

X₂YZ X = 3d, Y = 5f

X = 8A: Ni

Y = 4A: U

Z = 4B: Sn

Owing to the relative size of the actinide atoms, very few compounds form with 5f elements. At room temperature Ni₂USn has the L2₁ structure, but transforms at 220 K to a lower symmetry phase.

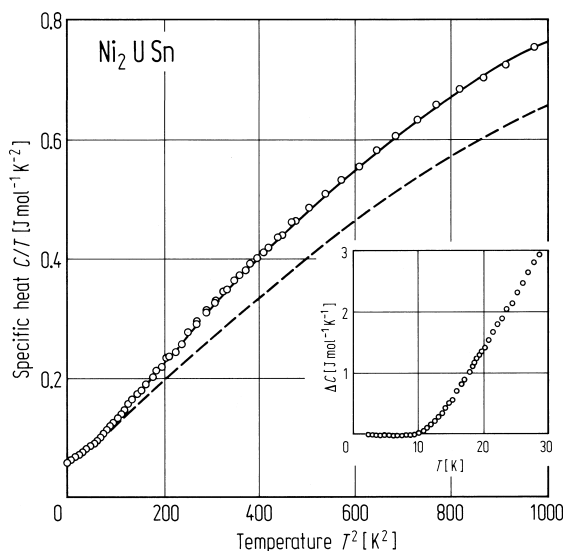


Fig. 361. Specific heat divided by temperature vs. temperature squared for Ni₂USn. The curve is the best overall fit, using electronic plus full Debye contributions. The broken curve is a better two-contribution fit to the low *T* (< 10 K) data. The inset shows the difference between this fit and the data [90E1].

1.5.5.8 Hyperfine fields

Since the previous review [88W1] a substantial amount of research has been undertaken to determine the hyperfine fields at all three sites. Measurements have also been undertaken as a function of pressure and on systems undergoing phase transitions. Detailed band structure calculations and predictions of hyperfine fields have also been published.

X₂YZ X = 3d, Y = 3d, 4d, 5d,

X = 8A: Co

Y = 4A: Ti, Zr, Hf; 5A: V, Nb; 6A: Cr; 8A: Fe

Z = 3B: Al, Ga; 4B: Si, Ge, Sn

Co₂YZ

The hyperfine field at the Z site has been investigated using ¹¹⁹Sn Mössbauer effect. Time differential perturbed angular correlating (TDPAC) measurements of Cd hyperfine fields have also been carried out. All the samples are ferromagnetic with the moment confined to the Co sites.

The ⁵⁹Co and ⁵⁵Mn NMR have been measured at 4.2 K by the spin echo technique. The measurements at the Y site were carried out by dilute substitution of Mn. The hyperfine field at the Y site was found to be 30-80 kOe higher than that in Co₂MnZ alloys with the same Z [89K1].

Table 73. Mössbauer effect and magnetisation results for Co₂YZ alloys [84R1].

Host	p_{Co} [μ_{B}]	$H(\text{Sn})$ [kOe]	IS [mm s ⁻¹]	$H(\text{Sn})/p$ [kOe μ_{B}^{-1}]
Co ₂ TiAl	0.35	29 ± 2	1.44 ± 0.03	83
Co ₂ TiGa	0.4	25 ± 2	1.42 ± 0.01	63
Co ₂ TiSn	0.87	+ 80		+ 92
Co ₂ VAl	0.92	$- 7 \pm 2$	1.47 ± 0.02	- 8
Co ₂ VGa	1.05	$- 12 \pm 2$	1.47 ± 0.02	- 11
Co ₂ VSn	0.31	+ 7		+ 23
Co ₂ CrAl	0.80 ± 0.02	49 ± 2	1.40 ± 0.02	61
Co ₂ CrGa	1.21 ± 0.02	$- 61 \pm 2$	1.41 ± 0.02	- 50

Table 74. Cd and Sn hyperfine fields measured in Co based Heusler alloys Co₂YZ. The values are extrapolated to 0 K and are quoted in kOe [87Y1].

