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Hyperfine fields and magnetic interactions in Heusler alloys

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Abstract. We have studied transition and noble metal site NMR spectra of stoichiometric, off-stoichiometric and substituted Heusler alloys. The hyperfine fields can be analysed consistently in terms of local and transferred contributions. The transferred fields are negative at near neighbour and second neighbour to a Mn site, and positive at third neighbour. In many cases excess Mn atoms substituted onto Z sites form antiferromagnetic good local moments in these ferromagnetic hosts, with strongly anomalous hyperfine field temperature dependences. Both the transferred fields and the Mn–Mn coupling follow the predictions of a Friedel-Anderson d resonance model correctly treated in the pre-asymptotic region. The local hyperfine fields at Mn sites are very similar to fields in dilute Mn alloys, while the local fields at Co sites are positive indicating unquenched local orbital moments on the Co atoms.

1. Introduction

'Heusler alloy' is a generic name for a family of intermetallic compounds of composition X_2YZ . These are ordered in an $L2_1$ superstructure built up on a basic BCC lattice (figure 1). Typically the X atoms are transition or noble metal elements of the Co, Ni or Cu columns of the periodic table, Y atoms are transition elements of the Mn, V or Ti columns and Z atoms are sp elements from columns III to V; thus for instance the original 'Heusler alloy' is Cu₂MnAl. Compounds containing Mn are always magnetically ordered, and are usually ferromagnetic with saturation



Figure 1. The crystal structure of a Heusler alloy X_2YZ .

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moments on the Mn atom of about $4\mu_B$. Co atoms if present are also magnetic with moments of 0.3 to $1\mu_B$. Other constituents are nonmagnetic (see Campbell 1975 for a summary).

The magnetic properties of the compounds where only Mn atoms carry moments are of interest because they provide excellent test cases for models of magnetic interactions in metals. The Mn-Mn distances are big (third-nearest-neighbour distance in the BCC structure) but in contrast to the situation in true dilute alloys such as **Cu**Mn the Mn atoms here are both structurally and magnetically ordered and are all in identical cubic environments. These compounds are thus half-way between dilute and concentrated magnetic systems.

In the present work we have studied NMR in both stoichiometric and off-stoichiometric samples of a number of Heusler alloys to obtain information on the magnetic interactions and also on the conduction electron polarisation induced by a magnetic atom on surrounding sites, which is a closely related property. We find that the results can be explained by a d resonance coupling model in which the preasymptotic region is correctly treated. We also find that the effective coupling of the Mn atom with the conduction electrons varies with the type of X site atom and that this variation can be correlated with data from dilute alloys.

We will not consider sp element hyperfine fields to avoid the problems associated with charge screening (Campbell and Blandin 1975).

Partial reports of some of this work have already been published (Le Dang Khoi et al 1977a,b).

2. Sample preparation and experimental techniques

The samples were all prepared by melting under argon in an induction furnace. They were crushed, remelted and again crushed to 100 μ m powder. This powder was annealed at an appropriate temperature and was either slow cooled or quenched to room temperature. For the heat treatments of the various compounds, we have followed the recipes given in the literature. Samples were x rayed to check that they were single phase. Compositions were chosen so that the samples were either stoichiometric (X₂YZ), off-stoichiometric (e.g. X₂Y_{1+x}Z_{1-x}) or with an impurity on one type of site (e.g. X₂Y_{1-x}Y'_xZ) with x typically 1%.

NMR spin echo measurements were made in zero field or in applied fields up to 10 kG at helium temperatures. For some samples additional spectra were taken at higher temperatures.

3. Experimental results

3.1. Stoichiometric samples

Hyperfine field values at 4.2 K for X and Mn nuclei are given in table 1, together with data on the ordering temperatures and magnetic moments per atom. Where X or Mn fields have already been measured by NMR on well ordered samples our results are in good agreement with earlier values. The NMR linewidth is a good indication of the degree of order of the samples; some compounds (such as Co_2MnSi , Pd_2MnSn and Cu_2MnAl) can be very well ordered if an appropriate heat treatment

Table 1. Magnetic properties and hyperfine fields in stoichiometric Heusler alloys. Results in italics are present work. For collected T_c , moment and hyperfine data, see Campbell (1975). Results marked (1) and (2) are from Endo *et al* (1976) and Endo *et al* (1977). More Co hyperfine field values are given by Vijayaraghavan *et al* (1977).

