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Mössbauer studies of hyperfine fields in disordered Fe_2CrAl

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Abstract. Heusler-like alloy Fe_2CrAl was prepared and studied. Structure determination was done by X-ray. The structure was found to conform to the B_2 type. Magnetic hyperfine fields in this sample were studied by the Mössbauer effect. The Mössbauer spectra were recorded over a range of temperature from 40 to 296 K. The Mössbauer spectra showed the co-existence of a paramagnetic part with a magnetic hyperfine portion at all recorded temperatures. Even with the distribution in the magnetic hyperfine field, the average hyperfine field follows the $(T/T_c)^{3/2}$ law. The paramagnetic part of the hyperfine field is explained in terms of the clustering of Cr atoms.

Keywords. Mössbauer spectroscopy; disordered alloy; magnetic hyperfine fields.

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1. Introduction

Heusler alloys are ternary alloys of stoichiometric composition bearing the general formula X_2YZ. In this class of alloys, X and Y are generally transition elements and Z an sp element. These alloys offer excellent systems for studying magnetic interactions. Large volumes of studies have been devoted to Heusler alloys bearing the general formula Pd_2YZ and Co_2YZ, with Y mostly being Mn [1,2]. Not many studies for Fe-based Heusler alloys have been reported.

In general, it can be seen that on preparing Heusler alloys X_2YZ with Pd as X, ordering is easily possible. It can even tolerate some amount of off-stoichiometric composition [3]. It was observed that there was more of a tendency for disorder in Co-based alloys as compared to the Pd-based ones. When X is Fe, few of these alloys show good ordering. In particular, in most Heusler-like alloys, irrespective of what element X is, when Z is a III B element, the possibility for forming disordered systems is greater [4].

Iron-based transition metal alloys show a great sensitivity to environmental effects [5], for instance, the definite site preference of Cr, Co or V in Fe–Al or Fe–Si systems even in the presence of disorder [6–9]. It is therefore interesting to study the trend of hyperfine fields in the stoichiometric alloy Fe_2CrAl. In this paper, we present the results of hyperfine interaction studies made on the Heusler-like alloy Fe_2CrAl.

2. Experimental

The samples were prepared by weighing out required amounts of the constituent materials in stoichiometric proportions. The materials used were of at least 99.99% purity (obtained from M/s Spex Inc., USA). These were then melted in argon (99% purity) atmosphere turning over the melted buttons and re-melting several times to ensure homogeneity. The buttons were then crushed and packed into quartz ampoules evacuated to 10^{-5} torr and kept for annealing. They were annealed at 800°C for 72 h and then further annealed at 200°C for three more days and allowed to cool down to room temperature in the furnace itself. X-ray studies were made at room temperature using Cu-Kα radiation. Mössbauer spectra for this sample were recorded using a 25mCi Co-57 (Rh) source over a temperature range of 296–40 K. Low temperature Mössbauer measurements were carried out using a closed cycle refrigerator. The temperatures were kept steady within 2 K.

The centroids of the Mössbauer spectra taken for this sample were seen to lie very close to the zero velocity channel. Curie temperature was therefore determined using the zero velocity thermal scan method. In addition, this method has the advantage that it does not require the application of any external magnetic field. As the Mössbauer spectra also showed co-existence of paramagnetic as well as hyperfine structures, this method is more suitable in the present case. The temperature was kept fixed within ± 0.5°C to ± 2°C at worst. The counts were collected for half a minute at each temperature after allowing for a 5-min stabilization time between each reading so as to ensure the establishment of proper temperature equilibrium. Figure 1 gives the curve obtained by plotting the counts obtained at zero velocity against temperature for this sample. It was seen that the Curie temperature is 297 ± 2 K.

3. Results and discussion

The X-ray diffractogram (figure 2) taken for this alloy showed that a single-phased alloy had formed. Preliminary studies on the effect of quenching and also of different annealing

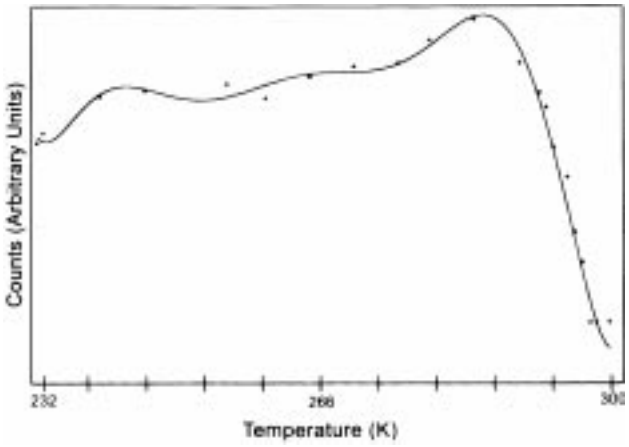

Figure 1. Zero velocity Mössbauer thermal scan for Fe_2CrAl.

