

Phase changes in $\text{Fe}_{72-x}\text{Al}_{28}\text{Cr}_x$ ($x = 0, 2, 4, 6$) alloys due to mechanical strain

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Abstract. $\text{Fe}_{72-x}\text{Al}_{28}\text{Cr}_x$ alloys ($x = 0, 2, 4, 6$) are made by arc melting a mixture of constituent elements in stoichiometric proportion, in argon atmosphere. The ingots so obtained are filed to make powder samples thereby giving them substantial mechanical deformation. It is observed that as-powdered samples show hyperfine field distribution typical of α -phase, where the atoms are randomly distributed on the available sites. Annealing at 900°C for 60 h leads to preferential occupation of lattice sites by the atoms and this results in better defined groups of hyperfine magnetic field (HMF) which can be associated with specific configuration in the neighbourhood of probe iron atoms. The average HMF is found to decrease sharply with increasing Cr concentration even though the net chromium concentration remains low (≤ 6 at%). The results show that cold working on samples is very important in changing the atomic ordering and must be taken into account if properties of equilibrium phases are probed.

Keywords. Iron aluminides; Mössbauer spectroscopy; phase transformation; mechanically driven transformation.

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1. Introduction

Iron–aluminium alloys with compositions close to Fe_3Al have been well studied by various researchers. In particular, $\text{Fe}_{72}\text{Al}_{28}$ alloy has drawn great attention because it has interesting magnetic and structural properties such as high magnetic permeability and has extremely good resistance to environmental degradation [1–8]. To alter different mechanical and magnetic properties in desired ways, a third element like Co, Ti, V, Mn, Cr is mixed in small proportions. Thus it has been shown that addition of Ti increases the order/disorder transition temperature [9,10] and expands the DO_3 region. Pandey *et al* [11,12] have shown that addition of Ti facilitates fast recovery from the mechanically stressed non-equilibrium phases. It was found that addition of Ti to Fe_3Al and Fe–Al is very effective in stabilizing the ordered phases DO_3 and B2 respectively.

Cr is another favorite element to add in $\text{Fe}_{72}\text{Al}_{28}$ in order to change the mechanical and magnetic properties. For example, addition of chromium in small proportions is known to increase the Curie temperature significantly [13]. In the present work we investigate the response of $\text{Fe}_{72-x}\text{Al}_{28}\text{Cr}_x$ samples on mechanical deformation and annealing.

2. Experimental

Alloys with nominal compositions $\text{Fe}_{72-x}\text{Al}_{28}\text{Cr}_x$ ($x = 0, 2, 4, 6$) were prepared by melting 99.99% pure metals in stoichiometric proportion using non-consumable electrode arc furnace under argon atmosphere. The buttons so formed were heat treated at 1000°C for a long time in order to achieve proper chemical homogeneity and then furnace-cooled to room temperature. The chemical composition of these alloys was found to be in stoichiometric proportion as shown by electron probe microanalysis (EPMA). Severe mechanical deformation was given to the cleaned ingots by filing them with a diamond file thereby producing powder samples. Portions of this powder were sealed in quartz tubes under argon atmosphere ($\sim 10^{-2}$ mbar) and were annealed at 900°C for 60 h. The as-filed powders as well as the annealed samples were subjected to Mössbauer spectroscopy and XRD. The Mössbauer spectra were recorded at room temperature using a constant acceleration Mössbauer spectrometer and ^{57}Co source in rhodium matrix. The spectra were analysed using computer programs developed at IIT Kanpur. Probability distributions of hyperfine magnetic field (HMF) were obtained using a program based on Window's approach [14,15].

3. Results and discussion

Fe rich Fe–Al alloys with compositions near to $\text{Fe}_{75}\text{Al}_{25}$ have mainly three equilibrium phases – disordered α , ordered DO_3 and B2. All these have the same basic crystal structure BCC. The BCC structure of Fe–Al alloys may be interpreted as one which is made of two interpenetrating simple cubic lattices normally called A-sublattice and B-sublattice [14]. The atomic arrangement in these lattice sites depends on the phase stability, which in turn depends on the composition and temperature [13]. In ideal DO_3 structure, the A-sublattice is fully occupied by the iron atoms, whereas iron and aluminium occupy alternate positions in the B-sublattice. In the B2 phase too, the A-sites are occupied by iron atoms, but the remaining iron and aluminium atoms are randomly distributed on the B-sites. In the α phase, iron and aluminium atoms are randomly distributed on all the available sites [14].