Compound X_2YZ	$T_{c}(\mathbf{K})$	$\mu_{\rm Mn}(\mu_{\rm B})$	$\mu_{\rm Co}(\mu_{\rm B})$	$H_{Mn}(\mathbf{kG})$	$H_{\mathbf{X}}(\mathbf{k}\mathbf{G})$
Cu ₂ MnAl	630	4.12		-214	-212
Cu ₂ MnSn	530	4.11		-231	-175
Cu ₂ MnIn	500	3.95		-233	-200
Ni ₂ MnSn	344	4.05		-317	-127
Ni ₂ MnGa	379	4.17	_	- 297	± 125
Ni ₂ MnIn	323	4.4		-302	± 141
Ni ₂ MnSb	360	3.27		-285	- 60
Pd ₂ MnSn	189	4·23		- 380	- 255
Pd ₂ MnSb	247	4.4		- 330	-88
Au ₂ MnAl	140	~		-352	± 1500
Co ₂ MnSi	985	3.57	0.75	- 337	-146
Co ₂ MnGe	905	3.61	0.75	- 339	-141
Co ₂ MnGa	694	3.01	0.52	-280	-173
Co ₂ MnSn	829			- 352	-155
Co ₂ VGa	349		1.05	$H_{\rm v} = -73$	+14.3
Co ₂ TiGa	130		0.40		+12.2
Co ₂ TiSn	359		1.03		$+21^{(1)}$
Co ₂ TiAl	138		0.37		$+16.5^{(2)}$

has been used; for certain others we have not been able to find a heat treatment which leads to samples with lines less than 2 or 3 MHz wide.

We can already note that there is a systematic variation of Mn field with the type of X neighbour: when X is Cu, the fields are low ($\sim -220 \text{ kG}$), when X is Ni the fields are intermediate ($\sim -300 \text{ kG}$) and when X is Pd or Au the fields are high ($\sim -370 \text{ kG}$). This is not due to large variations of the Mn moment, as the magnetic moments appear to be near $4 \mu_B$ in all cases. The compounds where X is Co must be considered separately because of the moment on the Co sites.

The Co fields in samples where Co is the only magnetic atom are invariably positive.

3.2. Off-stoichiometric and substituted samples

From this type of sample, we can obtain two sorts of information: first, the hyperfine field on the excess or impurity atom, and secondly the positions of the NMR satellite lines due to host atoms which are neighbours to the impurity atom (for convenience we will refer to NN (near neighbour), 2 NN (second near neighbour) etc). For instance, suppose that we prepare the compound $\text{Cu}_2\text{Mn}_{1+x}\text{Al}_{1-x}$ and that the x excess Mn atoms substitute randomly onto Al sites in the place of the x Al vacancies. In addition to the main host lines we will have typically:

(i) a Mn signal of intensity x (relative to the main Mn line) due to Mn atoms on Al sites.

(ii) a Cu satellite signal of intensity 4x (relative to the main Cu line) due to Cu on regular Cu sites having excess Mn as NN.

(iii) possibly a second Cu satellite signal of relative intensity $12x^2$ due to Cu sites with two Mn excess atoms at NN distance.

(iv) a different Cu satellite signal of relative intensity 12x due to Cu sites with excess Mn atoms at 4 NN distance.

(v) a Mn satellite signal of relative intensity 6x due to Mn on regular Mn sites which have excess Mn atoms at 2 NN distance.

etc.

At first sight it would seem that this type of nonstoichiometric sample would give an inextricable forest of NMR signals which would be quite impossible to interpret. In practice, if x is kept small the spectra can usually be understood quite easily as the lines remain narrow and the satellite frequency shifts fall off very fast with distance—in the example we have considered, the type (ii) Cu NN satellites are about 50 MHz from the main line, but the type (iv) Cu 4 NN satellites are only of the order of 1 MHz from the main line. Satellites can be identified with definite environments with confidence.