Alloy	H_{hf} (Cd) [kOe]	H_{hf} (Sn) [kOe]
Co ₂ TiAl	70(6)	29(2)
Co ₂ TiGa	- 108(6)	25(2)
Co ₂ TiGe	143(5)	
Co ₂ TiSn		+ 83
Co ₂ VAl	- 64(3)	- 7(2)
Co ₂ VGa	- 56(5)	- 12(2)
Co ₂ VSn		+ 7
Co ₂ CrAl		49(2)
Co ₂ CrGa		- 61(2)
Co ₂ ZrSn	180(5)	+ 103.5
Co ₂ NbSn		+ 15
Co ₂ HfSn		+ 106

Table 75. The Mn hyperfine field $H_{\text{hf}}(\text{Mn}^{\text{dil}}/\text{T})$ in Co₂(T_{0.95}Mn_{0.05})Z, the difference $\Delta H_{\text{hf}}(\text{Mn}/\text{T})$ which is defined for the compounds with the same Z by $H_{\text{hf}}(\text{Mn}^{\text{dil}}/\text{T}) - H_{\text{hf}}(\text{Mn})$ as in Table 77 and magnetic moments [89K1]. Mn^{dil}: dilute substitution of Mn.

Co ₂ TZ	p_{s} [$\mu_{\text{B}}/\text{f.u.}$]	p_{Co} [μ_{B}]	$H_{\text{hf}}(\text{Mn}^{\text{dil}}/\text{T})$ [kOe]	$\Delta H_{\text{hf}}(\text{Mn}/\text{T})$ [kOe]
Co ₂ TiGa	0.75	0.40	$- 321 \pm 2$	- 41
Co ₂ TiSn	1.93	1.03	$- 391 \pm 10$	$- 39 \approx - 47$
Co ₂ VAl	1.95	0.92	$- 357 \pm 5$	- 76
Co ₂ VGa	1.92	1.05	$- 367 \pm 5$	- 87
			- 367	
Co ₂ CrAl	1.55		$- 332 \pm 5$ (weak)	- 52
Co ₂ CrGa	2.36		$- 334 \pm 3$	- 54
Co ₂ FeAl	4.96		$- 349 \pm 5$	- 68
Co ₂ FeGa	5.13		$- 332 \pm 2$	- 52
Co ₂ FeSi	5.9		$- 367 \pm 2$	- 31

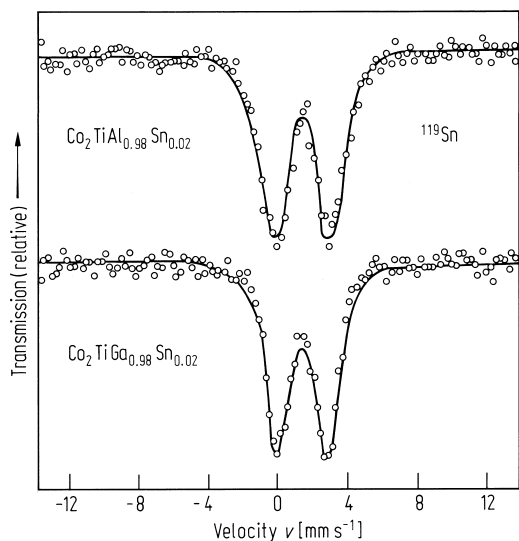


Fig. 362. ^{119}Sn Mössbauer spectra of $\text{Co}_2\text{TiAl}_{0.98}\text{Sn}_{0.02}$ and $\text{Co}_2\text{TiGa}_{0.98}\text{Sn}_{0.02}$ at 4.2 K [84R1].

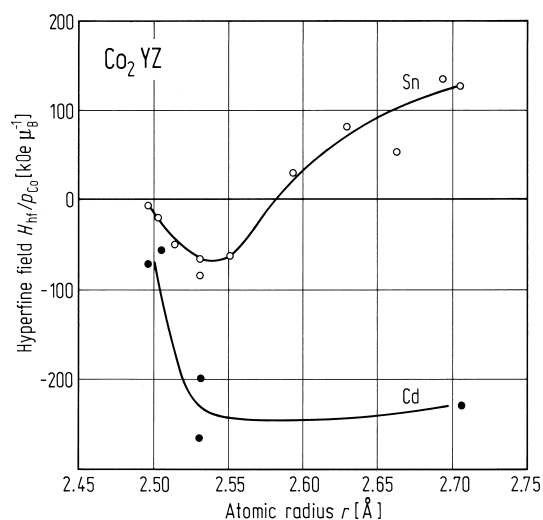


Fig. 364. Reduced hyperfine fields measured at Cd sites (TDPAC) and at Sn sites (Mössbauer) in Co-based Heusler alloys [87Y1].

Fig. 365. Conduction electron polarization in Co-based Heusler alloys calculated using the Campbell Blandin model [75C1] for Cd sites and for Sn sites [87Y1].

