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Mössbauer effect and magnetization studies of the $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ system in the $L2_1$ (X_2YZ) structure

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Abstract

We investigate the effect of deviations from the stoichiometric composition on the structural and magnetic properties of the $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ system. The ordered $L2_1$ structure was identified in all prepared alloys, and was found to coexist with a tetragonally distorted face-centred tetragonal (fct) phase. The Curie temperature is strongly composition dependent, and achieves its highest value in the alloy which has the smallest cell volume. The saturation magnetization and saturation moments at 4.2 K increase with the increase of the Cr concentration. Conversely, the highest average B_{hf} value at 300 K was obtained for the more Fe-rich alloy. It may be inferred from our results that the Fe atoms are carrying a non-null magnetic moment, which depends strongly on the composition in this system.

1. Introduction

Since the discovery of the ferromagnetic behaviour of ternary intermetallic compounds formed with nonmagnetic atoms and which adopt the $L2_1$ structure, Heusler alloys [1] have been the focus of attention of both experimentalists and theoreticians. Ideally these alloys have composition X_2YZ . From band structure calculations such systems have been predicted to be half-metallic: metallic in the spin majority band and semiconducting in the spin minority band structure with a gap near to the Fermi level. The existence of this gap in the minority-spin subband is a striking feature of these materials. The first compound which was predicted to be a half-ferromagnet was the Heusler alloy NiMnSb [2]. The interest in half-metallic ferromagnets stems from their potential for technological applications as spin valves. Heusler alloys possess a much higher ferromagnetic Curie temperature when compared with most other potential half-metallic materials. It is well established that the magnetic properties of these alloys depend

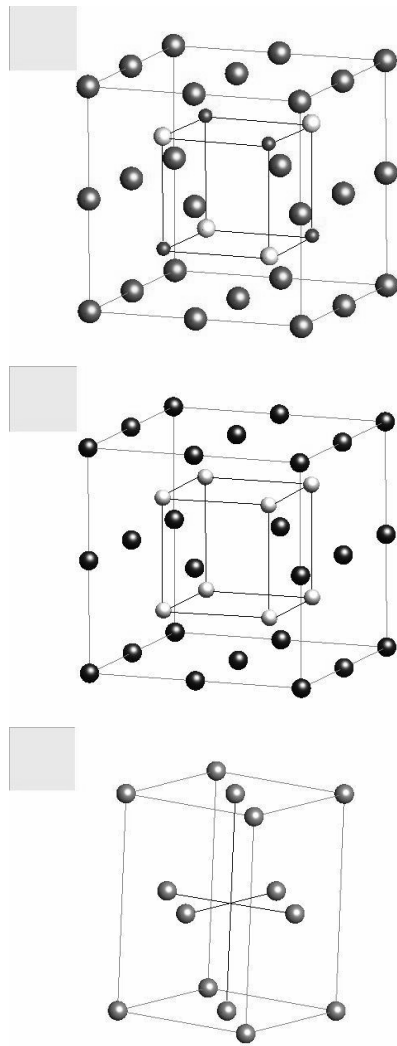


Figure 1. Top: $L2_1$ structure (X_2YZ); middle: $B2$ structure; bottom: fct structure. In a disordered $B2$ phase the Cr, Al atoms interchange positions randomly between Y and Z sites (inner cube).

sensitively on the degree of atomic order as well as on the conduction electron concentration. Moreover, several studies have been devoted to assess the effect of the valence electron number of the Z atoms on the magnetic properties of these alloys.

Recently there has been an upsurge of interest in ordered compounds containing Fe. Experimental findings have shown that the energetic splitting of the Fe 3s band is essentially different for each studied material, but without strong correlation effects [3]. Besides, the dispersion as well as the energetic position of the Fe 3s band varies as a function of the electron spin. Results of experiments with polarized radiation which have investigated the Fe 2p spectra of pure Fe have shown that the contributions of spin-up and spin-down electrons are different [4]. Fe_2CrAl alloy has been prepared and studied in the disordered $B2$ (simple cubic, sc) phase [5]. Mössbauer spectroscopy studies have shown the coexistence of a paramagnetic part (which has been ascribed to clustering of Cr atoms) with a magnetic hyperfine portion