Using the NMR data together with metallurgical information, we have found simple rules for substitutions in these compounds. In the off-stoichiometric samples Mn and Z atoms will substitute for each other but not on X sites. In samples where an impurity is introduced the impurity (if it goes into solution which is not always the case) will substitute onto the chemically most similar site, i.e. V or Ti impurities onto Mn sites, sp impurities onto Z sites and noble metal or column VIII impurities onto X sites. These are essentially the same rules as have been established for impurities substituting into the related compound Fe_3Si (Burch *et al* 1974).

The impurity site hyperfine fields are given for the various compounds in table 2 where we use the notation A/B to indicate an atom A on site B (e.g. Mn/Z for a Mn atom on a Z site).

One point can be made immediately. In all the compounds except Ni_2MnIn and those containing Co, Mn substituted onto Z sites has a strong positive hyperfine field, while in Ni_2MnIn and the Co compounds Mn/Z has a strong negative field. As the negative local core polarisation term can be expected to always dominate in the Mn hyperfine field, this indicates that the Mn/Z moments are antiferromagnetically and ferromagnetically aligned respectively in the two types of compound.

In some cases the temperature dependence of the main Mn line and the Mn/Z line were measured. For Pd₂MnSn and Ni₂MnSn we have already published the

Compound	Regular Mn/Y hyperfine field (kG)	Excess Mn/Z hyperfine field (kG)	X site impurity fields (kG)	Y site impurity fields (kG)
Cu ₂ MnAl	-214	+ 202		
Ni ₂ MnSn	- 316	+ 253		$H_{\rm v} = 15$
				$H_{\rm Nb} = +42$
Pd ₂ MnSn	- 380	+ 303	$H_{\rm Co} = -151$	$H_{\rm Nb} = 20$
Au ₂ MnAl	- 352	+284		
Ni ₂ MnIn	- 302	- 386		
Co ₂ MnSi	- 334	- 400		$H_{\rm v} = -50$
Co ₂ MnGa	-280	- 332	$H_{\rm Ni} = \pm 128$	
Co ₂ VGa				$H_{\rm Mn} = -367$

Table 2. Hyperfine fields at excess Mn on Z atoms and at impurity atoms in off-stoichiometric or substituted samples. The last two columns give the hyperfine fields measured at impurities substituted onto X or Y sites respectively in the various compounds.



Figure 2. The temperature variations of the resonance frequencies in a Co_2MnSi sample with excess Mn on Si sites. \bigcirc . main Mn line; +, main Co line; I, excess Mn on Si line.

results (Le Dang Khoi *et al* 1977b). For Co_2MnSi and Ni_2MnIn the temperature dependences are shown in figures 2 and 3.

4. Analysis of hyperfine fields and field shifts

The hyperfine field at a nucleus in this type of magnetic metal is always analysed as the sum of local and transferred terms. If the atom is magnetic there is a local field H_{loc} due to the moment on the atom itself, usually equal to about $-70\mu_0 kG$ for a 3d element with moment μ_0 . Secondly, the interaction between each local moment and the conduction electrons leads to an oscillating conduction electron polarisation (CEP) on surrounding sites; there is a CEP contribution to the field at an atom in a magnetic metal (whether the atom itself is magnetic or not) which is equal to the total s electron CEP at that site due to surrounding moments multiplied by the atomic hyperfine coupling constant A_i appropriate to that particular atom.

We will assume that the total hyperfine field at a given atom i is the sum of a series of terms

$$H_{i} = h_{0}^{i} \mu_{0} + h_{1}^{i} \Sigma \mu_{1} + h_{2}^{i} \Sigma \mu_{2} + \dots$$
(1)



Figure 3. The temperature variations of the resonance frequencies in a Ni_2MnIn sample with excess Mn on In sites.

where μ_0 , μ_1 , etc, are the local site moment, the NN moments, etc, and h_0^i , h_1^i ... are coefficients to be determined. The transferred field terms $h_1^i \mu_1$, $h_2^i \mu_2$... can be assumed to be due to the s CEP induced at atom *i* by the NN, 2 NN... neighbour moments. To compare results from different atoms we can divide the h_j^i values by A_i to obtain the induced s CEP that this coefficient represents. We will write

$$p_j^i = h_j^i / A_i \tag{2}$$

in units of polarised s electron per atom per $\mu_{\rm B}$ on neighbour j.

