Hyperfine interactions in Heusler systems

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Recently, there has been a new surge of interest in Heusler alloys because of possible use of these alloys as materials for spin electronic devices. Heusler alloys also offer excellent systems for studying magnetic interactions. These alloys can be held at various degrees of order and also allow systematic substitution of one or more of the constituents. The magnetic and transport properties of these alloys can, therefore, be modified through such methods. Hyperfine interactions studies in a disordered Heusler system Fe2CrAl using Mössbauer spectroscopy, have been presented. The disorder present in the system is reflected in the X-ray diffraction and Mössbauer spectra. The system behaves like a normal ferromagnet even in the presence of disorders.

Keywords: Mössbauer spectroscopy, Heusler alloys, Half-metals, Disordered alloy, Magnetic hyperfine interactions

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1 Introduction

Heusler alloys are ternary intermetallic systems made mainly from transition metal and sp-elements. The Heusler alloys have been of interest since 1903 when Heusler reported that ferromagnetic alloys could be made from non-ferromagnetic constituents Cu, Mn and main group elements such as Al and Sn. The ferromagnetic properties of these alloys were related to the chemical ordering and concentration of Mn atoms. In general, there are two types of Heusler systems. The first is the full-Heusler alloy, with chemical composition X2YZ, which crystallizes in the L21 structure. The other type is half-Heusler with composition XYZ, which crystallizes in the Clb structure. Typical X-site elements are transition metal elements Cu, Pd, Au, Co, Ni, Fe etc, Y-site elements are transition metal elements Ti, Zr, Hf, V, Mn, Cr etc. and Z may be any one of the large number of sp elements belonging to the IIIB-VB group. Typical s-p elements are Al, Sn, In, Sb, Ge or Ga etc. Most of these alloys, especially the X2YZ type, are ferromagnetic at room temperature. Though a large number of Heusler alloys are available as ferromagnetic systems, many of the alloys show other interesting properties like semiconducting, semimetallic, Pauli paramagnetic, antiferromagnetic and halfmetallic character.

Initial interest in Heusler systems was mainly limited to the study of the magnetic interaction process. The regular and well-defined crystal structure allows partial or total substitution of components in these systems. Earlier studies were mostly confined to the study of hyperfine fields and systematics in these alloys.

Recently, there has been a renewed surge of interest in Heusler systems due to possible technological application of these systems in the new emerging field of magneto electronics devices called spintronics. In spintronics systems, materials having nonequilibrium spin population are required for generation of spin polarization. One of the key issues for the realization of spintronics is the efficient electrical injection of spinpolarized carriers into semiconductors. The gap in the minority spin band in Heusler systems leads to 100% spin polarization of electron states at the Fermi level. Hence, these systems are emerging as strong candidates as possible materials for spin injection into semiconductors. Further, high Curie temperature in the range 200-1100K and compatibility with compound and element semiconductors, makes these materials as one of the most promising materials for spin electronics. Another area of technological applications of the Heusler systems is in shape memory alloys (SMA).
Shape memory alloys are materials that, after being strained, revert back to their original shape at a certain temperature. In Heusler systems like Ni$_2$MnGa, magnetic control of the structural transformation is exploited to prepare SMA systems which are more efficient compared to conventional temperature driven SMA’s. Thus, the unusual transport and magnetic properties of these materials, consisting of three components, open up possibilities to engineer new materials. Altering the composition, allows changes in electrical resistivity, thermal conductivity, Seebeck coefficients, heat capacity and magnetic properties of these alloys.

Though, Heusler systems are, in general, chemically well ordered, chemical disorder of various degrees can co-exist in these systems, depending on the constituent elements and heat treatment given to prepare these alloys. These disorders play a major role in altering the magnetic and electrical properties of these materials. Although many Heusler systems have been predicted to be half metallic ferromagnets, sensitivity of spin polarization to structural disorder is one of the difficulties in experimentally realizing a half metallic ferromagnetic state in many of these systems. While atomic disorder destroys high spin polarization in half Heusler systems like NiMnSb, no significant reduction in spin polarization has been detected in Co$_2$(Cr$_{0.6}$Fe$_{0.4}$)Al even in the presence of atomic disorder among Cr, Fe and Al. Theoretical investigation of atomic disorder-effects on half metallicity of the full-Heusler alloy Co$_2$(Cr$_{1-x}$Fe$_x$)Al shows that disorder between Cr and Al does not significantly reduce the spin polarization while disorder between Co and Cr makes a considerable reduction of the spin polarization. Thus, atomic disorders in Heusler systems play a crucial role in determining the spin polarization and hence, their utility as spin injection sources.