Compositions of our samples are close to $\text{Fe}_{72}\text{Al}_{28}$ which falls in magnetic DO_3 region [16]. In this phase, we expect two prominent six-line patterns with HMF 30 T and 21 T corresponding to iron on B- and A-sublattices respectively. The Mössbauer spectrum generated using the ideal DO_3 structure is shown in figure 1a. The corresponding p – B distribution calculated by our analysis program is shown in figure 1b. The oscillations in the wings are mathematical artifact due to program structure. As a small amount of Cr is substituted for iron, the phase is likely to change from magnetic to non-magnetic DO_3 . This would give a singlet/doublet

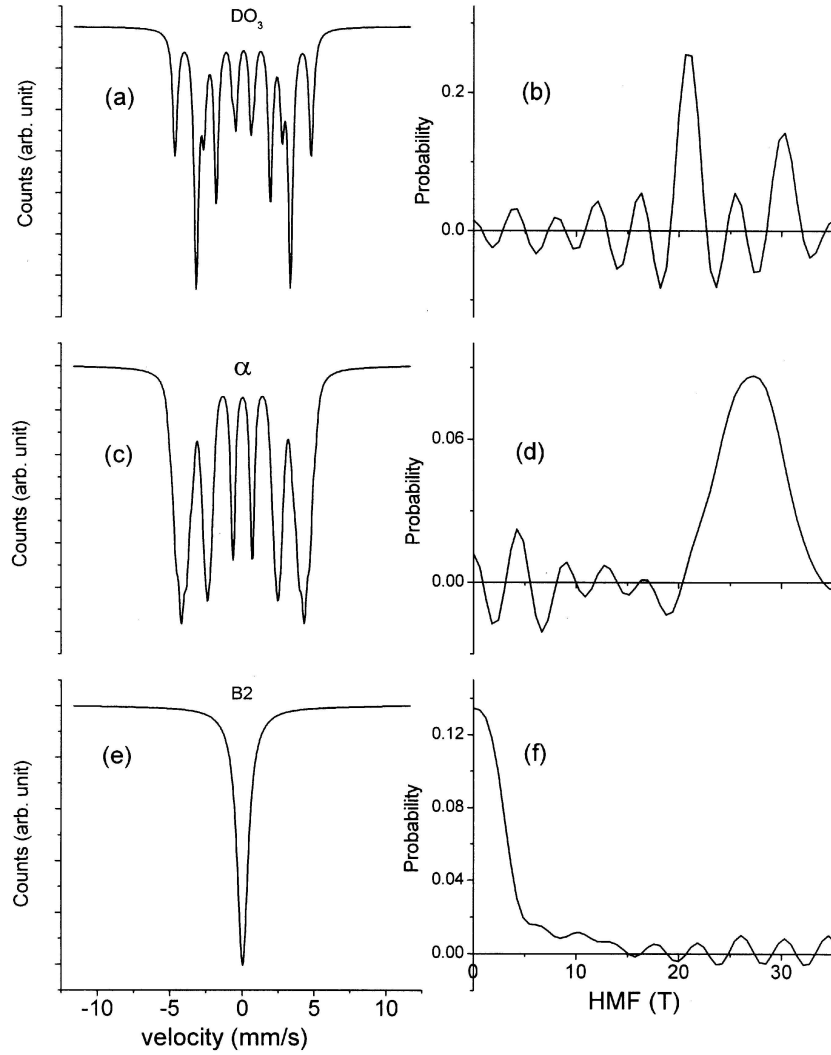


Figure 1. Mössbauer spectra and their corresponding p - B distributions for ideal DO_3 , α , and B2 phases.

component in the spectrum. However, the disordered α phase and the ordered B2 phase may also result during the filing and annealing processes. Hence, in order to understand the Mössbauer spectra of the samples in the present study, it will be useful to discuss the HMF and the resulting Mössbauer spectra in ideal α and B2 structures also. Figure 1c gives the expected Mössbauer spectrum corresponding to a perfectly random distribution (α phase) of atoms in $Fe_{72}Al_{28}$, generated by calculating the probabilities of different surroundings of iron using binomial distribution. For each surrounding, the expected value of HMF was calculated using the equation