We will now use the data to estimate the different hyperfine field terms at the various atoms and to draw general conclusions.

4.1. Nonmagnetic X atoms

In stoichiometric samples, these sites have as magnetic neighbours 4 Mn at NN distance, 12 Mn at 4 NN etc. If we replace one NN Mn by a nonmagnetic atom the X site field shift will be given by $\Delta H_x = -h_1^x \mu_{Mn}$ from (1). The field shift data show that the X site hyperfine field are dominated by the NN contributions, as the total field $H_x \simeq -4\Delta H_x$. We have the NN CEP values $p_1^x = -\Delta H_x/A_x \mu_{Mn}$ in table 3. The CEP in Cu compounds is rather stronger than in Ni or Pd compounds, and when the Z atom is Sb, p_1^x is much lower than the other cases.

and Watson and Bennett (1977). For Mn, p of $0.1^{10}_{0.0}$ represents about 1.8 kG.				
Compound	<i>p</i> ₁	<i>p</i> ₂	<i>p</i> ₃	
Cu ₂ MnAl	- 0.50	-0.25	+ 0.055	
Cu ₂ MnSn	-0.42			
Cu ₂ MnIn	-0.48			
Ni ₂ MnSn	-0.32	-0.3	+0.03	
Ni ₂ MnGa	-0.32	-0.27		
Ni ₂ MnIn	-0.36			
Ni ₂ MnSb	-0.12			
Pd ₂ MnSn	-0.33	-0.22	+0.012	
Pd_2MnSb	-0.11			
Au ₂ MnAl	-0.45			
Co ₂ MnSi	-0.46	-0.50	+0.02	

Table 3. The s conduction electron polarisation at NN, 2 NN and 3 NN sites around a polarised Mn moment in units of 10^{-2} s electrons per atom per μ_B on the Mn site. The p_i are defined by equations (1) and (2). A_i values were taken from Campbell (1969) and Watson and Bennett (1977). For Mn, p of $0.1^{\circ}_{.0}$ represents about 1.8 kG.

4.2. Mn site fields

We have estimated the transferred fields at regular Mn sites in two ways. First, if nonmagnetic V or Nb is substituted onto Mn sites, the impurity hyperfine field divided by A_i can be taken as giving the total s CEP at the Mn site due to the surrounding twelve Mn 3 NN atoms, so $H_i/A_i \simeq 12p_3\mu_{\rm Mn}$ where *i* is V or Nb. Secondly, the $\Delta H_{\rm Mn}$ satellite field shift corresponding to Mn/Y sites having a nonmagnetic atom substituted on one 3 NN Mn/Y neighbour site is equal to $-h_3^{\rm Mn}\mu_{\rm Mn}$, or $-A_{\rm Mn}p_3\mu_{\rm Mn}$. The two methods give consistent results for p_3 , and although p_3 varies considerably from one compound to another it has so far been found to be positive in all cases (table 3).

After estimating h_3^{Mn} in each case, we can obtain the local field due only to the Mn moment on its own site

$$H_{\rm loc}^{\rm Mn} = h_0^{\rm Mn} \simeq H_{\rm Mn} - 12 \, h_3^{\rm Mn} \, \mu_{\rm Mn} \,. \tag{3}$$

In table 4 we give H_{loc}^{Mn} values, and we compare with Mn hyperfine field values in the dilute alloys XMn.

We can use the Mn line satellite in samples with excess Mn on Z sites to estimate p_2 values. As we noted above, the sign of the strong hyperfine field observed at

Table 4. Local hyperfine fields at Mn sites H_{loc}^{Mn} . Estimated transferred fields have been subtracted from the measured fields, equation (3). References for fields at Mn in dilute XMn: (1), Cameron *et al* (1966); (2), Koi and Tsujimura (1963); (3), Gallop (1970) and Le Dang Khoi *et al* (1976).

