are valuable to prompt the development of improved theoretical approaches. In this work we present a detailed Mössbauer study of the alloy series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$: $0 \leq x \leq 0.15$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$: $0 \leq y \leq 0.20$.

The x-ray study of Fe_3Ga and Cr_3Ga_4 by Philippe *et al* [8] has shown that both alloys have base centred monoclinic structure with lattice dimensions $a = 10.102 \text{ \AA}$, $b = 7.666 \text{ \AA}$, $c = 7.881 \text{ \AA}$ and $\beta = 106.26^\circ$ for Fe_3Ga_4 . The unit cell contains 18 Fe atoms occupying four inequivalent sites Fe(1), Fe(2), Fe(3) and Fe(4) populated in ratios 2:4:4:8 respectively. A

study of the magnetization of Fe_3Ga_4 by Kawamiya and Adachi [9] showed complex behaviour indicating the coexistence of ferromagnetic and antiferromagnetic interactions with a Néel temperature $T_N = 392$ K. This study reported preliminary Mössbauer measurements at 300 and 80 K in which the spectra were fitted with four sextet components. For the alloy series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ an x-ray study by Al-Kanani and Booth [10] showed a crystallographic structure comparable to that of the parent alloy. No Mössbauer measurements of these series have been reported.

2. Experimental techniques

The alloy samples for Fe_3Ga , $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ were prepared by arc melting in an argon gas atmosphere as reported by Al-Kanani and Booth [10]. The x-ray measurements on $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ showed these alloys to be single phase and have the same crystal structure as the Fe_3Ga_4 alloy with comparable lattice parameters. In our experiments the above mentioned alloys were used as Mössbauer absorbers. The absorber samples were made by mixing optimum quantities of powdered alloy (about 24 mg cm^{-2}) with boron nitride powder. The mixture was enclosed homogeneously in polypropylene holders for measurements at temperatures $T < 300$ K. For measurements above room temperature the mixture was sandwiched evenly in the form of a circular disc between two thin aluminum foils which provided homogeneous temperature across the sample. For alloys with $T_C > 300$ K the samples were inserted in a temperature controlled Mössbauer furnace whose temperature could be controlled with an accuracy of ± 1 K.

The spectrometers used were equipped with sources of ^{57}Co in a rhodium matrix driven in a double ramp mode by a constant acceleration transducer. The folded spectra showed flat background. The spectrometers were calibrated using a $25 \mu\text{m}$ α -iron foil at room temperature. Isomer shifts were measured relative to these calibrations.

The magnetic spectra recorded at 4.2 K were measured in a helium bath cryostat. The magnetic spectra were fitted to the minimum number of sextet components required to give an acceptable fit. In this fitting of spectra of polycrystalline samples the relative areas of the outer:middle:inner doublet constituents of the sextet were fixed as 3:2:1. For Fe_3Ga_4 in which four sextet components were required, the area ratios of these components were fixed at 2:4:4:8 reflecting the iron atom population of the sites in the unit cell. For samples of the series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ and $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ variations on this area ratio were allowed to model any site selectivity of substitution of the Ti and Cr atoms. In fitting the singlet spectra seen at 300 K for $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$: $y \geq 0.10$ the relative areas of the components were fixed at the values obtained from fits to the 4.2 K magnetic spectra.

The magnetic transition temperature T_C observed by the collapse of the hyperfine field was determined for each alloy by thermal scan used previously by Kobeissi [11]. As a check on the T_C measurements, the line width was measured as a function of temperature just below and above T_C where the paramagnetic phase shows a narrow line whose width is independent of temperature.

3. Results and discussion

3.1. Parent alloy Fe_3Ga_4

3.1.1. *Mössbauer spectra at 4.2 and 300 K.* Mössbauer spectra taken at 4.2 and 300 K are shown in figure 1. The crystal structure with four inequivalent iron sites leads to the expectation of spectra with at least four distinct components. Acceptable fits were obtained

with four sextet components whose parameters are listed in table 1. These fits broadly followed those of Kawamiya and Adachi [9] but in this work the relative component areas were more rigorously constrained to the ratios 2:4:4:8 of the crystal structure. Fitting with five or more components did not improve the overall fit and accordingly we feel justified in associating the four fitted components with iron atoms at the specified crystal sites.