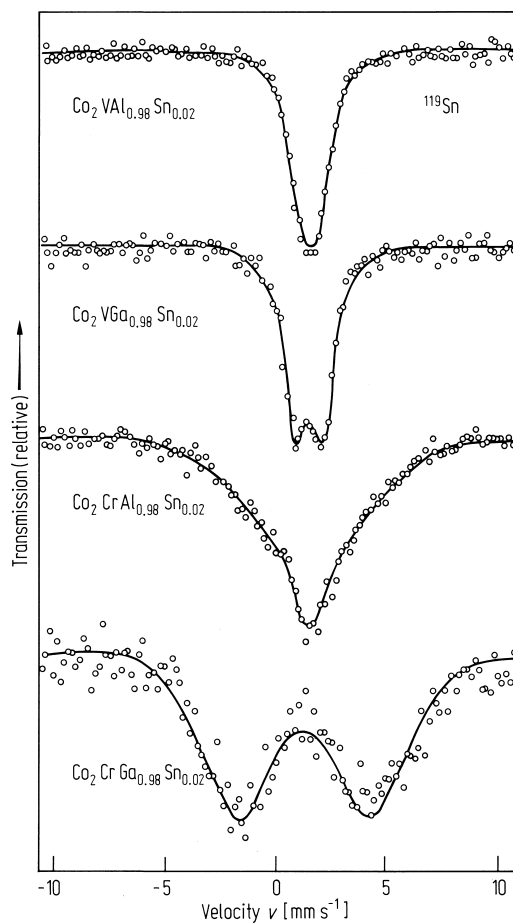
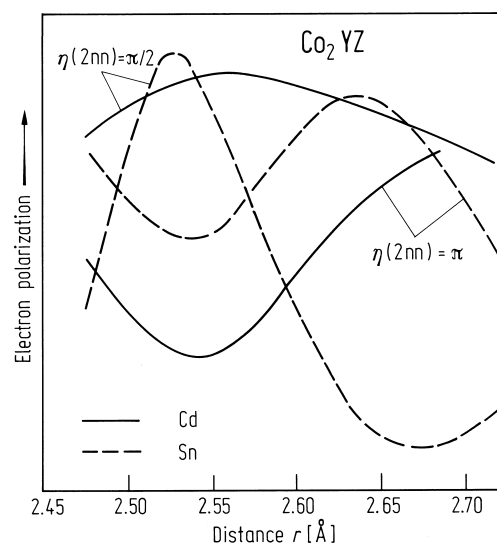
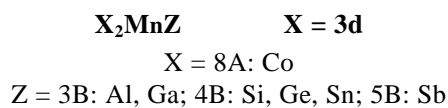


Fig. 363. ^{119}Sn Mössbauer spectra for the Co-based Heusler alloys Co_2VAl , Co_2VGa , Co_2CrAl and Co_2CrGa in which 2 % of Sn has been substituted for either Al or Ga [84R1].



**Co₂MnZ**

All compounds in this series order ferromagnetically with high Curie temperatures. The moment per formula unit is close to 5 μ_B for Z = 4B and approximately 4 μ_B for Z = 3B. The compound containing Sb does not form a single phase system but contains Co_{1.5}MnSb and free cobalt.

Table 76. The Co hyperfine field ($X_{0.95}Co_{0.05}$)₂MnZ which is denoted by $H_{hf}(Co^{dil}/X)$, the difference $\Delta H_{hf}(Co/X)$ which is defined for the compounds with the same Z by $H_{hf}(Co^{dil}/X) - H_{hf}(Co)$ as in Table 77 and magnetic moments [89K1].

X_2MnZ	p_{Mn} [μ_B]	p_{Co} [μ_B]	$H_{hf}(Co^{dil}/X)$ [kOe]	$\Delta H_{hf}(Co/X)$ [kOe]
Ni ₂ MnGa	4.1		-155 ± 5	17
Ni ₂ MnSn	3.75	0.75	-149 ± 3	-7
Ni ₂ MnSb	3.71		-129 ± 3	9
Cu ₂ MnSn	4.0	0.4	-144 ± 5	12
Pd ₂ MnSn	4.21	1.0	-151	5

Table 77. The Co and Mn hyperfine fields in some Co₂MnZ alloys [89K1].