Compound	H ^{Mn} for Mn on Y sites	H_{loc}^{Mn} for Mn on Z sites	Mn field in dilute XMn alloy
Cu ₂ MnAl	-270	+ 310	- 280 in CuMn ⁽¹⁾
Ni ₂ MnSn	- 335	+ 370	- 325 in NiMn ⁽²⁾
Pd ₂ MnSn	- 390	+410	-400 in PdM n ⁽³⁾
Au ₂ MnAl	- 380	+400	-400 in AuMn ⁽⁴⁾
Co ₂ MnSi	- 330	- 280	

Mn/Z atoms tell us if the excess moment is antiferromagnetically or ferromagnetically polarised. The value of the field shift for the Mn/Y atoms having a Mn/Z second neighbour is equal to $(- \text{ or } +) h_2^{Mn} \mu_{Mn}$, allowing us to estimate h_2^{Mn} and hence p_2 .

4.3. Mn at Z sites

The absolute values of the Mn/Y and Mn/Z fields are not identical (table 2); this turns out to be mainly due to their different transferred field terms. For the regular Mn/Y, the nearest magnetic neighbours are twelve Mn atoms at 3 NN distance, while for the excess Mn/Z the nearest magnetic neighbours are six Mn atoms at 2 NN distance pointing either in the same or the opposite direction to the Mn/Z moment. To estimate the Mn/Z transferred field we assume the same value of h_2^{Mn} as for a Mn/Y site in the same compound, so

$$H_{\rm Mn/Z} = H_{\rm loc}^{\rm Mn/Z} \mp 6 h_2^{\rm Mn} \mu_{\rm Mn}$$

ignoring further neighbour terms. Analysed in this way, the $H_{loc}^{Mn/Z}$ values that we find are similar to the $H_{loc}^{Mn/Y}$ values in each compound (except for the positive sign when the Mn/Z moments are antiferromagnetic): table 4. This means that the excess Mn atoms have about the same magnetic moment as the regular Mn atoms.

4.4. Compounds containing Co

The interpretation of the X = Co compounds has to include the local and transferred fields due to the Co moments as well as to the Mn moments (if any).

The fields due to the Mn atoms were obtained as in the other compounds; the fields due to the Co moments were found by substituting nonmagnetic Ni or Cu atoms onto Co sites.

We can note that the values of the field on the nonmagnetic V atoms in Co_2VGa and in Co_2MnSi are negative because of the transferred fields from the NN Co moments. The field is less negative in Co_2MnSi because of the positive term from the 3 NN Mn neighbours.

The transferred field values in the X = Co compounds are very similar to the values for the other compounds, but H_{loc}^{Co} is always strongly *positive* instead of negative as is the case when the usual core polarisation term dominates. This is so both in the compounds where Co is the only magnetic atom and in compounds containing Mn. For the former the total transferred field at the Co sites is relatively weak, so the Co field is actually positive (Le Dang Khoi *et al* 1977a).

4.5. Summary

We can sum up the results of this section:

(i) The analysis of the hyperfine fields in terms of a sum of local and transferred fields (equation (1)) can be done consistently for each compound and gives coherent results for the whole set of compounds.

(ii) The s electron CEP values (table 3) indicate that in all the compounds the induced CEP around a Mn site is negative at NN and 2 NN distance and positive at 3 NN distance. The NN polarisation p_1 and the 3 NN polarisation p_3 are rather weaker when X is Pd or Ni than when X is Cu, and p_1 is much weaker when Z is Sb.

(iii) The local Mn fields H_{loc}^{Mn} vary from -280 kG when X is Cu to -400 kG when X is Pd or Au. In table 4 we compare H_{loc}^{Mn} with Mn fields in the dilute binary alloys XMn, and we see that the fields in corresponding systems are equal within the experimental error.

(iv) The sign and magnitude of H_{1oc} at Mn/Z atoms show they have practically the same moment as the regular Mn atoms, but in many hosts they are anti-ferromagnetically polarised.

(v) The local Co fields H_{loc}^{Co} are positive.