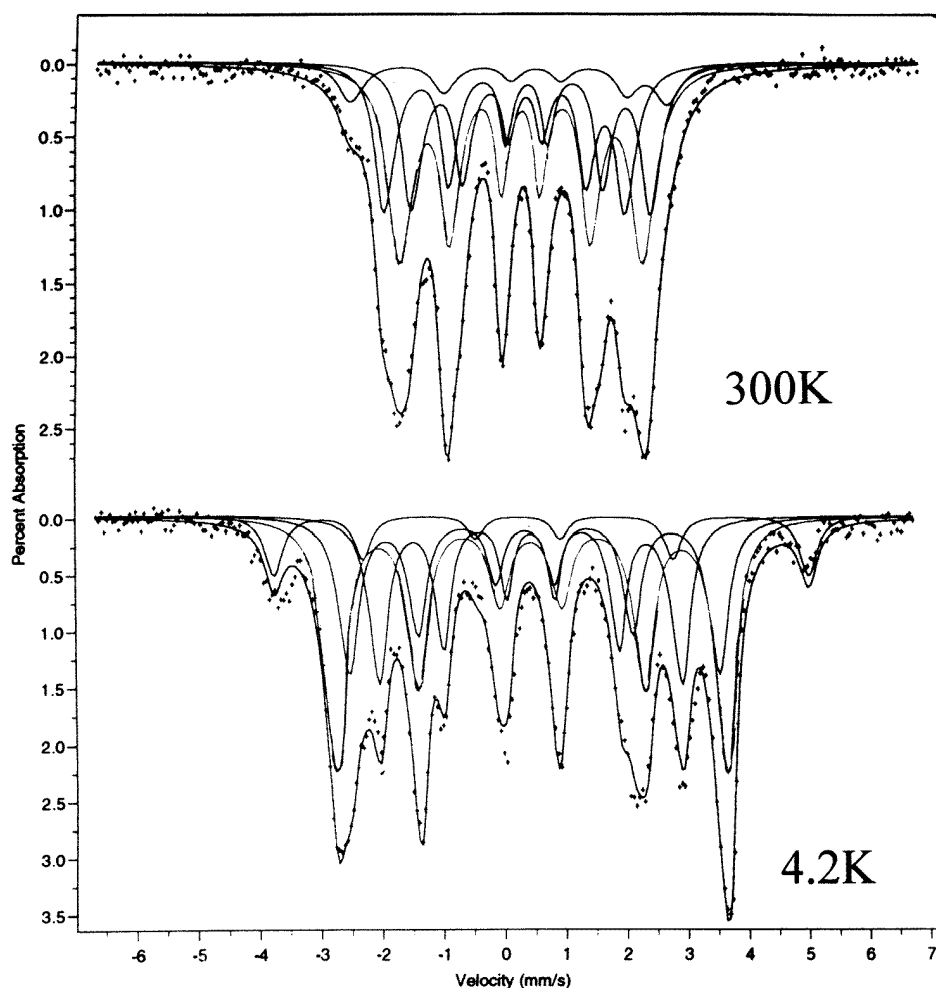


Figure 1. Mössbauer spectra of the alloy Fe_3Ga_4 at 300 K (top) and at 4.2 K (bottom). Each spectrum is fitted with four sextet components.

The values of relative area fix unambiguously the sextet components associated with iron sites Fe(1) and Fe(4). In order to associate the sextet components with sites Fe(2) and Fe(3) values of hyperfine field were considered in association with the environment of nearest neighbours reported by Philippe *et al* [8]. The near neighbour environments of all four iron sites are listed in table 2 in which the number and distance of neighbour atoms for a given iron site is read across the row corresponding to that site. For example the environment around site Fe(1) consists of four iron atoms in site Fe(4) at a distance of 2.576 Å and gallium atoms in

Table 1. Values of the isomer shift δ (mm s⁻¹), quadrupole shift Δ (mm s⁻¹), hyperfine field B_{hf} (kG), linewidth Γ (mm s⁻¹) and relative component area A (%) for the fits to the Mössbauer spectra taken at 4.2 and 300 K on samples of the series (Fe_{1-x}Ti_x)₃Ga₄ with $0 \leq x \leq 0.15$. Errors in δ , Δ , Γ , B_{hf} and A for the largest area component, Fe(4), are ± 0.01 , ± 0.02 , ± 0.02 mm s⁻¹, ± 3 kG and $\pm 2\%$ respectively; for the smallest area component, Fe(1), the errors are several times larger.