In general, ordering is easily possible in Heusler alloys X$_2$YZ with Pd as X. It is observed that there is more of a tendency for disorder in Co-based alloys as compared to Pd based alloys, especially if Z site elements are Sn or Al. When X is Fe, few of these alloys show good ordering. In particular, in most Heusler alloys, irrespective of what the element X is, when Z is a IIIB element, the possibility of forming disordered systems is greater. Iron based transition metal alloys show a great sensitivity to environmental effects. For instance, Cr, Co or V in Fe-Al or Fe-Si systems show definite site preference even in the presence of disorder.

Extensive studies have been carried out on Heusler systems using hyperfine interaction methods, to understand the coupling mechanisms responsible for magnetic hyperfine fields at non-magnetic sites. Atomic disorders present in the system will be reflected as a distribution in the hyperfine fields. Hyperfine interaction in a iron based Heusler system, Fe$_2$CrAl using Fe-57 Mössbauer spectroscopy has been studied in the present paper. The system is one of the iron based Heusler alloys theoretically predicted as a half-metallic ferromagnetic system. Since the hyperfine fields in iron based transition metal alloys are very sensitive to the environmental effects resulting from the structural disorders, it is interesting to investigate the hyperfine interactions in this system especially in the presence of disorders.

2 Experimental Details

Studies of hyperfine interactions in the Heusler system involves preparation of the alloy from the constituent elements, structural characterization using X-ray diffraction, magnetic characterization by measuring bulk magnetic properties and measurement of hyperfine interaction at specified sites using hyperfine interactions tools like Mössbauer spectroscopy, perturbed angular correlation technique, nuclear magnetic resonance methods etc. In the present study, we have used Fe-57 Mössbauer spectroscopy to investigate hyperfine interactions at iron sites in Fe$_2$CrAl system.

2.1 Material Preparation

Heusler alloys are usually prepared by melting the constituent metallic elements in argon atmosphere using an argon arc furnace. The melting procedure is repeated three to four times to ensure homogeneity. During melting, precaution is to be taken to compensate for the loss of material due to sublimation. The quantity of material to be added for compensation depends on the constituent elements and the duration of first melting. Alloys prepared from arc melting require annealing to remove structural disorders and defects. The arc-melted ingots are sealed in evacuated quartz ampoules and put in a furnace maintained at a selected annealing temperature. Annealing temperatures are normally selected above the temperature of formation of other phases of the constituent elements. The duration of annealing can be decided from the changes in the intensity and width of the X-ray diffraction lines of samples subjected to different time periods of annealing. After annealing, the material can
be either slow cooled in the furnace if no intermediate phase formation is possible, or quenched into room temperature to avoid formation of intermediate phases. The alloys so obtained are usually powdered and used for measurements. The Fe$_2$CrAl Heusler alloy has been prepared by arc melting the iron, chromium and aluminium of high purity (99.99%). The chromium and aluminium in the form of chunks were wrapped in the iron foil to reduce any loss of aluminium by evaporation and melted by striking arc for a period of one minute. The ingot obtained from the first melting was melted repeatedly six times to ensure homogeneity. The weight loss of the Fe$_2$CrAl alloy prepared by the above procedure shows a weight loss of 0.5% only which is well within the acceptable level for samples prepared by arc melting. The arc-melted ingots are annealed at 800°C for one week. After annealing, the samples were slow cooled to room temperature in the furnace. Powdered samples were used for X-ray diffraction, magnetization and Mössbauer studies.

2.2 X-ray diffraction studies

X-ray diffraction studies of the alloy were carried out for structural investigations using Cu-Kα radiation. X-ray and lattice parameters calculated from X-ray measurements for Fe$_2$CrAl is presented in Table 1. The crystal structure of the fully ordered alloys is of the L21 structure and is shown in Fig. 1. The lattice consists of four fcc sub lattices. The unit cell is that of fcc lattice with four atoms as basis with A at (0,0,0), B at (1/2,1/2,1/2), C at (1/4,1/4,1/4) and D at (3/4,3/4,3/4). In Fm3m symmetry, Bragg reflections with non-zero structural amplitudes occur when Miller indices are all either odd or even. X-ray diffraction pattern will show three types of reflections with structure amplitudes as follows:

(i) $h$, $k$, $l$ all odd
e.g. $F(1,1,1)=4 \left| (f_A-f_C)^2+(f_B-f_D)^2 \right|^{1/2}$