5. Discussion

5.1. Heusler alloys not containing Co

As we stated in the Introduction, the Heusler alloys provide a remarkable testbed for the verification of models for magnetic interactions in metals. The Mn–Mn distances are such that direct d–d overlap is certainly negligible so the magnetic coupling is indirect, through the conduction electrons. The sites other than Mn are nonmagnetic and even when X is Ni or Pd, it is reasonable to suppose that the local d states are full, so that the compounds can be regarded as having well defined well separated local d moment sites in an sp band host. Important information on the magnetic coupling was obtained from the magnon dispersion curves of Pd₂MnSn and Ni₂MnSn which gave the Mn–Mn coupling as a function of separation up to about 12 Å (Noda and Ishikawa 1976). The data showed positive interactions at 3 NN distance and oscillations at large distances.

The present results give information on the CEP itself at NN, 2 NN and 3 NN distances, and on the Mn-Mn coupling at 2 NN separation, as well as providing the local hyperfine fields at the Mn atoms.

The CEP around a magnetic site and the magnetic interactions through the CEP have traditionally been discussed in terms of the asymptotic RKKY interaction. Some time ago it was suggested that a more realistic approach would be to use the Friedel-Anderson d resonance model for magnetic impurities in metals (Caroli and Blandin 1966). However, as calculations were still made in the asymptotic limit, applications to any but very dilute systems were opened to question. Recently, d resonance approach calculations have appeared which should be valid in the pre-asymptotic region. The calculations were done keeping the approximation of a free-electron-like conduction band but instead of an s wave scattering potential, a k to k' scattering with the correct d symmetry is used (Geldart 1972, Jena and Geldart 1973, Alloul 1974, Malmström *et al* 1976a, b, Price *et al* 1976).

In the asymptotic limit for the d resonance model the CEP at distance r from a magnetic site is equal to $p(r) = \delta n_1(r) - \delta n_1(r)$ where

$$\delta n_{\sigma}(r) = -\frac{5}{4\pi^2 r^3} \sin \phi_{\sigma} \cos(2k_{\rm F}r + \phi_{\sigma})$$

 ϕ_{σ} being the d phase shift at the Fermi level for spin σ . In the same limit the coupling strength between two identical moments separated by distance R is

$$J(R) = -\frac{25}{8S^2} \frac{E_F}{\pi (k_F R)^3} \sum_{\sigma} \sin \phi_{\sigma} \cos(2k_F r + 2\phi_{\sigma})$$

where S is the local spin.



Figure 4. Calculated curves for conduction electron polarisation p(r) and magnetic site coupling J(r) in a **CuMn** type of system, using the d resonance model: (\cdots) , -J(r) from Malmström *et al* (1976a,b); (----), p(r) from Geldart (1972) and Alloul (1974); (--), asymptotic expression.

For magnetic Mn sites $\phi \uparrow$ will be near π and $\phi \downarrow$ will be small so in the asymptotic region p(r) and -J(R) should oscillate almost in phase (i.e. the effective RKKY coupling J_{sd} is negative). For the preasymptotic region curves calculated numerically on the d resonance model with parameters appropriate to Mn in a Cu-like host are shown in figure 4. The d state width Δ was chosen as 1 eV, and $k_F = 1.35$ Å⁻¹. We see that p(r) and -J(R) curves get badly out of phase with each other in this range as well as deviating strongly from the asymptotic formula curve.

We can compare the calculated values with the present experimental results.

5.1.1. Conduction electron polarisation. The calculated p(r) curves are compared with the experimental p_s values in figure 5. As the hyperfine fields are sensitive only to s electron polarisation the amplitudes of p(r) and p_s cannot be directly compared. However, the important conclusion to be drawn is that the calculated p(r) curve gives good agreement with experimental data as to the order of magnitude of p_s and to its variation with r. It is clear that a detailed fit to each compound could be achieved by dint of minor adjustments of Δ and k_F . In the compounds with



Figure 5. (a) Calculated conduction electron polarisation per atom p(r) around a Mn site in Cu using d resonance model (Geldart 1972 and Alloul 1974). (b) Measured s electron polarisation per atom $p_s \mu_{Mn}$ around a Mn site in various Heusler alloys (the factor μ_{Mn} is because we have defined p_s as s polarisation per μ_B on the Mn site): \bigcirc , Cu₂MnAl; \triangle , Ni₂MnSn; \square , Pd₂ MnSn and O, Co₂MnSi. Arrows indicate near, second and third neighbour distances.