(Fe _{1-x} Ti _x) ₃ Ga ₄	Site	4.2 K					300 K					
		δ (mm s ⁻¹)	Δ (mm s ⁻¹)	B_{hf} (kG)	Γ (mm s ⁻¹)	A %	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	B_{hf} (kG)	Γ (mm s ⁻¹)	A (%)	T_C (K)
$x = 0$	1	0.50	0.40	273	0.33	11	0.33	-0.25	163	0.30	11	385 ± 1
	2	0.48	0.14	188	0.35	22	0.37	0.16	137	0.27	22	
	3	0.49	-0.02	154	0.31	22	0.37	-0.19	109	0.25	22	
	4	0.49	-0.01	199	0.39	45	0.33	-0.07	124	0.37	45	
$x = 0.05$	1	0.52	0.36	273	0.36	10	0.31	-0.29	147	0.36	10	384 ± 2
	2a	0.50	0.11	184	0.41	21	0.34	-0.05	111	0.31	20	
	2b	0.37	0.50	19	0.25	7	0.27	0.00	16	0.37	11	
	3	0.49	-0.04	150	0.28	21	0.34	-0.03	100	0.36	20	
$x = 0.10$	4	0.48	0.02	196	0.38	41	0.34	-0.04	128	0.38	39	386 ± 2
	1	0.53	0.37	271	0.38	9	0.25	-0.45	144	0.38	8	
	2a	0.45	0.11	141	0.92	21	0.25	0.17	106	0.57	23	
	2b	0.37	0.32	14	0.25	9	0.28	0.00	15	0.26	16	
$x = 0.15$	3	0.50	-0.07	153	0.28	15	0.34	-0.12	103	0.22	13	385 ± 2
	4	0.48	0.05	194	0.38	45	0.34	-0.05	124	0.38	39	
	1	0.46	0.45	272	0.39	10	0.31	-0.35	146	0.31	9	
	2a	0.32	-0.22	70	0.57	20	0.24	0.00	22	0.24	19	
	2b	0.34	0.32	15	0.27	11	0.27	0.00	13	0.24	16	
	3	0.49	-0.02	152	0.25	13	0.32	-0.08	104	0.32	12	
	4	0.46	0.06	194	0.40	46	0.34	-0.02	122	0.34	43	

sites Ga(1), Ga(2) and Ga(3) at specified distances. It is seen that site Fe(3) has two iron and nine gallium neighbours while site Fe(2) has four iron and six gallium neighbour atoms. On the assumptions that magnetic coupling between iron atoms will act to increase the hyperfine field and that electron sharing between iron (3d) electrons and non-magnetic gallium atoms will act to reduce the hyperfine field, the component with the lower hyperfine field is associated with the Fe(3) site.

Table 2. Numbers/distances (Å) of near neighbour atoms to each separate Fe site in Fe_3Ga_4 . These data are taken from Philippe *et al* [8].

Site	Fe(1)	Fe(2)	Fe(3)	Fe(4)	Ga(1)	Ga(2)	Ga(3)	Ga(4)
Fe(1)				4/2.576	2/2.602	2/2.649	4/2.651	
Fe(2)		1/2.954	1/2.745	2/2.756	1/2.462		1/2.475	2/2.506 2/2.498
Fe(3)		1/2.745		1/2.599	1/3.412	1/2.471 1/2.715	2/2.542	2/2.640 2/2.560
Fe(4)	1/2.576	1/2.756	1/2.599	1/2.903 1/3.091	1/2.494 1/2.479	1/2.530	1/2.570 1/2.582	1/2.534 1/2.579

The high values of isomer shift listed in table 1 show the influence of the gallium neighbours as the mean value of isomer shift at 300 K ($\sim 0.35 \text{ mm s}^{-1}$) is close to the value 0.37 mm s^{-1} measured for iron in a gallium host [12]. The difference in isomer shift values between 4.2 and 300 K is accounted for by the second order Doppler shift. Quadrupole shift values are small and not well defined because of the complexity of the fit but the change of sign in the value for the Fe(1) component between 4.2 and 300 K is clearly seen in the spectra.

3.1.2. Determination of the transition temperature T_C . The 300 K spectrum of figure 1 shows magnetic order. On increasing the temperature to just below T_C the spectrum evolved to a very broad single line indicating the near collapse of the hyperfine field. Further increase in the temperature caused progressive narrowing of the line which then remained constant above T_C , indicating a total collapse of the hyperfine field. As confirmation of this result, the centroid velocity transmission (CVT) method was used [9]. Both methods showed a steep decrease showing a sharp transition at a value of $T_C = 385 \pm 1 \text{ K}$ in reasonable agreement with the Néel temperature $T_N = 392 \text{ K}$ determined by the magnetization measurements of Kawamiya and Adachi [9].