$$B = B_0 - n_1\Delta B_1 - n_2\Delta B_2$$

with $B_0 = 33$ T, $\Delta B_1 = 2.4$ T and $\Delta B_2 = 0.5$ T [17]. Here n_1 and n_2 represent the number of aluminium atoms in the nearest-neighbour (NN) and the next-nearest neighbour (NNN) shells. The spectrum in figure 1c is a superposition of different sextets corresponding to these B values with intensity proportional to the calculated probability. The corresponding p - B distribution is shown in figure 1d. The ideal B2 structure belongs to FeAl composition where each Fe atom has six iron atoms in the NNN shell and no iron atom in the NN shell. This gives rise to a single line Mössbauer spectrum as indicated in figure 1e. The corresponding p - B distribution (figure 1f) shows a strong peak at low values of B (<10 T). Even when the composition is non-stoichiometric, B2 structure gives a single line most likely due to smaller crystallite size.

From the above analysis we see that a double peak in p - B distribution at around 30 T and 21 T signifies DO_3 phase, a peak below 10 T shows B2 phase and a very broad single peak spanning the range ~ 20 –30 T shows the dominance of α phase.

3.1 As-filed powder

As mentioned above, from the composition of the samples, we expect them to be in DO_3 order. Powdering of the well-annealed ingots by filing, however, changes the situation drastically. Figure 2 shows the Mössbauer spectra of all four powdered samples, for $x = 0, 2, 4$ and 6, and their corresponding p - B distributions. The characteristic HMFs of 30 T and 21 T are not seen in any of the four samples. The p - B distribution shows a very broad peak centered around 25 T with some smaller humps and kinks for each sample. This resembles well with the model p - B distribution of α phase shown in figure 1d. Increasing chromium substitution shifts the p - B distribution towards left, showing a general reduction in HMF which is consistent with the known fact that chromium substitution for Fe in the nearest-neighbour shell of the probe ^{57}Fe atom reduces the effective HMF [18].

Thus filing has introduced significant plastic deformation by changing the equilibrium configuration drastically. The spectra suggest that samples have changed from the equilibrium DO_3 phase to the α phase where the atoms occupy all sites randomly. The four spectra are qualitatively very similar to each other. This means that any effect of chromium substitution is overshadowed by the plastic deformation created by filing.

3.2 Annealed samples

The powders were annealed at 900°C for 60 h in inert (argon) atmosphere. It is expected that any effect of defect/deformation introduced during filing will be annealed out at this temperature and during the slow cooling, the sample will acquire its equilibrium configuration. This annealing treatment is the same as that given to the ingots after their preparation in arc furnace. Thus the annealed powder is also expected to have the same ordering characteristic as the ingots before filing.

