Hyperfine field distributions in disordered Mn_2CoSn and Mn_2NiSn Heusler alloys

N LAKSHMI*, ANIL PANDEY and K VENUGOPALAN

Department of Physics, Mohanlal Sukhadia University, Udaipur 313 001, India

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Abstract. Heusler alloys, Mn_2CoSn and Mn_2NiSn , were prepared and characterized by X-ray studies. Mössbauer studies using Sn-119 were carried out to investigate the hyperfine fields present at the Sn site in these alloys. The hyperfine field distribution in these alloys as well as X-ray studies point to the chemical disorder present in both alloys. Co-existence of a paramagnetic portion along with the magnetic hyperfine part was observed in Mn_2CoSn even at low temperatures, while this was not found in Mn_2NiSn spectra. Hyperfine fields at Sn site were calculated using Blandin and Campbell model and compared with the experimental results.

Keywords. Hyperfine field distribution; Heusler alloys; Sn-119 Mössbauer spectroscopy.

1. Introduction

The Heusler alloys are generally ternary alloys of stoichiometric composition bearing the general formula, X_2YZ . In this class of alloys, X and Y are transition elements like Ni, Co, Pd, Pt, Fe etc and Z is an *sp*-element like Si, Al, Ge etc. These alloys offer excellent systems for the study of the mechanism of magnetic interactions. Magnetic properties of X_2YZ alloys arise from magnetic moments on transition metal atoms located on either the X or Y sites. Extensive studies have been carried out using Heusler alloys by employing hyperfine methods to understand the coupling mechanism responsible for magnetic hyperfine fields at non-magnetic sites (Brooks and Williams 1974; Dunlap *et al* 1981; Dunlap and Jones 1982; Jha *et al* 1983; Ritcey and Dunlap 1984; Carbonari *et al* 1993). The hyperfine field systematics in cobalt based Heusler alloys are quite different from systematics in Heusler alloys which contain only Mn as the magnetic atom (Delyagin *et al* 1981; Dunlap and Stroink 1982). In cobalt rich Heusler alloys of the form Co_2MnZ , which contain 25% of Mn, magnetic moment exists at two inequivalent lattice sites. In these alloys Mn carries about $4 \mu_B$ magnetic moment, while Co carries moments ranging between 0.3 and $1 \mu_B$, depending on the Z element (Webster and Ziebeck 1973). The Blandin–Campbell model has been used fairly successfully to describe hyperfine fields at the Y site in Co_2YZ type of alloys (Carbonari *et al* 1996). However, the success of this model is doubtful to explain the hyperfine fields at the Z site in the

case of Heusler alloys of the type, Co_2MnZ (Dunlap and Jones 1982). In this context, it is interesting to study the behaviour of hyperfine fields in Mn rich Heusler alloys. We have, therefore, prepared and studied Mn_2CoSn and Mn_2NiSn and also tested the applicability of the Campbell–Blandin model in these alloys. Further, these alloys are known to exhibit a good amount of chemical disorder (Surikov *et al* 1990) and it is, therefore, interesting to observe the behaviour of hyperfine fields in the presence of disorder.

2. Experimental

The starting materials for the preparation of the alloys were obtained from M/s Spex Industries Inc., USA. These were of at least 99.99% purity. Mn and Sn were in the form of granules while Co and Ni were in the form of sheets. The constituent materials were weighed out in the desired atomic ratio and melted together in an arc furnace in a flowing argon atmosphere. Weight loss in both materials was observed to be less than 1%. It was seen that the materials were hard and brittle. They were crushed and ground to fine powder. They were then sealed into quartz ampoules evacuated to 10^{-5} torr and kept in a furnace at 800°C for 7 days. They were then allowed to cool down to room temperature in the furnace itself.

Approximately 300 mg each of the powdered materials was used for X-ray characterization of the prepared alloys. X-ray diffraction studies of the samples were done at room temperature with a Philips X-ray diffractometer using $\text{CuK}\alpha$ radiation. The Curie temperatures for Mn_2CoSn and Mn_2NiSn were determined using an a.c. susceptibility equipment.