3.2. The alloy series $(Fe_{1-x}Ti_x)_3Ga_4$

3.2.1. Mössbauer spectra at 4.2 and 300 K. Mössbauer spectra recorded at 4.2 and 300 K for the series $(Fe_{1-x}Ti_x)_3Ga_4$: $0.05 \leq x \leq 0.15$ are shown in figures 2 and 3 respectively. All spectra required five sextet components for an acceptable fit and similar behaviour was observed at 4.2 K and at 300 K. The parameters of the fits are listed in table 1. It is seen that the hyperfine parameters associated with sites Fe(1), Fe(3) and Fe(4) change little with x but that the hyperfine field for the other two components shows a progressive collapse as x is increased. Also the relative area of the component associated with site Fe(3) decreases as x is increased—seen in the spectra as a decrease in the area of the line at $\sim 3 \text{ mm s}^{-1}$. This suggests a situation where Ti atoms substitute selectively on the Fe(3) site and affect the hyperfine field on the Fe(2) site. In these data the matching of component area ratios with iron occupation of Fe sites is best, though not perfectly, achieved if both components with collapsing hyperfine

field are associated with the Fe(2) site. Confirmatory evidence for the likelihood of preferential substitution of Ti atoms on the Fe(3) site arises from the values in table 2 where the fact that the Fe(3) site has the largest mean separation between site atom and neighbours (both iron and gallium) matches the relatively large radius of titanium (145 pm compared to 124 pm for iron).

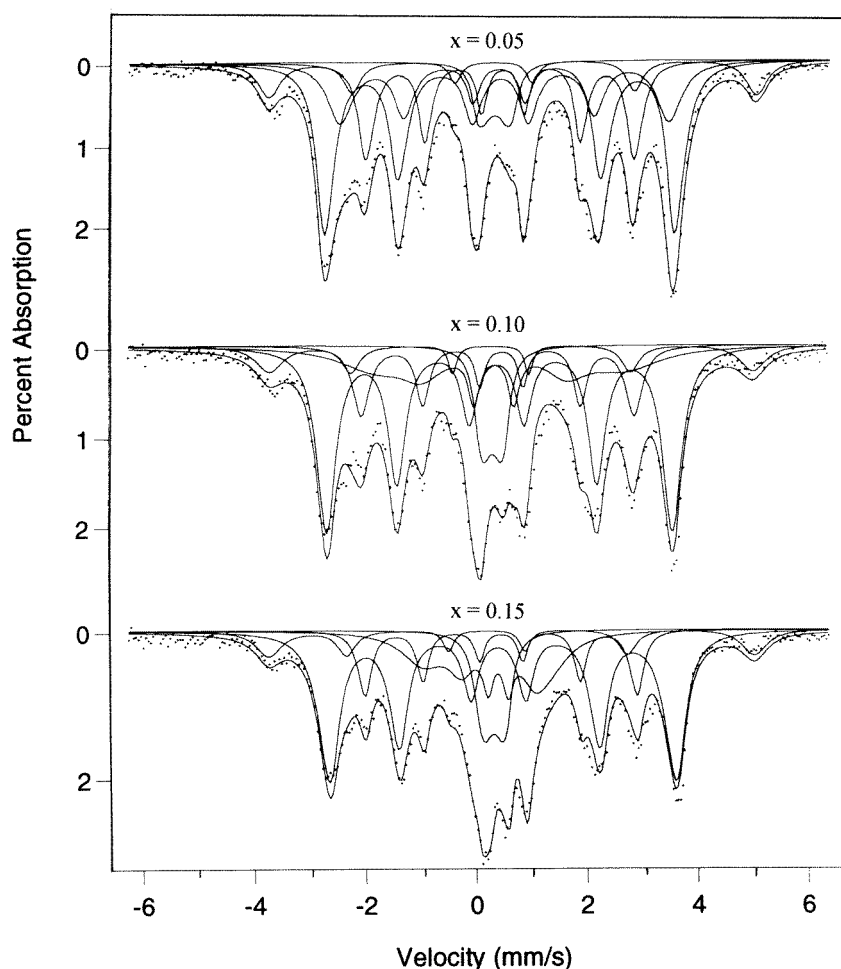


Figure 2. Mössbauer spectra of the series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ taken at 4.2 K.