for this alloy show that in no case was the ordered L_{21} structure formed. The structure was found to conform to the B_2 type. A fully ordered Heusler structure is of the L_{21} type. This structure consists of four sets of interpenetrating fcc planes A, B, C and D (shown in figure 3). The A and C sublattices are equivalent and are occupied by Fe atoms, sublattice B by Cr atoms and sublattice D by Al atoms. However, this sample has a B_2 structure. Cr and Fe have, therefore, randomly entered the A[C] and B sites. The lattice parameter 2*a* was found to be 5.807 Å. The density of Fe_2CrAl was measured to be 6.25 g/ml by using a standard relative density method. The density calculated from the measured lattice parameter is in agreement with this value. Table 1 gives the details of the X-ray measurement carried out

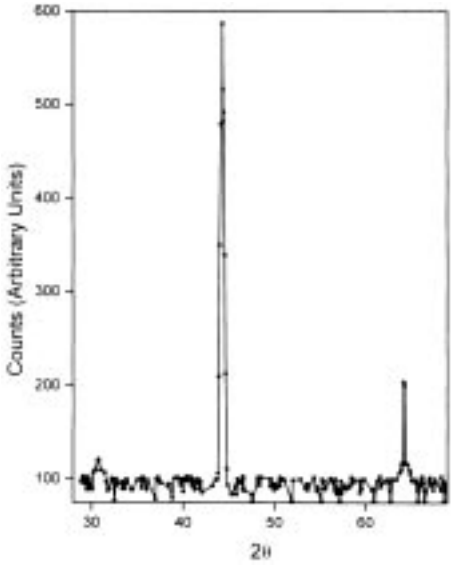

Figure 2. XRD pattern of Fe_2CrAl.

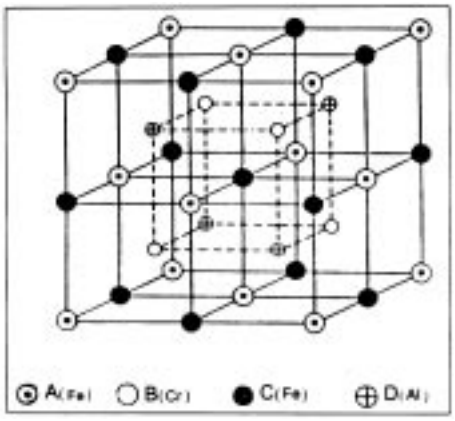

Figure 3. Crystal structure for ordered Fe_2CrAl (L_{21} structure).

Table 1. X-ray parameters for Fe_2CrAl.

2θ (°)	I/I_0	$d_{\text{experimental}}$ (Å)	hkl	$\Delta 2\theta$ (°)
30.8	4.00	2.90	200	0.00
44.1	100	2.05	220	−0.02
64.1	12.48	1.45	400	−0.03
64.2	6.50	1.45	331	−0.07

on this sample. Difference between the experimentally determined values of 2θ and the calculated theoretical value for a B_2-type structure are given as $\Delta 2\theta$ in this table.

Mössbauer spectra were recorded at temperatures 40, 70, 108, 145, 202, 241, 252, 264, 291 and 296 K. An immediate point of interest in the Mössbauer spectra was the co-existence of a paramagnetic portion with the magnetic hyperfine part in all the spectra, down to 40 K. These were fitted using the Window's [10] method of fitting for a distribution in the hyperfine fields. The linewidths were constrained to have widths corresponding to α-iron. Figures 4 and 5 give the Mössbauer spectra as well as the hyperfine field distribution curves for 40, 70, 108, 145, 202 and 296 K. The distribution curves show one high intensity peak at low field values and one low intensity peak at higher field values. Both these are broadened with $\Delta H/H$ in excess of 30%. In addition to these, there is a peak corresponding to the zero magnetic field. Our studies on the disordered series $Fe_{3-x}Cr_xAl$ [6] showed that Cr preferentially entered into the high field site in the disordered Fe_3Al. This site is the one which has 2–3 neighbor Al. The high-field component in this sample has a very low intensity as compared to the low-field main peak. This shows that a few probe Fe atoms are surrounded by nearly three other Fe atoms. In a perfectly ordered sample of Fe_2CrAl, the iron atom should have only Cr atoms as nearest neighbors and there should have been only one peak (the lower one) in the hyperfine distribution. The presence of the second high field peak as also the large $\Delta H/H$ values show the considerable disorder present in this sample.