*Author for correspondence

The samples for the Mössbauer measurements were prepared by weighing out the required amount of the powdered material and packing into copper rings after thoroughly mixing with boron nitride. The quantity of material used was such as to have a thickness of 9 mg/cm^2 of Sn. The source used was a 5 milli Curie Sn^{119} in CaSnO_3 matrix. This allowed measurement of the hyperfine field at the Sn site as tin is a component of these alloys. Data were accumulated for an average of 72 h. Low temperature studies were performed using a closed cycle refrigerator.

3. Results and discussion

X-ray diffraction spectra were analysed and the peaks were indexed using the PDP program (Calligaris 1990). It was observed that each of the alloys had formed in the single phase. Well ordered Heusler alloys have the $L2_1$ structure (figure 1), whereas the structure in both cases was seen to conform to the $B2$ type observed for the typically disordered Heusler alloys. The lattice parameter, $2a_0$, for Mn_2CoSn is $6.011 \pm 0.02 \text{ \AA}$ and that for Mn_2NiSn is $6.082 \pm 0.01 \text{ \AA}$. Using the a.c. susceptibility apparatus, Curie temperature for Mn_2CoSn was found to be $610 \pm 5 \text{ K}$ and that for Mn_2NiSn to be $530 \pm 5 \text{ K}$.

Mössbauer spectra recorded at 50 K and 670 K of the Mn_2CoSn sample annealed at 800°C for 7 days are shown in figure 2. Figure 3 gives the Mössbauer spectra recorded at 50 K and 590 K for Mn_2NiSn .

3.1 Mn_2CoSn

From figure 2, which gives the Mössbauer spectra at 50 K and 670 K of the Mn_2CoSn sample, it is observed

Figure 1. Heusler $L2_1$ structure.

that the spectrum at 50 K has a broad magnetic hyperfine component with the presence of a central paramagnetic peak for Mn_2CoSn . Mössbauer spectrum of this sample recorded at 670 K showed only a single peak, which rules out presence of another phase containing Sn contributing to the hyperfine spectrum. The room temperature Mössbauer spectrum was first fitted for a single sextet with a central paramagnetic peak. If the Mn_2CoSn were perfectly ordered, only a single field would be seen by the Sn nucleus. However, the width of the peaks of the sextet was six times more than the line width of natural tin. This clearly indicates that the hyperfine magnetic field at Sn site has a distribution rather than a single value. To look for any possibility of improving chemical order in the alloys, we had further annealed the sample at 400°C for periods of 2, 4 and 6 days. Mössbauer spectrum at room temperature was recorded at the end of each annealing period.

Mössbauer spectra below the Curie temperature for this sample annealed for different durations show broad hyperfine spectra. The spectra were, therefore, fitted using a program which fits for distribution of magnetic hyperfine fields based on the Window's (1971) method. The number of cosine terms used was eight. The width of the sextets was constrained to be that of tin. Three

Figure 2. Mössbauer spectra of Mn_2CoSn at 50 K and 670 K.

distinct field components in addition to a zero probability component (corresponding to the paramagnetic portion in the spectrum) were seen (figure 4). The values of the components H_1 , H_2 and H_3 , fractional widths $\Delta H/H$ as well as the average field values are given in table 1.

The trend of the hyperfine field distribution shows that the dominant component at 90 kOe, which was present in the sample before any annealing was done, decreases on annealing. Instead, the higher field components increase in the sample annealed at 400°C for two days. The four and six days annealed samples show distributions in which all the three components have nearly equal amplitudes as well as peak positions. The values of the average hyperfine fields are also nearly the same for the three spectra. This suggests that further annealing increases the disorder.

The sample showed an increase in the average hyperfine field component, H_{av} , from 94.84 to 130.14 kOe over a period of six days annealing at 400°C. Since no further changes were seen, the sample annealed at 400°C for 6 days was used for temperature studies of Mn_2CoSn . Mössbauer spectra using Sn^{119} were recorded over a temperature range of 50–670 K.