(ii) $h$, $k$, $l$ all even. There are two different conditions which are as follows:

(a) $(h+k+l)/2=2n+1$
e.g. $F(200)=4 |f_A+f_C+f_B+f_D| \quad \ldots (1)$

(b) $(h+k+l)/2 =2n$
e.g. $F(220)=4 |f_A+f_C+f_B+f_D|$

In Eq. (1), $f_A$, $f_C$, $f_B$ and $f_D$ are the average scattering factors of atoms situated on the corresponding lattice sites. Reflections for which $(h+k+l)/2=2n$ are the principal reflections. The intensity of these reflections are unaffected by the state of chemical ordering because, as seen from expression (b) of Eq. (1) case (ii) above, all the average scattering factors simply add up and so any interchange in positions will not affect the structure amplitude. The other two groups are superlattice reflections, which are sensitive to chemical ordering. Johnston and Hall and Ziebeck and Webster have studied in detail the effects of different types of disorder on the structure amplitudes of ternary alloys of the Heusler type.

In Fe$_2$CrAl, the X-ray diffraction pattern does not show the superlattice lines corresponding to (111) within the detectable limit of 1%, whereas the even superlattice line (200) is observed. In Fe$_2$CrAl system, the even super lattice lines are unaffected by the Cr-Al disorder and intensities are reduced due to random disorder present in the system. The preferential disorder between Cr and Al will not cause reduction in intensities of even superlattice lines but the intensities of odd super lattice lines get affected. Complete disorder between Cr and Al in this alloy, therefore, reduces the intensity of the odd super lattice line (111) below the detectable limit resulting in a B2 type of structure.

| Table 1—X-ray and Lattice parameters for Fe$_2$CrAl Heusler alloy |
|-------------------|------------------|--------------|
| alloy             | 20   | hkl | I/Io | a (Å) |
| Fe$_2$CrAl        | 30.8 | 200 | 4.0  |       |
|                   | 44.1 | 220 | 100.0|       |

<table>
<thead>
<tr>
<th>alloy</th>
<th>64.2</th>
<th>331</th>
<th>6.50</th>
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Fig. 1—Heusler L21 structure
2.3 Magnetization measurements

The Curie temperature and magnetic moment carried by atoms in the alloys can be determined from magnetization studies. However, the bulk magnetization studies can only provide magnetic moment per molecule irrespective of the number of magnetic atoms in a formula unit whereas neutron diffraction measurement can be carried out to obtain magnetic moment carried by the transition metal element\(^7\). A vibration sample magnetometer (VSM) has been used to measure Curie temperature and magnetic moment per formula unit for the Fe\(_2\)CrAl alloy. While determining the Curie temperature, a very small field of about 50 Oe was used. The measurements were made over a range of temperatures from room temperature to a few degrees kelvin above the transition temperature. Saturation magnetization at room temperature was measured by noting the magnetic moment at room temperature over varying fields. Magnetization measurement shows that Fe\(_2\)CrAl alloy is ferromagnetic with Curie temperature of 297K. The total magnetic moment per formula unit is 1.45 \(\mu_B\) for Fe\(_2\)CrAl.

2.4 Mössbauer measurements

\(^{119}\)Sn and \(^{121}\)Sb Mössbauer spectroscopy have been extensively used to measure hyperfine fields at the Z site in full and half Heusler systems\(^7\). In the present study, we have used 57Fe Mössbauer spectroscopy to study hyperfine fields at the iron site in Fe\(_2\)CrAl alloy. Mössbauer studies were performed using a 25mCi Co-57(Rh) source mounted on a Mössbauer drive operated in constant acceleration mode. Low temperature measurements were carried out using a closed cycle refrigerator. The temperatures were kept steady within 2K.