X = Cu the transferred fields are stronger than in the other compounds showing a stronger s-d mixing on the magnetic site (higher d state width Δ) than in the other cases. As we will see, other evidence supports this. The effective k_F value may also change from compound to compound.

It is interesting to note that the experimental $p_s(r)$ values are rather similar to values which can be extracted from data on Fe metal containing impurities (Stearns 1966, Grüner *et al* 1972, Vincze and Campbell 1973) or on dilute Cu-based magnetic alloys (Boyce and Slichter 1974).

5.1.2. Mn-Mn coupling. The fact that we have observed antiferromagnetically oriented Mn/Z moments in all of these compounds except Ni₂MnIn indicates that the Mn/Z coupling with the surrounding host moments is negative. For three of the compounds, Pd₂MnSn, Ni₂MnSn and Ni₂MnIn, we have measured the temperature dependence of the Mn/Z hyperfine field, which is in each case quite different from that of the main Mn field (figure 3 and Le Dang Khoi *et al* 1977b). Some years ago, a molecular field model was proposed for the variation of the hyperfine field of a magnetic impurity with a well defined spin in a ferromagnetic host (Jaccarino *et al* 1964) but the model was applied to physically unsuitable cases (see Campbell 1970). The present systems are very well suited to this type of model, and we have used a molecular field approach to obtain the effective coupling of the Mn/Z moment to the host lattice. Assuming that the dominant coupling is with the six 2 NN Mn neighbours, we have estimated the 2 NN Mn-Mn coupling in these compounds (table 5).

For Pd_2MnSn and Ni_2MnSn spin wave dispersion measurements have been made to obtain the Mn-Mn coupling J(R) for R between about 4.5 Å and 12 Å (Noda and Ishikawa 1976). The results plus the 2 NN distance values are given in figures 6(b) and (c) where it can be seen that there is a strong resemblance to the calculated curve of figure 6(a). In particular the calculations (Malmström *et al* 1976a,



Figure 6. (a) Calculated Mn-Mn coupling as a function of distance in CuMn (Malmström et al 1976a,b). (b) Measured Mn-Mn coupling in Pd_2MnSn . (c) Measured Mn-Mn coupling in Ni_2MnSn . In (b) and (c), \bullet indicates values from Noda and Ishikawa (1976), \bullet indicates the present work, using molecular field approximation.

b) predict a negative coupling for $R \leq 3$ Å, and suggest that the exact value of J at this distance would be very sensitive to the exact parameters appropriate to each particular compound. Indeed the J (2 NN) estimated for Pd₂MnSn and Ni₂MnSn are rather different from each other, and in Ni₂MnIn the Mn/Z moment is actually ferromagnetically coupled in contrast to the other cases. It may be relevant that the average number of conduction electrons is probably smaller for Ni₂MnIn than for the other compounds studied.

Again, fits could be made with different model parameters and $k_{\rm F}$ at least for small R where the details of the real conduction bandstructure should be relatively unimportant. For higher values of R the assumption of a free-electron-like conduction band may be too much of an oversimplification; it is not clear that one would expect a fit with a single effective value of $k_{\rm F}$ over a wide range of R as the real bandstructure of the metal should come into play.

5.1.3. Mn local hyperfine fields. As we have noted above, the Mn field due to its own local moment H_{loc}^{Mn} in a Heusler alloy is very similar to the Mn hyperfine field

Table 5.			
Compound	T _c	Excess Mn coupling J (2 NN)	
Pd ₂ MnSn	189 K	-0.91 meV	
Ni ₂ MnSn	344 K	-0.47 meV	
Ni ₂ MnIn	323 K	+0.70 meV	

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in the corresponding dilute Mn alloy. Also, there is a definite correlation between $H_{\rm loc}^{\rm Mn}$ and the Curie temperature. The compounds having the highest Curie temperature have the lowest $H_{\rm loc}^{\rm Mn}$ values and vice versa. In addition, in the compounds where $H_{\rm loc}^{\rm Mn}$ is lowest the neighbour conduction electron polarisations p_1 and p_3 are highest. This suggests that $H_{\rm loc}^{\rm Mn}$ depends on the effective s-d coupling on the Mn site; the stronger this coupling the higher $T_{\rm c}$ and the neighbour CEP, but the lower $H_{\rm loc}^{\rm Mn}$. The value of the s-d mixing seems to be principally determined by the near neighbour environment of the Mn atom.