Two possible reasons for the co-existence of a paramagnetic part with the magnetic hyperfine fields in this sample can be thought of. One reason could be the presence of two separate chemical phases in the sample, one of which is paramagnetic, and the other, ferromagnetic. The other reason could be due to a spread in the relaxation times of the iron atoms in the alloy while being chemically single phased. In our case X-ray has ruled out the presence of any other phase. A preliminary neutron diffraction study carried out in the sample rules out the existence of two different types of magnetic sublattices while confirming the structure determined by X-ray. Moreover, the centroids of the paramagnetic as well as hyperfine components coincide and the area of the paramagnetic portion varies with temperature. The coexistence of paramagnetic peak well below the Curie temperature points to the wide spread in the relaxation time in the system. Such a relaxation phenomenon is also seen in Fe_3Al system. For instance, Czer *et al* [11] have studied the ordering transformation in the Fe_3Al alloy by Mössbauer effect. They found that the paramagnetic and hyperfine peaks co-exist below the Curie temperature of the disordered alloy within a large interval of temperature. They ascribed this to the fluctuations that occurred in the number of next neighbor atoms. These fluctuations in the neighborhood of the iron atoms led to an appreciable dispersion of the relaxation time resulting in the simultaneous appearance of the hyperfine and paramagnetic peaks. In the series $Fe_{3-x}Cr_xAl$, it was observed that at about $x = 0.5$, a paramagnetic peak, co-existent with the hyperfine spectrum

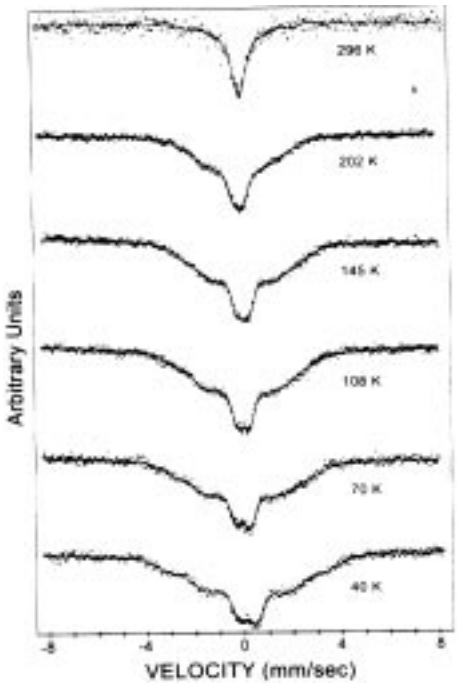

Figure 4. Experimental and fitted Mössbauer spectra at 40, 70, 108, 145, 202 and 296 K.

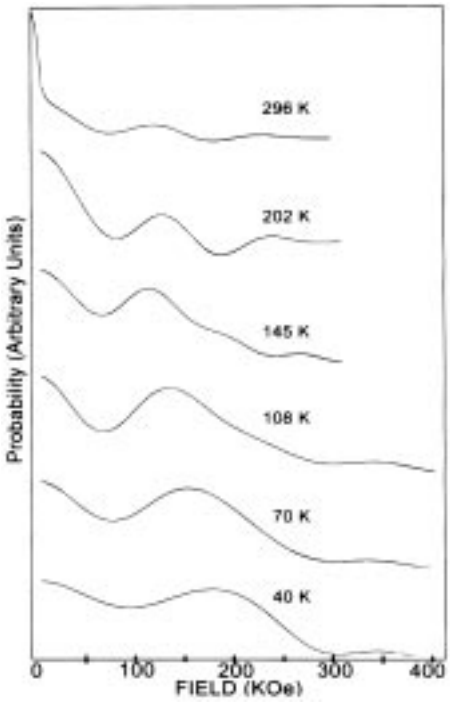

Figure 5. Hyperfine field distribution at 40, 70, 108, 145, 202 and 296 K.

had started appearing [6]. The effect of the addition of Cr above a certain percentage into Fe_3Al resulted in the preferential population of Cr atoms into the sites which would have been normally occupied by Fe in an ordered system. The coexistence of paramagnetic peak in the Fe_2CrAl can therefore be understood to be due to the clustering of Cr atoms.