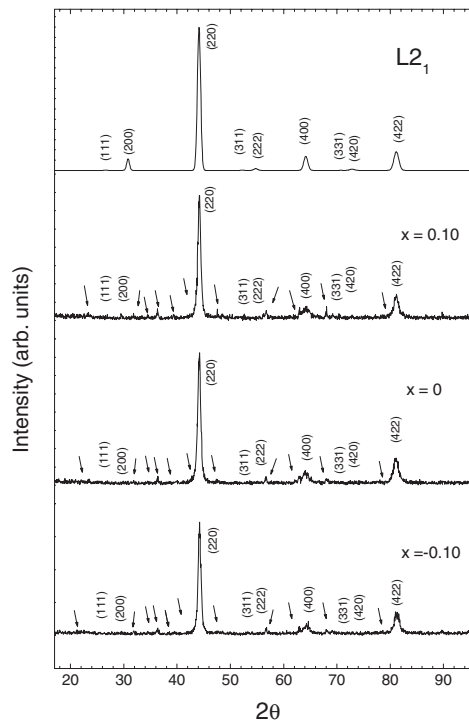


Figure 2. X-ray spectra of $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ alloys. The (hkl) Bragg reflections of the $L2_1$ structure are indicated. The arrows indicate the peaks of an fct structure. A simulation of a hypothetical $L2_1$ structure is shown at the top.

at several temperatures between 40 and 296 K. The average hyperfine field B_{hf} follows the $(T/T_C)^{3/2}$ law. The Curie temperature was determined as 297 K, and the lattice spacing was found to be $2a = 5.807 \text{ \AA}$. In the present contribution, we investigate the structural and magnetic properties of the $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ system by x-ray diffraction, Mössbauer spectroscopy, calorimetric and magnetization measurements. Since few experiments dedicated to studying the magnetic behaviour of Fe_2CrAl alloys exist, this work is intended to be a contribution to this matter.

2. Experimental procedure

Polycrystalline $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ compounds were prepared by arc-melting the high-purity starting materials Fe, Cr and Al, in an argon atmosphere and annealing at 1200 K for 3 days, then at 673 K for more 3 days, and afterwards cooling the samples in the furnace itself. Since the weight loss after melting and heat treatment was less than 0.6% the nominal composition was accepted as being accurate. The x-ray diffraction analysis was carried out on powdered polycrystalline samples with Cu $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). The Curie temperatures were determined by scanning magnetization versus temperature $M(T)$ curves with a magnetobalance above room temperature (300 K). The Mössbauer spectra were obtained at 300 and 23 K with transmission geometry in a conventional spectrometer, operating with constant acceleration mode, using a 50 mCi $^{57}\text{Co}/\text{Rh}$ source. The standard is natural α -iron, for which all quoted isomer shifts are reduced to its centroid. Hysteresis loops were registered at 4.2 K in a field up to

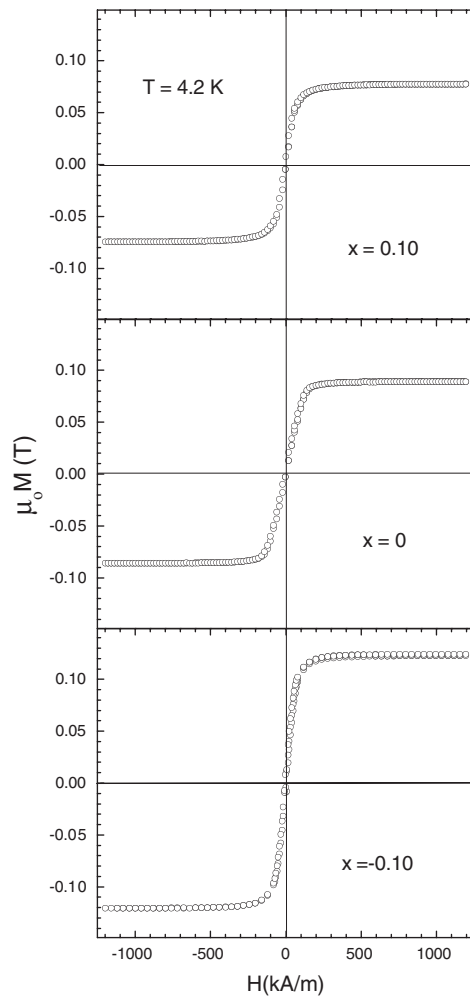


Figure 3. The magnetic field dependence of the magnetization in $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ alloys at 4.2 K.