All spectra up to 523 K, showed the presence of a magnetic hyperfine part coexisting with a paramagnetic component. This was seen even at the lowest temperature

recorded for this sample. The spectrum recorded at 670 K showed a single line with a width of natural tin as expected. Hyperfine field distributions for all the spectra show the presence of three field components (called the H_1 , H_2 , and H_3 components) in addition to a zero field (H_0) corresponding to the paramagnetic component. At 50 K, the first two are more intense as compared to the third. With increasing temperature, it was observed that H_1 and H_2 reduce while there is not much change in the third over the temperature range considered. $\Delta H/H$ values point to the considerable disorder present at the sites associated with each field. The disorder most probably arises from the disorder in the arrangement of Mn in the nearest neighbour positions. This result is consistent with the result from the spin echo studies (Surikov *et al* 1990) carried out on Mn_2CoSn . They observed that although the chemical structure is Heusler like, considerable degree of disorder was present in this alloy as shown by the presence of a number of high frequency peaks in the spin echo spectrum. In the Mn_2CoSn alloys, only a single hyperfine field will be seen by Sn nucleus, if Mn and Co occupy *A* and *B* sites, respectively in the perfectly ordered $L2_1$ structure (figure 1). Large distribution in magnetic fields observed from Mössbauer studies showing a spread in magnetic hyperfine field indicates that Mn is almost equally divided between *A* and *B* sites.

Figure 3. Mössbauer spectra of Mn_2NiSn at 50 K and 590 K.

Figure 4. Hyperfine field distribution of Mn_2CoSn and Mn_2NiSn at 50 K.

The non zero probability amplitude corresponding to zero field arises from the paramagnetic contribution to the Mössbauer spectrum. The co-existence of a paramagnetic peak well below the Curie temperature points to the wide spread in relaxation times in the system. Such a spread in the relaxation time can arise from the fluctuation of a number of next neighbour atoms carrying magnetic moment in the neighbourhood of the Sn probe. So the coexistence of paramagnetic peak in Mn_2CoSn can be understood to be due to clustering of Mn atoms around Sn.

3.2 Mn_2NiSn

Mössbauer spectra of the sample annealed at 400°C for 2 days did not show any change compared to that before annealing. So the sample heated at 400°C for 2 days was used for recording Mössbauer spectra at 50 K, 220 K, 395 K, 468 K and 590 K. The field distributions for the spectra recorded below the Curie temperature show the presence of three field components. Hyperfine field distribution parameters obtained from field distribution analysis are shown in table 2. From the hyperfine field distribution parameters given in table 1, it can be seen that at low temperatures, the hyperfine field distribution is made of three components: H_1 at 137 kOe with about

100% field distribution, a second field component, H_2 , at 185 kOe with about 40% distribution and a third field component, H_3 , at 255 kOe with only 27% field distribution. The paramagnetic probability at low temperature is zero indicating the absence of any relaxation phenomena in the case of Mn_2NiSn unlike in the Mn_2CoSn system. The large distribution in the hyperfine field again points to Mn atoms in Mn_2NiSn system to be divided between A and B sites.

The hyperfine magnetic fields at non-magnetic probes, Sn, at substitutional sites in Heusler alloys are understood in terms of conduction electron polarization via Fermi contact term. Conduction electron polarization varies sinusoidally with distance from the transition element where magnetic moment is assumed to be localized. The value of the average number of conduction electron, n_0 (Dunlap and Stroink 1982) is given by

$$n_0 = (1/4) [2(L_X - 2D_X + \mu_X) + (L_Y - 2D_Y + \mu_Y) + N_Z]. \quad (1)$$

Here L_X and L_Y are the number of outer shell electrons and D_X and D_Y the number of spin down outer electrons in X_2YZ alloys. N_Z is the electrons contributed to the conduction band by the Z element. The Fermi vector, k_F , is given by

$$k_F = (1/a_0) [48p^2 n_0]^{1/3}. \quad (2)$$

Here a_0 is the lattice parameter.