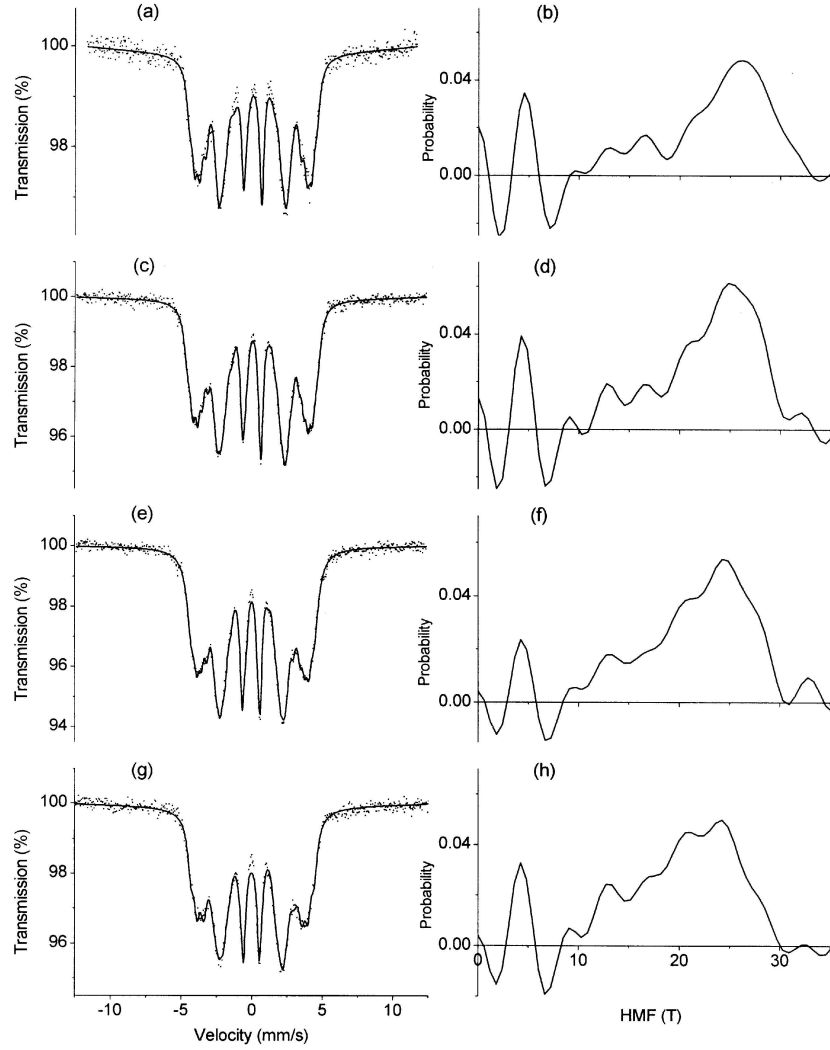


Figure 2. Mössbauer spectra and their corresponding p - B distributions for as-filed powders of $Fe_{72-x}Al_{28}Cr_x$ samples. (a), (b) correspond to $x = 0$, (c), (d) to $x = 2$, (e), (f) to $x = 4$ and (g), (h) to $x = 6$.

Comparison of annealed sample and filed sample can therefore be used to know the effect of filing alone.

Figure 3 shows the Mössbauer spectra and p - B distribution of these annealed samples. All these spectra could be fitted to well-resolved sextets and a superposing doublet. This is because the system has become much better ordered having specific atomic environments around iron nuclei.

It is known that getting an ideally pure DO_3 phase with just two environments is very difficult and during the cooling process other iron environments are picked up.

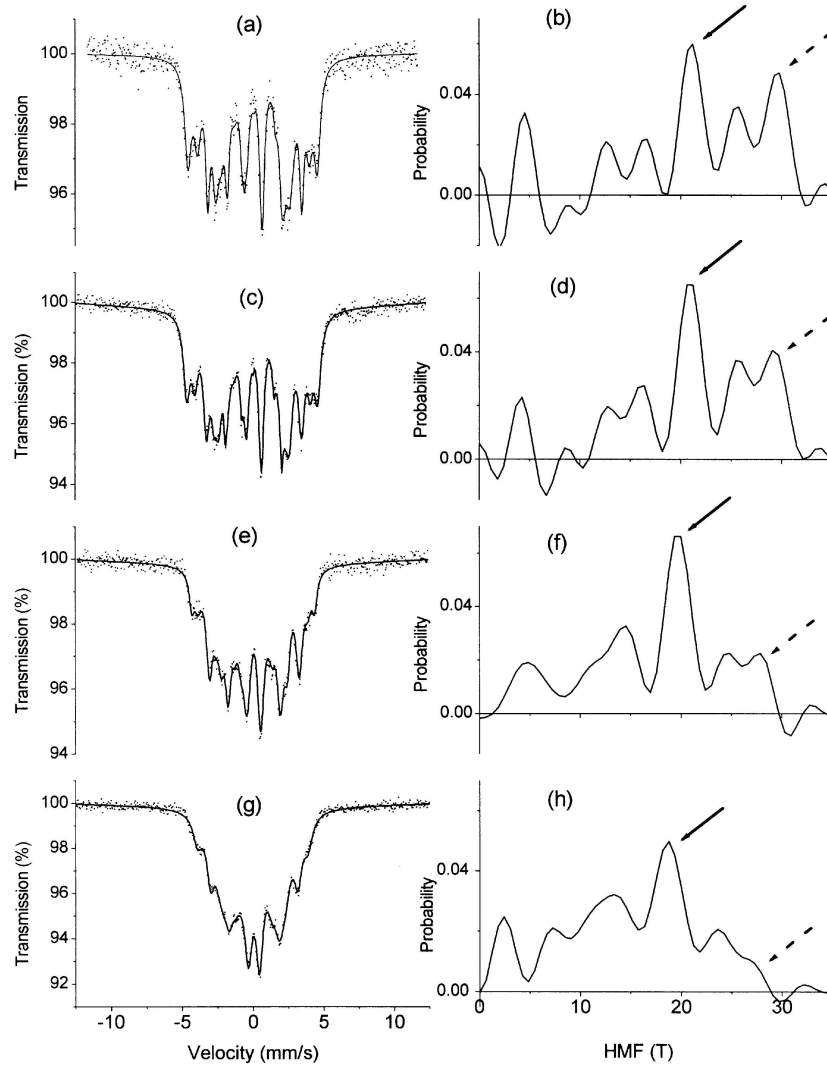


Figure 3. Mössbauer spectra and their corresponding p - B distributions of $\text{Fe}_{72-x}\text{Al}_{28}\text{Cr}_x$ samples annealed at 900°C for 60 h. (a), (b) correspond to $x = 0$, (c), (d) to $x = 2$, (e), (f) to $x = 4$ and (g), (h) to $x = 6$. Solid arrow corresponds to DO_3 -A peak and dashed arrow corresponds to DO_3 -B peak.