1250 kA m^{-1} using a vibrating sample magnetometer. Magnetization curves were registered in a field-cooled (FC) and zero field-cooled (ZFC) sequence by using a superconducting quantum interference device from 4.2 K to 400 K in a field of 20 G.

3. Results and discussion

X-ray diffraction studies showed that all samples possess the $L2_1$ phase, which appears mixed with a minor phase, identified as fct. An illustration of $L2_1$, $B2$ and fct structures is shown in figure 1. The diffractograms of the studied alloys are shown in figure 2, and the corresponding lattice parameters are listed in table 1. A simulation of a $L2_1$ structure with $a = 5.806 \text{ \AA}$ was performed and is shown on top of figure 2 for the sake of comparison. As can be seen in table 1, in the ordered $L2_1$ phase the lattice parameter decreases slightly in the off-stoichiometric alloys. An earlier reported value for the $L2_1$ phase is $a = 5.805 \text{ \AA}$ [6], whereas for the disordered $B2$ (sc) phase the reported value is $2a = 5.807 \text{ \AA}$ [5]. A satisfactory agreement exists between the

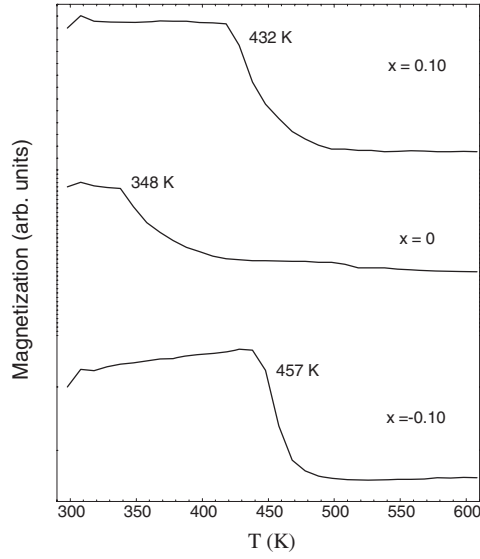


Figure 4. Transitions measured with a magnetobalance.

Table 1. Lattice parameter, saturation magnetization and saturation moments at 4.2 K, Curie temperature, average magnetic hyperfine field and most probable field value at 300 and 23 K for $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ alloys.

x	Structure	a (Å)	$\mu_0 M_s$ (T) (4.2 K)	μ_s (μ_B) (4.2 K)	T_C (K)	$\overline{B_{hf}}$ (T) (300 K)	$(B_{hf})_{mp}$ (300 K)	$\overline{B_{hf}}$ (T) (23 K)	$(B_{hf})_{mp}$ (23 K)
0.10	$L2_1$	5.806	0.077	1.301	432	14.40	17.45	17.14	18.70
	fct	4.584 (a)			219				
		4.959 (c)							
0	$L2_1$	5.811	0.089	1.508	348	12.07	8.63	16.31	19.71
	fct	4.575 (a)			152				
		4.977 (c)							
-0.10	$L2_1$	5.802	0.124	2.091	457	13.05	9.30	17.39	20.29
	fct	4.560 (a)			131				
		4.971 (c)							

results given in table 1 and those reported in the literature for the ordered phase. For the fct phase the increase of the Fe concentration leads to a compression in the c -direction, although the unit cell volume remains practically the same. With the increase of the Cr concentration the lattice is compressed in the xy -plane, and the cell volume decreases.