The contribution to the hyperfine field arising from polarization of the conduction band at a particular probe site due to a magnetic moment located at r_i is given according to Blandin and Campbell (BC) (1975) model by

$$p(r_i) \propto (1/r_i^3) \cos(2k_F r_i + 2\mathbf{d}_0 + \mathbf{h}), \quad (3)$$

where $2\mathbf{d}_0$ accounts for the perturbations to the conduction-electron density from the effective charge of the impurity atom and $\mathbf{h}$ the preasymptotic factor.

From the value of magnetic moment of an atom located at r_i and $p(r_i)$, the hyperfine field can be calculated as

$$H = \sum_i \mathbf{m}_i p(r_i). \quad (4)$$

In Co_2MnSn (Dunlap and Jones 1982), for which the average number of conduction electron, $n_0 = 1.57$, the free electron Fermi vector is $1.51 \text{ \AA}^{-1}$. The corresponding values for perfectly ordered Mn_2CoSn (if it is assumed that all the Mn atoms are at the X site, $\mu_{\text{Mn}} = -2 \mu_B$ and $\mu_{\text{Co}} = 0.6 \mu_B$), the average number of conduction electron, $n_0 = 1.05$ and Fermi vector, $k_F = 1.3 \text{ \AA}^{-1}$.

If X–Y disorder exists, Mn atoms can occupy Y site. In general, magnetic moment of Mn in X_2YZ alloys is nearly $4 \mu_B$. In many cases it is reported that Y–Z disorder exists. So in this alloy, the Sn atom can also occupy Co site which will lead to different discrete

Table 1. Internal magnetic fields, fractional widths of the fields and paramagnetic probability for Mn_2CoSn .

Temperature (°K)	50	220	305	423	523
H_{av} (kOe)	121.50	101.50	120.57	94.00	58.10
H_1 (kOe)	120.00	85.00	90.00	95.00	57.00
ΔH_1 (kOe)	70.00	40.00	50.00	40.00	40.00
H_2 (kOe)	180.00	165.00	180.00	155.00	147.00
ΔH_2 (kOe)	70.00	60.00	55.00	30.00	40.00
H_3 (kOe)	260.00	255.00	230.00	230.00	207.00
ΔH_3 (kOe)	40.00	50.00	50.00	40.00	20.00
Paramagnetic probability	0.04	0.07	0.08	0.14	0.38

Table 2. Internal magnetic fields, fractional widths of the fields and paramagnetic probability for Mn_2NiSn .

Temperature (°K)	50	220	305	395	468
H_{av} (kOe)	137.75	132.95	130.06	107.84	79.72
H_1 (kOe)	70.00	70.00	65.00	65.00	50.00
ΔH_1 (kOe)	70.00	60.00	60.00	60.00	30.00
H_2 (kOe)	185.00	160.00	170.00	150.00	120.00
ΔH_2 (kOe)	75.00	75.00	90.00	75.00	40.00
H_3 (kOe)	255.00	225.00	220.00	215.00	185.00
ΔH_3 (kOe)	70.00	70.00	50.00	65.00	35.00
Paramagnetic probability	—	—	—	0.13	0.49

Table 3. Hyperfine fields calculated for different values of magnetic moments at X and Y sites using BC model.

Sample	μ_{Mn}		μ_{Co}		Hyperfine field (kOe)
	X	Y	X	Y	
Mn ₂ CoSn	2	—	0.6	—	— 21.4
	— 2	4	0.6	—	62.0 ^a
	4	—	0.6	—	251.0
	— 2	0	0.6	—	0.34
	— 2	4	0.6	0.6	56.46 ^b
	— 2	4	0.6	0.6	24.92 ^c
	2	—	—	—	16.00
Mn ₂ NiSn	— 2	4	—	—	68.0 ^d
	4	—	—	—	247.0
	— 2	0	—	—	0.065

^aAssumed that up to 3 nn of Mn, 50% Mn is replaced by Co;