To get a good fit to the spectrum, five to six sextets together with a doublet was needed. As a typical case, we present the Mössbauer parameters for the annealed $\text{Fe}_{72}\text{Al}_{28}$ sample (table 1). The largest contribution (relative area 30%) comes from iron atoms occupying the A-site substitutionally and surrounded by four Fe and four Al atoms in the neighbouring B-site. This is clear from the HMF value of 21 T. This environment shows that large part of the sample has obtained DO_3 structure on annealing. The iron atoms in B-sites in such DO_3 regions give rise to the component

Table 1. Mössbauer parameters of $Fe_{72}Al_{28}$ powder annealed at $900^\circ C$ for 60 h in inert argon atmosphere.

IS (mm/s)	QS (mm/s)	HMF (T)	LWD (mm/s)	Area (%)
0.13	1.23		0.27	9
0.03	0.01	29.7	0.44	25
0.03	0.05	25.7	0.54	18
0.20	-0.002	21.0	0.45	30
-0.46	0.37	16.7	0.30	8
0.60	-0.08	12.6	0.48	10

with 29.7 T of HMF. In ideal DO_3 case, the areas corresponding to the iron atoms in A- and B-sites should be around 67 and 33% respectively. The present value of area (30% and 25%) shows that while B-sublattice is by and large intact and is occupied by alternate iron and aluminium atoms, some disordering is left in A-sublattice. This results in less than eight iron atoms in the nearest-neighbour shells of iron sitting in B-sublattice. Such a case results in the HMF of 25.7 T. The iron atoms displaced from the B-sublattice will create HMF components larger than 21 T. We also have a small contribution of doublet (relative area of about 6%). This signifies iron environments with less than four iron atoms in its neighbour shell.

The above results are also reflected in the p - B distribution shown in figure 3b. The characteristic DO_3 doublet is prominently present in this distribution together with other smaller peaks.

The behaviour of the sample $Fe_{70}Al_{28}Cr_2$ (figures 3c, 3d) is very similar to that of $Fe_{72}Al_{28}$ described above. Here also, we have the two characteristic DO_3 peaks in the p - B distribution, larger for the A-sublattice and smaller for the B-sublattice. It can be easily seen from figure 3d that the ratio of area of HMF peak in the B-sublattice to that in the A-sublattice is decreased on chromium substitution.

The p - B distributions for $x = 4$ and $x = 6$ of the annealed samples show a strong peak corresponding to the A-sublattice of DO_3 structure but the corresponding peak for B-sublattice is much reduced. Table 2 shows the relative areas of the component

Table 2. Relative area under the DO_3 peaks in the p - B distribution of annealed samples. A_1 is the area under the peak corresponding to the A-sublattice and A_2 that under the peak corresponding to the B-sublattice of DO_3 phase.

x	HMF of DO_3 -A peak (T)	Area A_1 (%)	HMF of DO_3 -B peak (T)	Area A_2 (%)	Area of other components (%)	A_2/A_1
0	21.0	30	29.7	25	45	0.83
2	20.8	32	29.1	22	46	0.69
4	19.7	37	28.0	12	51	0.32
6	18.7	30	26.4	7	63	0.23