The value of the average hyperfine field (H_{av}) obtained for different temperatures of this sample were plotted against the temperature. The curve obtained was extrapolated to obtain the value of the average hyperfine field at 0 K (H_{zero}). The plot of the reduced hyperfine fields, i.e., $H_{\mathrm{av}}/H_{\mathrm{zero}}$ vs. reduced temperature $(T/T_{\mathrm{c}})^{3/2}$ was then plotted. The same quantity was expressed by the Brillouin function for a particular spin value J, in this instance for $J = 0.5$, 1 and 2 (figure 6). As can be observed, the experimental curve for this sample passes below the curves but lies closest for the value of $J = 2$. Grandjean and Gerard [12] who have observed this over- or under-Brillouin curve behavior in their studies of $Fe_{2-x}Mn_xAs$, have put forward two possible explanations. The under-Brillouin zone magnetization curves cannot be explained by a theoretical model with localized moments. They put forward one explanation that the value of the proportionality constant between the magnetization and the hyperfine field, which is generally independent of temperature, is not so. The other was that an itinerant magnetism, which may be applied to all compounds, must be considered. The second possibility is the more plausible one as within the same type of solution, there is very little probability that the nature of the proportionality constant vary. A plot of $H_{\mathrm{av}}/H_{\mathrm{zero}}$ vs. $(T/T_{\mathrm{c}})^{3/2}$ (figure 7) gave a straight line showing

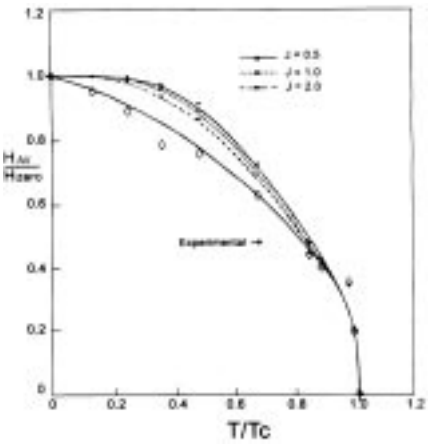

Figure 6. Reduced hyperfine field $H_{\rm av}/H_{\rm zero}$ vs. reduced temperature $T/T_{\rm c}$ and Brillouin functions for $J = 0.5$, 1 and 2.

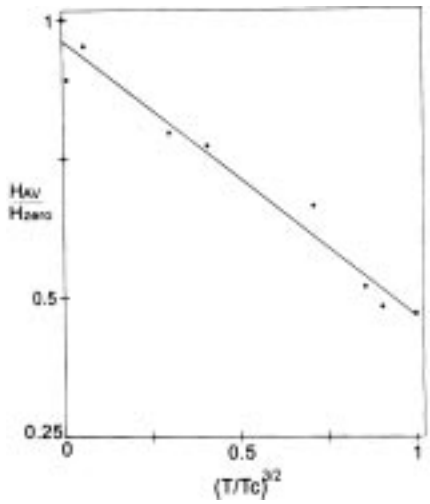

Figure 7. Reduced hyperfine field $H_{\rm av}/H_{\rm zero}$ vs. $(T/T_{\rm c})^{3/2}$.

that this alloy also followed the Bloch's [13] $T^{3/2}$ law. The hyperfine field in a ferromagnetic sample is proportional to the magnetization. In this particular sample however, the presence of a relaxation phenomenon observed in the Mössbauer spectra would make the direct quantitative evaluation of the proportionality constant difficult. A rough estimate of the exchange interaction energy for this sample was worked out to be 6.4×10^{-3} eV.

In conclusion we can see that the compound Fe_2CrAl has formed a single-phased Heusler-like alloy. Even in the limit of chemical disorder, this compound shows interesting magnetic properties. This is evident from the co-existence of a paramagnetic part with the magnetic hyperfine portion. The reason for this co-existence is most likely due to the clustering of Cr atoms. Even then, the overall behavior is like a regular ferromagnet as is evidenced by the validity of the $T/T^{3/2}$ law when the average hyperfine field is taken into account.

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