Co ₂ MnZ	$H_{hf}(Mn)$ [kOe]	p_{Mn} [μ_B]	$H_{hf}(Co)$ [kOe]	p_{Co} [μ_B]	T_C [K]	a [Å]
Co ₂ MnAl	280.5	3.01	-177 -175.1	0.5	693	5.756
Co ₂ MnGa	280.0 -280	3.01	171.8 -173	0.52	694	5.770
Co ₂ MnSi	335.9 -337	3.57	145.0 -146	0.75	985	5.654
Co ₂ MnGe	339.4 -339	3.61	140.2 -141	0.75	905	5.743
Co ₂ MnSn	344.1 -352	3.58	156.0 -155	0.75	829	6.000
Co ₂ MnSb	339	3.76	-138	0.75	600	5.929

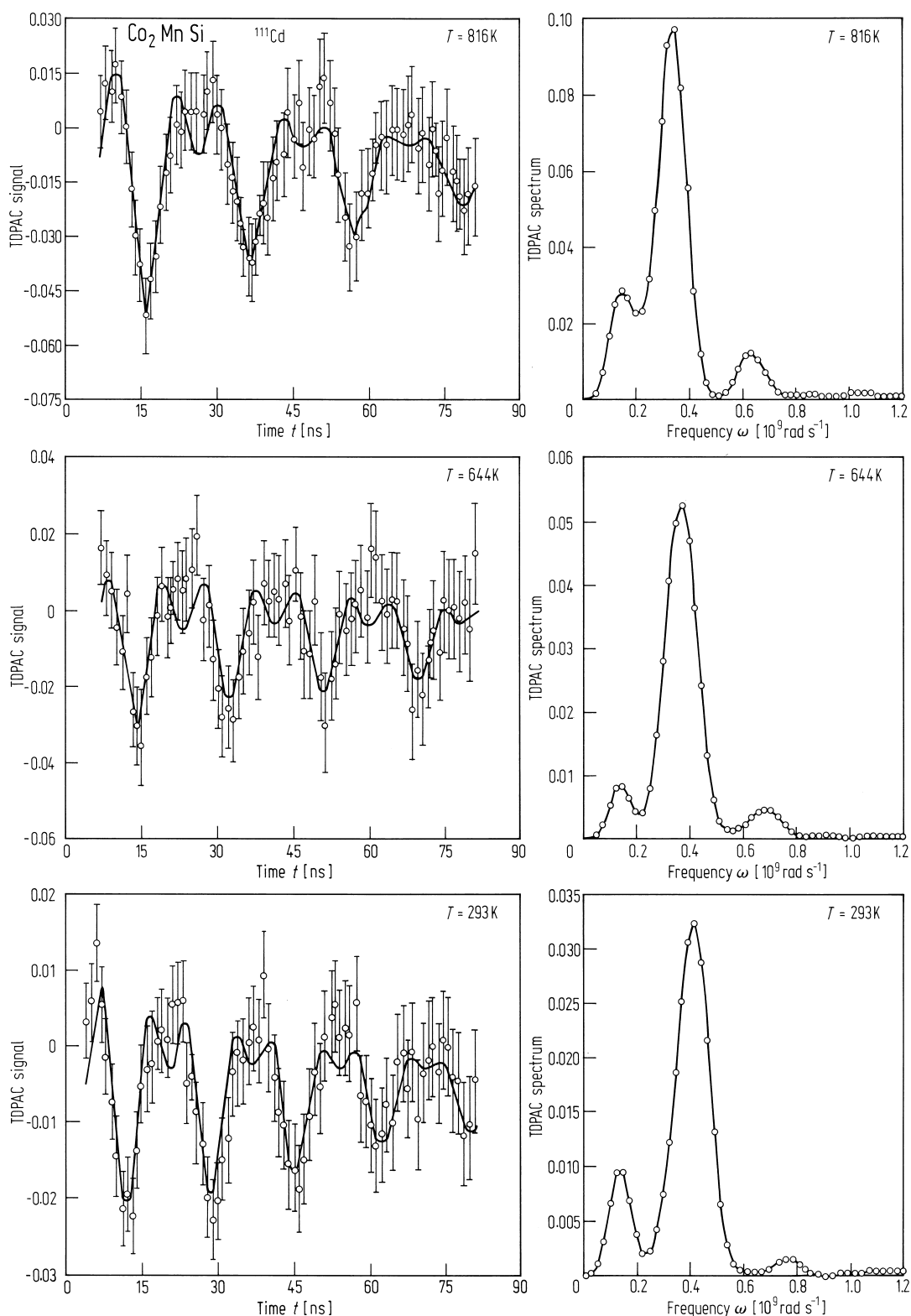


Fig. 366. TDPAC spectra and Fourier transforms for ^{111}Cd in Co_2MnSi at 816 K, 644 K and 293 K [89J1].