It is seen from table 2 that occupation of an Fe(3) site by a titanium atom reduces the number of magnetic neighbour atoms on an iron atom on all Fe(2) sites from four to three which would be expected to reduce the hyperfine field. The perturbation in position of neighbouring gallium atoms when the large titanium atom occupies an Fe(3) site may also reduce the hyperfine field on neighbouring Fe(2) atoms. The same arguments may be used to predict a reduction in hyperfine field in iron atoms occupying the Fe(4) site—which is not observed. In this case titanium substitution on an Fe(3) site reduces the number of iron neighbours for an Fe(4) site from five to four and presumably any indirect perturbation of gallium atom positions around the Fe(4) site does not act to reduce the hyperfine field.

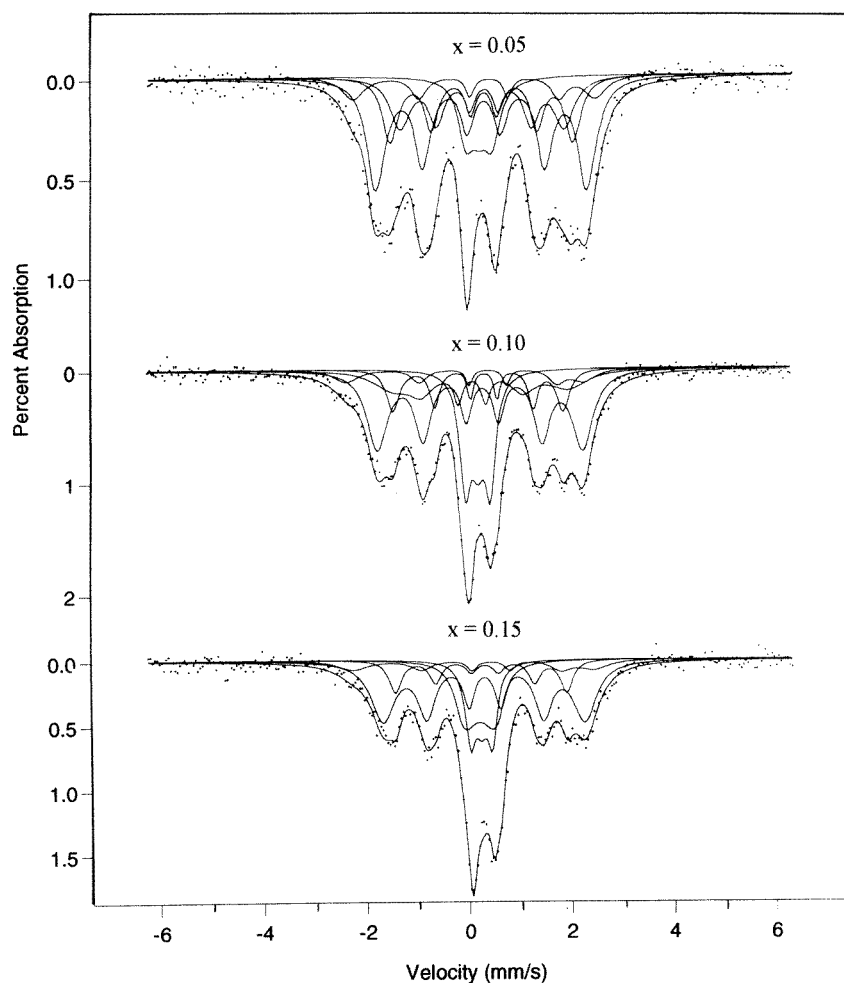


Figure 3. $(Fe_{1-x}Ti_x)_3Ga_4$ spectra taken at room temperature.

3.2.2. *Determination of the ordering temperature T_C .* Transition temperatures, T_C , for alloys with $0.05 \leq x \leq 0.15$ were obtained using the same methods as for Fe_3Ga_4 . The graphs of CVT versus temperature for the determination of T_C are shown in figure 4 and the values are listed in table 1. The graphs give the same transition temperature for all values of x which is the same as the value of the parent alloy to within the experimental error. This complements the measurements of the hyperfine field components discussed in the previous section where no appreciable change occurred with x in three of the four sites.