The hysteresis loops recorded at 4.2 K are plotted in figure 3. A typical ferromagnetic behaviour is seen in all of them. No remanence is observed, nor any coercive field. All these alloys saturate under the applied field, and the saturation magnetizations M_s as well as the saturation moments μ_s are included in table 1. M_s decreases in the more Fe-rich alloy and increases in the more Cr-rich alloy. Results of first-principles calculations for spin magnetic moments in Fe_2CrAl yielded -0.093 , 1.108 and $-0.011 \mu_B$, for Fe, Cr and Al atoms, respectively [7]. Thus, Fe is practically paramagnetic in Fe_2CrAl , whereas the Cr atoms are responsible for the spin moment. According to experimental results the saturation moment of this compound at 4.2 K is $1.67 \mu_B/\text{FU}$ (or equivalently, ≈ 0.099 T) [6]. The result obtained for

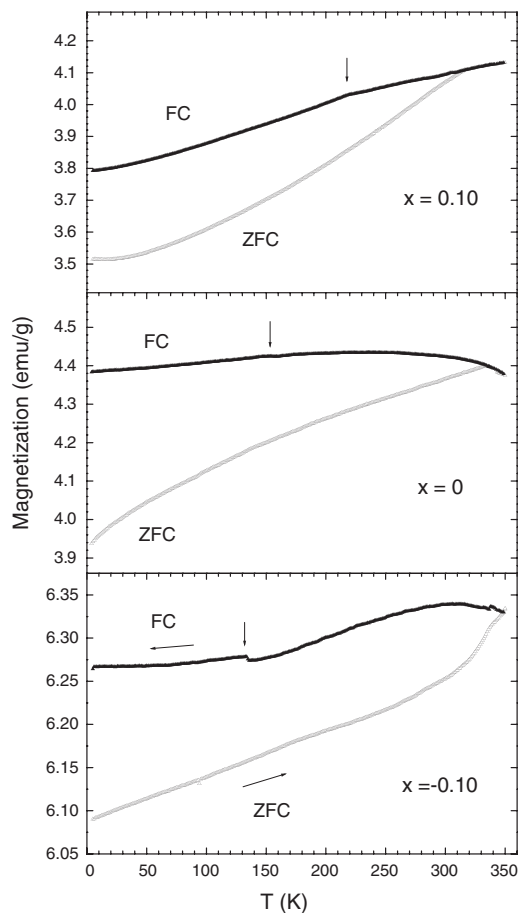


Figure 5. Magnetization measurements: field cooling (FC) and zero-field cooling (ZFC). The measuring field is 20 Oe. The vertical arrows are indicating detected transitions.

μ_s shown in table 1 for $x = 0$ agrees fairly well with the reported value. As can be seen, the increase of the Cr concentration leads to an increase of the total magnetization in these alloys, as a result of the larger contribution which arises from the Cr atoms which are carrying the largest moments.

In order to determine the ferromagnetic Curie temperature T_C of these alloys we performed magnetization versus temperature measurements with a magnetobalance. The registered traces are shown in figure 4, and the corresponding transition temperatures are listed in table 1. It can be seen that the Curie temperature increases in the off-stoichiometric alloys, in excess of both Fe and Cr, thus following the decrease of the unit cell volume. Hence, the largest T_C value (457 K) was achieved for the alloy with $x = -0.10$ which has the smallest lattice spacing (5.802 Å). The magnetic field dependence of the magnetization at lower temperatures is shown in figure 5. These $M \times T$ curves were registered first in the ZFC state and then in the FC state. The steep decrease of the magnetization with decreasing temperature indicates that a spin-glass behaviour is expected in these alloys at low temperatures. A feature which can be observed in the FC curves in figure 5 is a kink appearing at about 219, 152 and 131 K, for $x = 0.10$, 0 and -0.10 , respectively. These weak transitions are thought to be associated to the fct phase,