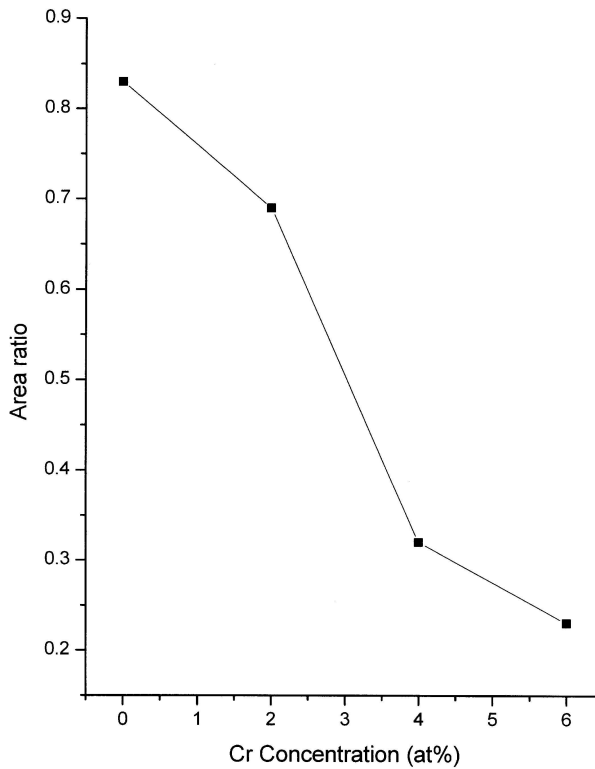


Figure 4. Variation of the ratio of relative area under the peak corresponding to the DO₃-B sublattice to that under the peak corresponding to the DO₃-A sublattice in the p - B distribution with increase of Cr concentration.

peaks making up the p - B distribution for all samples. These areas are obtained from the discrete fitting to the data. The variation is shown in figure 4.

The intensity of the B-sublattice peak is sharply reduced as the chromium concentration is increased from $x = 0$ to 2, 4 and 6. One possibility is that chromium atoms are preferentially occupying the A-sublattice, so that the iron atoms sitting at B-sites do not find eight iron atoms in their NN shell. However, this interpretation does not explain several observations. The maximum concentration of chromium is only 6%. If we use binomial distribution, the probability of zero Cr substitution in the NN shell is 0.61 and that of one Cr substitution is 0.31. The probability of two or more Cr substitution in the NN shell is only 0.08. In such a case we should have only a small reduction in the intensity of the B-sublattice peak and there should be an appearance of component with HMF 2 T less than the main B-sublattice peak. No such thing has been observed.

Also the intensity of the A-sublattice peak is roughly the same (area 30–35%). This also shows that not much change has occurred in the population of iron atoms in the A-site. This means that the iron atoms at the A-sublattice are producing HMF much smaller than the usual HMF (~ 30 T) at the probe ^{57}Fe nucleus at B-sites. We propose that, the effective magnetic moment of the A-site iron

atoms is gradually reduced when chromium is substituted. Cr as such is an antiferromagnetic material and may change the spin direction of the iron atoms in its nearest-neighbour environment. If chromium goes dominantly at B-sites, it can affect the spin direction of the A-site iron (which is its nearest-neighbour) resulting in a highly reduced HMF at the B-site iron atoms. The presence of chromium in B-site will reduce the value of HMF of B-site iron atom through next-nearest-neighbour interaction, where each substitution reduces the HMF by about 2 T [18] which is consistent with the observed results.

So, a general reduction of HMF and a sharp reduction of area in p - B distribution corresponding to the B-site probe ^{57}Fe , can both be explained by assuming that chromium is preferentially going in the B-sublattice and that the magnetic interaction changes the spin alignment of the nearest-neighbour A-site iron.

4. Conclusion

The phase structure of $Fe_{72-x}Al_{28}Cr_x$ alloys are severely changed by cold working to make powder from well-annealed ingots in equilibrium phases. The ordered DO_3 phase is almost destroyed during filing and in its place α -phase appears. This phase is not stable at room temperature and hence the equilibrium properties do not hold in the powder form unless further heat treatment is given. Annealing at $900^\circ C$ for 60 h restores the equilibrium DO_3 phase to a great extent.

The above observation is important for the Mössbauer spectroscopists where most of the transmission experiments are done with the sample in the powder form. If powder is made by a process which can introduce plastic deformation, there is a good chance of altering the phase structure drastically and any inference drawn from such an experiment will only be pertinent to the metastable structure of the sample developed during the powdering process.

Chromium substitution in dilute quantities has quite intense effect on the magnetic interactions in $Fe_{72-x}Al_{28}Cr_x$ samples. It seems that the chromium atoms preferentially occupy the B-sublattice of the Fe_3Al structure and change the spin structure of the eight nearest-neighbour iron atoms in the A-sublattice. This sharply reduces the intensity of the high HMF component (~ 30 T) in the DO_3 structure but leaves the low HMF component (~ 20 T) as it is, and the overall value of HMF reduces slightly on chromium substitution.

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