3.3. The alloy series $(Fe_{1-y}Cr_y)_3Ga_4$

3.3.1. *Mössbauer spectra at 4.2 and 300 K.* Mössbauer spectra recorded at 4.2 and 300 K for the series $(Fe_{1-y}Cr_y)_3Ga_4$: $0.05 \leq y \leq 0.20$ are shown in figures 5 and 6 respectively. All the magnetic spectra required only four components for an acceptable fit. The parameters of all the fits are listed in table 3. It is seen that in these spectra there is no collapse of hyperfine

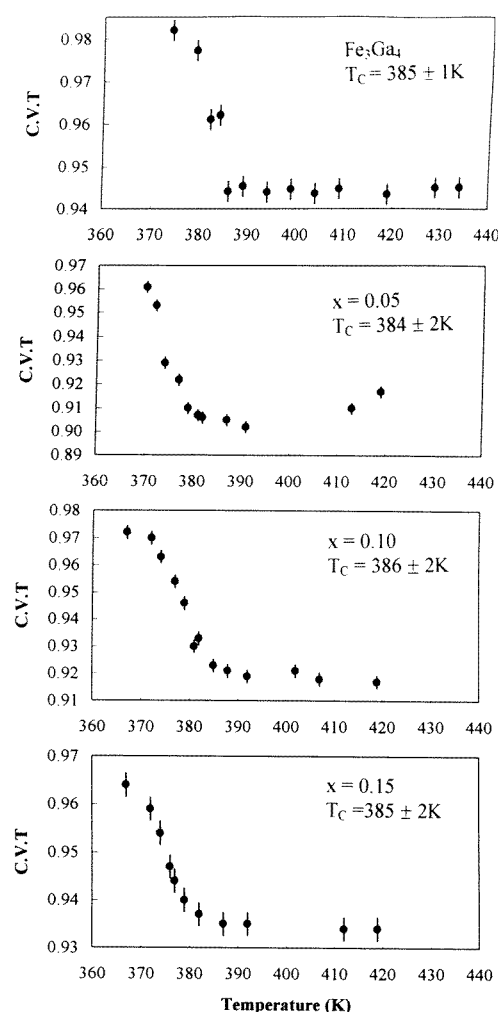


Figure 4. Determination of the transition temperature T_C of samples in the series $(\text{Fe}_{1-x}\text{Ti}_x)_3\text{Ga}_4$ using the thermal scan. The top curve for Fe_3Ga_4 is for comparison. The sharp drop in this curve at T_C for Fe_3Ga is contrasted with the rounding of the curve for the Ti doped alloys. No change in T_C with x is observed.

field in any component but a general decrease as y increases. In fitting the spectra the areas of the sextet components were allowed to vary but the values show that the relative areas stay broadly similar to those of the parent alloy and do not change appreciably with increasing y . There is thus no evidence from the Mössbauer spectra for site selectivity in the substitution of chromium atoms for iron. The apparent decrease in area of the component for the Fe(1) site is not well established as the small area of this component means that it has little effect on the overall fit. Added weight for the assumption of substitution without site selectivity arises from the essentially equal atomic radii of chromium and iron (125 and 124 pm respectively) and the fact that Fe_3Ga and Cr_3Ga_4 are isostructural [8]. In fitting the non-magnetic spectra of $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$: $y \geq 0.10$ at 300 K consistency was maintained by fixing the areas of

the four doublet components from the corresponding magnetic spectra at 4.2 K. While these fits are not unique the values for the quadrupole splittings are compatible with the quadrupole shifts of the magnetic spectra.