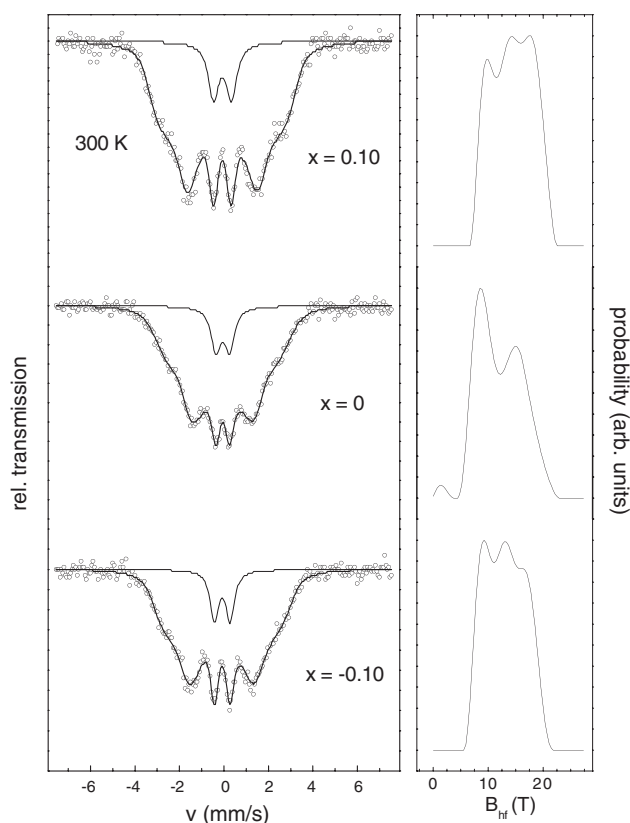


Figure 6. Left: Mössbauer spectra at 300 K of $Fe_{2+x}Cr_{1-x}Al$ alloys; right: histograms of magnetic hyperfine field distribution.

which has been identified from the x-ray diffraction analysis. Since no antiferromagnetic or paramagnetic component was detected in the hysteresis loops at 4.2 K this phase is expected to be another ferromagnetic entity which is present in these alloys coexisting with the ordered $L2_1$ phase.

The Mössbauer spectra of the studied compounds at room temperature are plotted in figure 6. These were fitted with a hyperfine field distribution in order to take into account those contributions which arise from both ordered $L2_1$ and fct phases. The linewidths were constrained to that of pure body-centred cubic (bcc) Fe. A histogram of 75 sextets was adopted to build up the distribution profile; these are shown to the right in figure 6. The centre of the block of sextets is located at -0.08 mm s^{-1} (average isomer shift). In addition, a doublet was used to fit the envelope of each spectrum. The average field \overline{B}_{hf} and most probable field $(B_{hf})_{mp}$ values are also included in table 1. It can be noted in figure 6 that similar shapes were obtained for the distributions of both the histograms and the spectra profiles. However, these are completely different from those earlier obtained for the $B2$ phase, which confirms the distinct nature between the $B2$ and $L2_1$ phases in these alloys [5]. Even for the results at low temperature there is no resemblance between the spectra profile in both cases. In the work of Lakshmi *et al* [5] the distribution curves have shown a prominent peak at low field values in addition to a low intensity peak at higher field values. In the case of a perfectly ordered sample, Fe_2CrAl should present only one peak in the field distribution, considering that Fe should have