This type of dependence of H^{Mn} on J_{sd} has already been discussed for the dilute Mn alloys. Davidov *et al* (1975) have attempted to interpret the Mn hyperfine fields in AgMn and CuMn by a partial wave analysis using data from other measurements on these alloys. Because of a number of uncertainties their discussion remained qualitative but they pointed out the association between less negative Mn hyperfine fields and higher d partial wave strengths. The present results confirm that it is no accident that lower Mn hyperfine fields correlate with higher Mn–Mn interactions and higher Kondo temperature.

5.2. Co compounds

The properties of these compounds are complicated by the magnetic moment on the Co site. The Co-Co 2 NN interaction is strong enough for the Co₂YZ compounds to have Curie temperatures above 300 K even when no Mn is present, and the Co₂MnZ compounds can have Curie temperatures of 900 K, indicating a positive NN Co-Mn interaction. Mn on Z site moments align ferromagnetically in these compounds. We can consider that the effective molecular field on the excess Mn moment is the sum of a positive term due to the Co neighbours (the NN Co environment is the same as for a regular Mn atom) and another term due to the 2 NN Mn neighbour shell. The temperature dependence of the Mn/Z hyperfine field in Co₂MnSi shows that the total molecular field is relatively weak, so we can deduce that the Mn-Mn coupling is negative but not strong enough to counteract the ferromagnetic Co neighbour term.

The transferred fields due to the Mn moments in the X = Co compounds seem to be rather similar to those in the X = Cu compounds. The transferred fields due to Co moments (Le Dang Khoi *et al* 1977a) are similar in magnitude, except that the p_2 term seems relatively stronger. However the analysis of the satellite field shifts in these compounds is complicated by the possibility that a change of neighbour environment may alter the Co moments to some extent as well as affecting the transferred fields directly.

The positive H_{loc}^{Co} values suggest that there is a strong local orbital moment on the Co sites in these compounds, so that the negative core polarisation local field which normally dominates at d sites with local moments is swamped by a positive orbital term. The size of H_{loc}^{Co} would be compatible with an orbital moment of about $0.5 \mu_{\rm B}/\text{atom}$. Positive hyperfine fields or Knight shifts have been observed at Co in a number of dilute alloys, but Heusler alloys provide the first examples of strong orbital contributions in concentrated metallic compounds of Co.

The basic reason for the existence of these local orbital moments is still unclear but it is probably relevant that the Co d states are certainly narrow in energy because the Co atoms are not near neighbours in the Heusler alloys.

6. Summary

We have given an account of the analysis of large numbers of NMR spectra in stoichiometric, off-stoichiometric and substituted Heusler alloys. We were interested in obtaining as much information as possible on the basic mechanisms of magnetic interactions in these systems, which provide a useful link between concentrated and dilute magnetism in metals.

(i) The hyperfine fields can be analysed consistently in terms of local and transferred contributions. From the transferred terms we find that the conduction electron polarisation is negative at near and second neighbour to a Mn site, and positive at third neighbour.

(ii) In all cases but Ni_2MnIn excess Mn atoms substituted onto Z sites have well defined local moments which are coupled antiferromagnetically to the shell of regular Mn neighbours surrounding them at 2 NN distance. In Ni_2MnIn the coupling is ferromagnetic. The temperature variations of these well defined local magnetic impurities in a ferromagnetic lattice can be analysed on a molecular field model.

(iii) Both the conduction electron polarisations and the Mn–Mn couplings follow the predictions of a Friedel–Anderson d resonance model where the d character of the magnetic sites is correctly treated so as to obtain results valid in the preasymptotic region down to near-neighbour distance.

(iv) The local hyperfine fields at a Mn site due to its own local moment can be correlated with the strength of the effective s-d coupling; comparisons can be made with dilute XMn alloys.

(v) The local hyperfine fields at Co nuclei due to the Co moment are positive, indicating unquenched local orbital moments on the Co atoms.

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