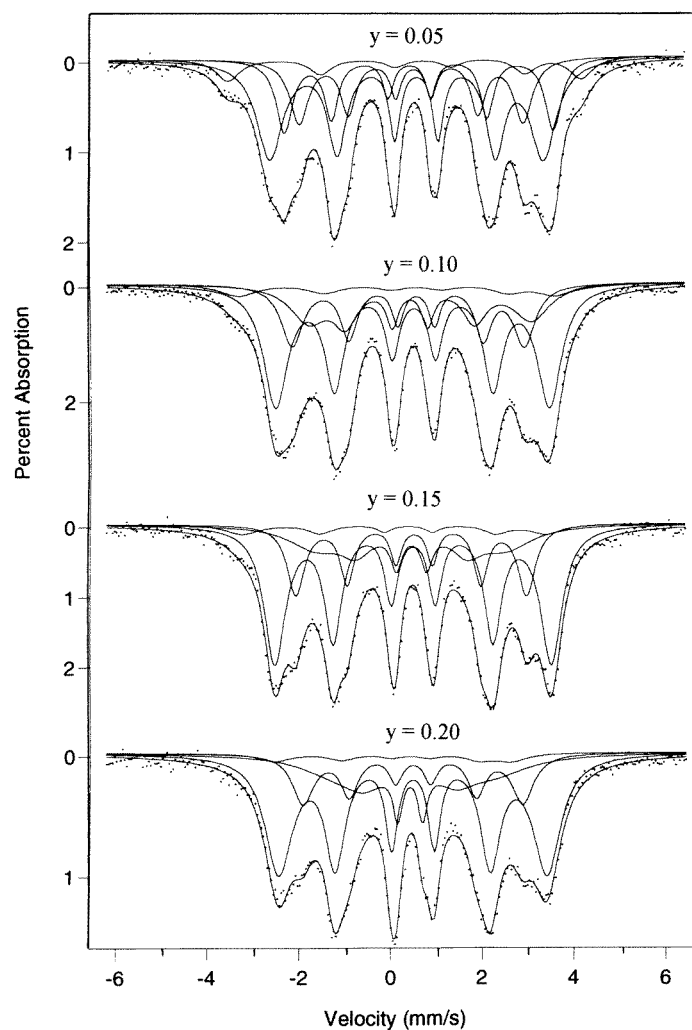


Figure 5. Mössbauer spectra of the series $(Fe_{1-y}Cr_y)_3Ga_4$ as recorded at 4.2 K.

3.3.2. Determination of the transition temperature T_C as a function of y . As in the case of the Ti series, the thermal scan method was used to determine T_C for the Cr series. For the concentration range $0.10 \leq x \leq 0.20$ we employed an He flow cryostat with temperature control system whose accuracy was ± 0.5 K. The values of T_C obtained for each Cr concentration y are listed in table 3. It is seen that in this alloy series the ordering temperature T_C decreases steadily with increasing chromium concentration.

Table 3. Values of isomer shift δ (mm s^{-1}), quadrupole interaction Δ (mm s^{-1}), hyperfine field B_{hf} (kG), linewidth Γ (mm s^{-1}) and relative component area A (%) for fits to the Mössbauer spectra taken at 4.2 and 300 K on samples of the series $(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$ with $0.05 \leq y \leq 0.20$. Errors in the values are similar to those in table 1.

$(\text{Fe}_{1-y}\text{Cr}_y)_3\text{Ga}_4$	Site	4.2 K					300 K					T_C (K)
		δ (mm s^{-1})	Δ (mm s^{-1})	B_{hf} (kG)	Γ (mm s^{-1})	A (%)	δ (mm s^{-1})	Δ (mm s^{-1})	B_{hf} (kG)	Γ (mm s^{-1})	A (%)	
$y = 0.05$	1	0.50	-0.39	239	0.58	9	0.33	-0.11	104	0.26	9	349 ± 2
	2	0.51	0.22	182	0.35	22	0.35	-0.04	73	0.28	22	
	3	0.46	-0.04	152	0.39	22	0.35	0.02	53	0.42	22	
	4	0.45	-0.21	185	0.49	47	0.34	-0.05	88	0.47	47	
$y = 0.10$	1	0.33	-0.42	215	0.87	8	0.29	0.72	0	0.25	8	263 ± 2
	2	0.46	-0.17	158	0.44	22	0.31	0.17	0	0.21	22	
	3	0.52	0.22	151	0.65	22	0.41	0.24	0	0.24	22	
	4	0.48	-0.03	186	0.51	48	0.32	0.32	0	0.35	48	
$y = 0.15$	1	0.22	-0.30	206	0.66	7	0.30	0.73	0	0.25	7	226 ± 2
	2	0.47	-0.06	157	0.37	21	0.32	0.15	0	0.22	21	
	3	0.44	-0.01	130	0.86	21	0.38	0.20	0	0.24	21	
	4	0.48	0.00	187	0.46	51	0.33	0.33	0	0.32	51	
$y = 0.20$	1	0.23	-0.37	161	0.70	5	0.28	0.67	0	0.25	5	160 ± 2
	2	0.48	0.00	149	0.46	18	0.30	0.16	0	0.22	18	
	3	0.48	0.12	106	1.09	23	0.40	0.22	0	0.24	23	
	4	0.48	0.00	182	0.52	54	0.33	0.32	0	0.34	54	