^bassumed that up to 6 nn, one atom of Mn is replaced by Co and one Co atom by Mn; ^cassumed that up to 6 nn, 50% Mn is replaced by Co atom and 50% Co atom by Mn; ^dassumed that up to 3 nn of Mn, 50% Mn is replaced by Ni atom.

magnetic fields. Sn atom occupying Y site will have higher magnetic field due to $4\mu_{\text{B}}$ Mn and $0.6\mu_{\text{B}}$ Co as their neighbours, compared to Sn atom occupying Z site, which has $2.0\mu_{\text{B}}$ Mn as 1 nn, $4.0\mu_{\text{B}}$ Mn as 2 nn and $0.6\mu_{\text{B}}$ Co as 3 nn. This implies that Sn at Y site will see a higher magnetic field. However, the values calculated for this combination using BC model do not agree with the observed H_{av} values. As a good deal of chemical disorder has been observed in these samples, it would be pertinent to examine whether the BC model could explain some of these field distributions.

Table 3 gives the values of hyperfine field calculated by using (4) for different combinations of disorder. Assuming that 50% of Mn atoms (X atoms) up to 3 nn are replaced by Y atoms and taking $\mu_{\text{Mn}} = -2.0\mu_{\text{B}}$ at X-site, $\mu_{\text{Mn}} = 4.0\mu_{\text{B}}$ at Y-site and in the case of Mn₂CoSn, $\mu_{\text{Co}} = 0.6\mu_{\text{B}}$, one gets a field of 62 kOe for Mn₂CoSn and 68 kOe for Mn₂NiSn. This could be related to the first peak at 90 kOe in the hyperfine field distribution curve for Mn₂CoSn and to the first peak at 75 kOe for Mn₂NiSn. The other two field components in the hyperfine field distribution curves for both the alloys could not be

reconciled on the basis of BC model even allowing for chemical disorder.

4. Conclusions

The present study shows that it is difficult to produce order in Mn₂NiSn and Mn₂CoSn alloys. The hyperfine field distribution indicates an almost equal distribution of X and Y atoms between the A and B sites of the Heusler structure. The presence of a paramagnetic contribution in the hyperfine spectrum of Mn₂CoSn indicates a spread in the relaxation times pointing to the clustering of Mn atoms. Application of Blandin–Campbell model to these alloys shows that the observed hyperfine fields cannot be satisfactorily explained on the basis of this model even allowing for chemical disorder.

References

- Brooks J S and Williams J M 1974 *J. Phys. F: Metal Phys.* **4** 2033
- Calligaris M 1990 *X-ray powder diffraction and its applications, P.D.P. version 1x1, ICTP, SMR/455-1*
- Campbell I A and Blandin A 1975 *J. Magn. Mater.* **1** 1
- Carbonari A W, Pendl Jr. W, Attili R N and Saxena R N 1993 *Hyperfine Interact.* **80** 971
- Carbonari A W, Saxena R N, Pendl Jr. W, Mestnik Filho J, Attili R N, Souza S D and Olzon-Dionvsio M 1996 *J. Magn. Mater.* **163** 313
- Delyagin N N, Zonnenberg Y D, Krylov V I and Nesterov V I 1981 *Hyperfine Interact.* **11** 65
- Dunlap R A and Jones D F 1982 *Phys. Rev.* **B26** 6013
- Dunlap R A and Stroink G 1982 *J. Appl. Phys.* **53** 8210
- Dunlap R A, March R H and Stroink G 1981 *Canadian J. Phys.* **59** 1577
- Jha S, Seyoum H M, Demarco M, Julian G M, Stubbs D A, Blue J W, Silva M T X and Vasquez A 1983 *Hyperfine Interact.* **15/16** 685
- Ritcey S P and Dunlap R A 1984 *J. Appl. Phys.* **55** 2051
- Surikov V V, Zhordochkin V N and Astakhova T Yu 1990 *Hyperfine Interact.* **59** 469
- Webster P J and Ziebeck K R A 1973 *J. Phys. Chem. Solids* **34** 1647
- Window B 1971 *J. Phys.* **E4** 401