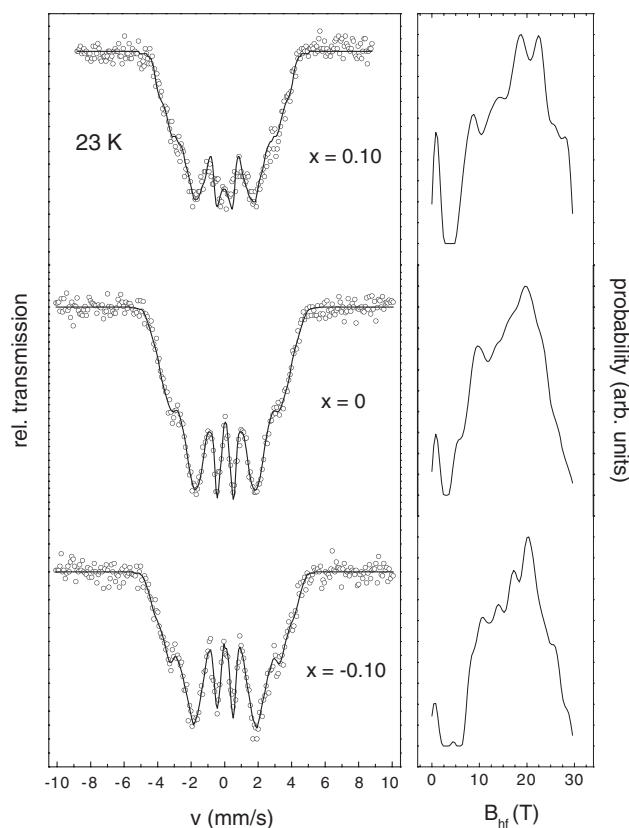


Figure 7. Mössbauer spectra at 23 K of $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ alloys.

only Cr atoms as nearest neighbours. Hence, the presence of a second peak in the distribution reveals a considerable disorder in the sample in that case. At 296 K the higher peak occurred for $B_{\text{hf}} \approx 12$ T, and at 4.2 K this was shifted to about 18 T [5].

In the present work, as can be seen in table 1, for $x = 0$ there was obtained an average B_{hf} of 12.07 T. In the more Fe-rich sample this has the largest value of 14.40 T, whereas for the more Cr-rich alloys it is 13.05 T. As one sees, the behaviour of B_{hf} does not follow by any means the behaviour of the saturation magnetization. In the distribution profile the highest peak indicates the most probable field $(B_{\text{hf}})_{\text{mp}}$, which presents similar values for both $x = 0$ and -0.10 and increases steadily for $x = 0.10$, as can be seen in table 1. The $(B_{\text{hf}})_{\text{mp}}$ value is expected to be reflecting the contribution which arises from the Fe sites which represent the most probable configuration in these alloys and which, in its majority, belongs to the main phase, e.g., the $L2_1$. The paramagnetic doublet, which is shown as a component subspectrum in figure 6 (dotted line), is associated with the fct phase, for which the magnetic transitions were detected in the $M \times T$ curves below 220 K, as shown in figure 5. At 300 K, the quadrupolar splitting of this doublet is nearly constant at about 0.7 mm s^{-1} , the isomer shift is -0.089 mm s^{-1} , and the subspectral area in all of them is $\approx 8\%$. Thus, it is confirmed from Mössbauer spectroscopy that our samples consist mostly of the ordered $L2_1$ phase.

In figure 7 are shown the spectra collected at 23 K. As one sees, the distribution of histograms is enlarged and includes new contributions from both higher and lower fields. This can be explained by taking into account that at 23 K more Fe sites contribute to the total

field, since at this temperature the fct phase is below its disordering (Curie) temperature. The paramagnetic doublet observed at 300 K is expected to be converted into sextets to include the contribution of this magnetic phase at low temperature. The average field $\overline{B_{\text{hf}}}$ and most probable field $(B_{\text{hf}})_{\text{mp}}$ values at 23 K are also listed in table 1, where it can be seen how these values become closer, as a result of the increase of the magnetic contributions which arises from the Fe sites in both ferromagnetic phases. The increased number of peaks which appears in the distribution of histograms indicates an increased number of field values (sextets) which compose the overall spectrum envelope. From this one may infer that the fct phase is a disordered phase, in which several configurations of Fe sites are contributing with different field values. Nevertheless, the small peak which appears in the distribution profile at lower fields indicates that a small contribution is also arising from Fe sites whose B_{hf} values are nearly zero, which also confirms that in this system the Fe atoms are indeed carrying a small magnetic moment. As a conclusion, the results of the present investigation indicate that the ordered $L2_1$ phase can stabilize in the $\text{Fe}_{2+x}\text{Cr}_{1-x}\text{Al}$ system at compositions around stoichiometric. A ferromagnetic behaviour was identified at room temperature. The Curie temperature increases with the decrease of the lattice parameter in the off-stoichiometric alloys. Our results also indicate that the Fe atoms are indeed carrying a non-null magnetic moment, which is expected to depend strongly on the composition in this system. A spin-glass behaviour was observed at low temperatures. It is noteworthy that a spin-glass behaviour has also been reported recently for a bcc $\text{Fe}_2\text{Cr}_{0.33}\text{Al}$ alloy [8].

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