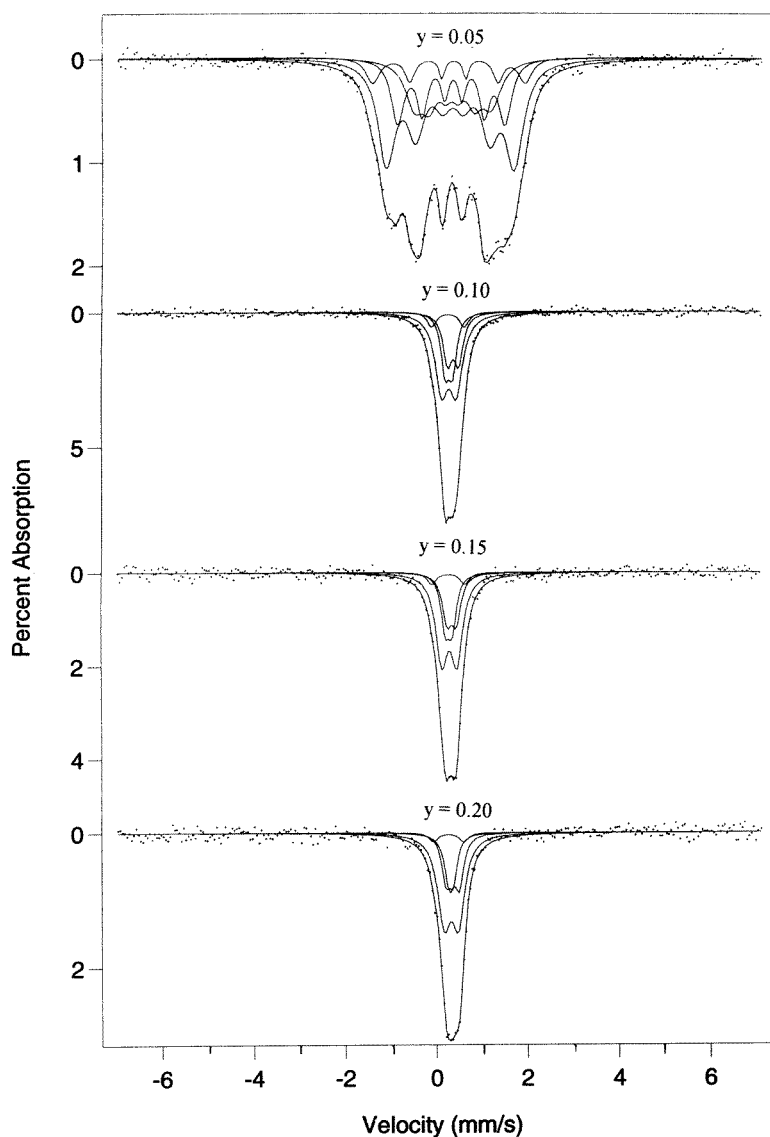


Figure 6. Spectra of the series $(Fe_{1-y}Cr_y)_3Ga_4$ recorded at room temperature. For $y > 0.05$, a total collapse of the hyperfine fields is clearly seen in these spectra in contrast with those of $(Fe_{1-x}Ti_x)Ga_4$.

4. Conclusion

In the alloy series $(Fe_{1-x}Ti_x)_3Ga_4$ evidence has been obtained that the titanium atoms substitute preferentially on the Fe(3) site whereas in the alloys $(Fe_{1-y}Cr_y)_3Ga_4$ the chromium atoms appear to substitute on iron sites without site preference. In this latter case the random substitution of non-magnetic chromium atoms for magnetic iron atoms weakens the magnetic ordering interactions by increasing the mean distance between magnetic atoms and (assuming a connection between hyperfine field and atomic magnetic moment) reducing the magnetic

moments on the iron atoms. It is thus expected that as the chromium content y is increased the ordering temperature T_C will decrease. This is observed in the values of T_C listed in table 3. The situation is less straightforward in the titanium substituted series where site preference diminishes the iron atom population of site Fe(3) and reduces the hyperfine field—and hence the magnetic moment of iron atoms on site Fe(2). In this case the values of T_C listed in table 1 show no change of ordering temperature with titanium atom content x . This indicates that in the complex competition of ferromagnetic and antiferromagnetic interactions present in these alloys [5, 7, 13] the weakening or eliminating of some of the competing magnetic interactions involving Fe(2) and Fe(3) sites does not affect the overall magnetic ordering.

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