3 Results and Discussion

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 40K. The spectra were fitted using the Window's28 method of fitting for a distribution in the hyperfine fields. The line widths were constrained to have widths corresponding to α-iron. Figs 2 and 3 show 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 a low intensity peak at high fields for 40, 70, 108, 145, 202 and 296 K.
peak at higher field values. Both these are broadened with $\Delta H/\langle H \rangle$ 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($x$)Al show that Cr preferentially enters into the high field site in disordered Fe$_3$Al. This site is the one which has 2-3 neighbour 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 3 other Fe atoms. In a perfectly ordered sample of Fe$_3$CrAl, the iron atom should have only Cr atoms as the nearest neighbours and there should have only been one peak (the lower one) in the hyperfine distribution. The presence of the second high field peak as also the large $\Delta H/\langle H \rangle$ values show the considerable disorder that is 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 a second one, which is ferromagnetic. The other reason could be 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 persistence of the paramagnetic peak well below the Curie temperature points to the wide distribution in the relaxation times in the system. Such a relaxation phenomenon is also seen in Fe$_3$Al system. For instance, Czer et al. have studied the ordering transformation in Fe$_3$Al alloy using 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 occur in the number of next neighbour atoms. These fluctuations in the neighbourhood of the iron atoms lead 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($x$)Al, it is observed that at about $x = 0.5$, a paramagnetic peak, co-existent with the hyperfine spectrum starts appearing. The addition of Cr above a certain percentage into Fe$_3$Al results in the preferential substitution of Cr atoms into sites which are normally occupied by Fe in an ordered system. The co-existence of paramagnetic peak in the Fe$_3$CrAl can, therefore, be understood to be due to the clustering of Cr atoms.

The values of the average hyperfine field ($H_{av}$) obtained at different temperatures have been plotted against temperature. The curve obtained is then extrapolated to obtain the value of the average hyperfine field at 0K ($H_{zeta}$). The plot of the reduced hyperfine fields, i.e., $H_{av}/H_{zeta}$ versus reduced temperature ($T/T_c$)$^{3/2}$ is then plotted. The same quantity is expressed by the Brillouin function for a particular spin value $J$, in this instance for $J = 0.5$, 1 and 2 (Fig. 4). As can be observed, the experimental curves pass below the theoretical curves with the curve corresponding to $J = 2$ being the closest. Grandjean and Gerard, who have observed this over or under-Brillouin curve behaviour in their studies of Fe$_{2-x}$Mn$_{x}$Al, have put forward two possible explanations. The under Brillouin zone magnetization curves cannot be explained by a theoretical model with localized moments. One explanation that they put forward is 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 is that an itinerant magnetism,

\[ Fig. 4—\text{Reduced hyperfine field } H_{av}/H_{zeta} \text{ versus reduced temperature } T/T_c \text{ and Brillouin functions for } J = 0.5, 1 \text{ and } 2\]
which may be applied to all compounds, must be considered. The second possibility is the more plausible since, within the same type of solution, there is very little probability that the nature of the proportionality constant vary. A plot of $H_{av}/H_{zero}$ versus $(T/T_c)^{3/2}$ (Fig.5) shows a straight line which indicates that this alloy also follows Bloch's $T^{3/2}$ 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 is worked out to be $6.4 \times 10^{-3}$ eV.

Using full potential screened Korringa-Kohn-Rostoker method, Galanakis et al. studied the full Heusler alloys based on Co, Fe, Rh and Ru. They have predicted that Fe$_2$CrAl Heusler alloy would be a half-metallic system. The atomic magnetic moments at Fe, Cr and Al were calculated as $-0.093 \text{ìB}$, $1.108 \text{ìB}$ and $-0.011 \text{ìB}$ with total spin magnetic moment in Fe$_2$CrAl as $0.910 \text{ìB}$ which is very near to the integer value (1.0 1B) of magnetic moment expected for half metallic ferromagnets. The theoretical calculation shows that the Fe in Fe$_2$CrAl is practically paramagnetic. This is contrary to the result obtained from the Mössbauer studies. The magnetic moment measured in Fe2CrAl is 1.451B, which is much higher than the theoretically predicted value of 0.910B and deviates much from the Slater-Pauling behaviour observed in half-metallic ferromagnets. Since the energy gaps in the minority band in full Heusler systems are extremely small due to states localized only at the Fe sites, disorders present in the system are expected to introduce density of states (DOS) in the gap and the system will tend to behave as a normal ferromagnet.

4 Conclusions

The hyperfine interaction studies in Heusler system can reveal the disorders present in the system through a distribution in the hyperfine fields. In addition to the hyperfine fields, interesting magnetic properties like clustering of atoms around the probe atoms which can give rise to co-existence of paramagnetic portion along with the usual hyperfine spectrum Even in the presence of high degree of disorder present in the system, the overall behaviour is like a regular ferromagnet as is evidenced by the validity of the $T^{3/2}$ law when the average hyperfine field is taken into account. The disorder present in the alloy is expected to destroy the half-metallic property of Fe$_2$CrAl as evidenced from the non-integer value of magnetic moment and the deviation from the Slater-Pauling behaviour and the system behaves as a normal ferromagnet.

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