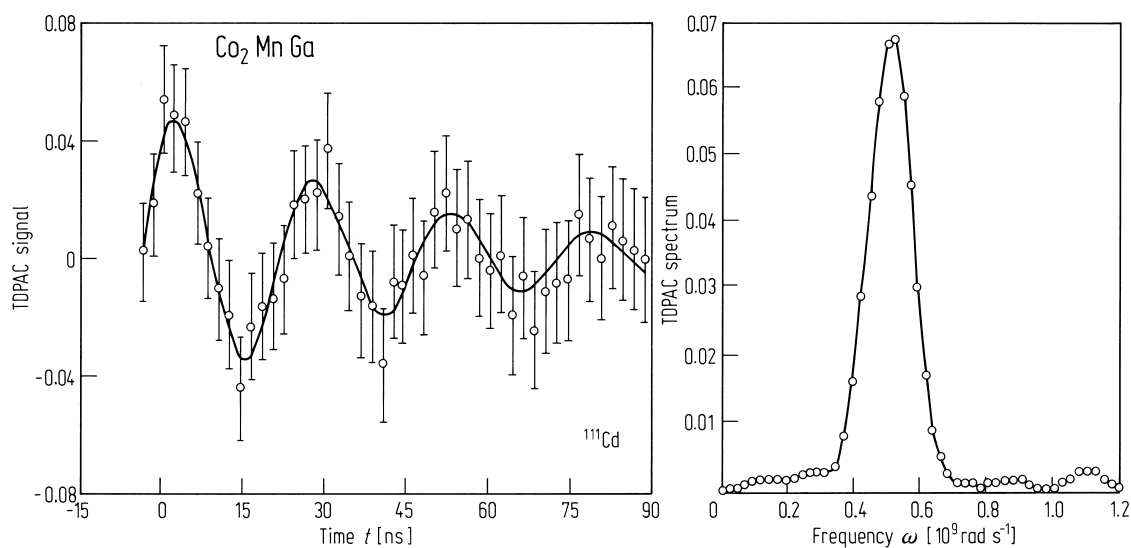


Fig. 367. Room temperature TDPAC spectrum and its Fourier transform for ^{111}Cd in Co_2MnGa with an external polarising field applied [89J1].

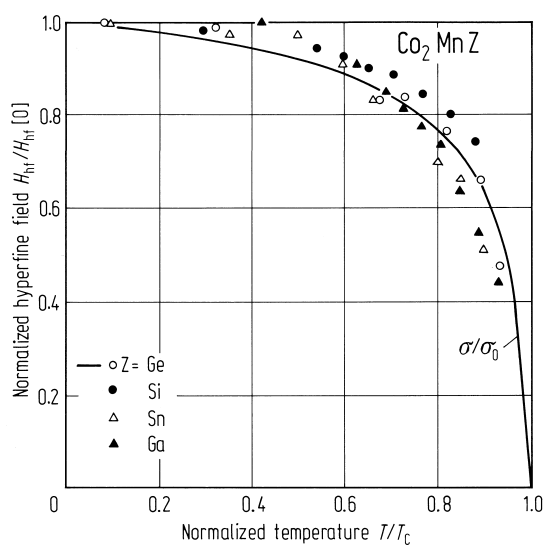


Fig. 368. Hyperfine field at ^{111}Cd sites vs. temperature for Co_2MnZ alloys. The solid line represents the thermal variation of the magnetisation of Co_2MnGe [89J1].

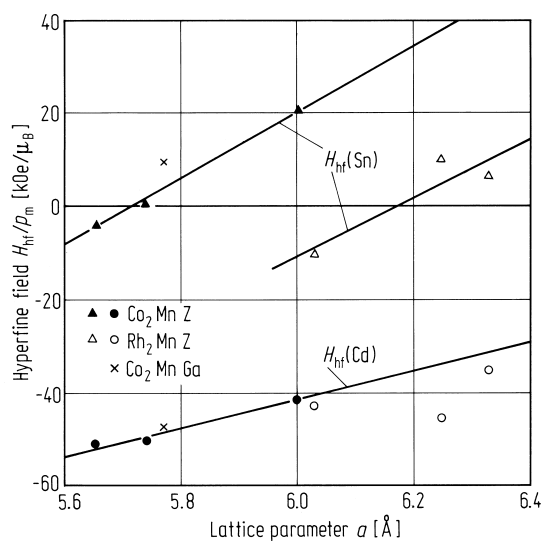


Fig. 369. Hyperfine field normalised to the total magnetic moment per formula unit vs. lattice parameter. Straight lines are fitted respectively to the Cd and Sn hyperfine field in Co_2MnZ and to the Sn hyperfield in Rh_2MnZ ($Z = \text{Si, Ge, Sn}$) [87J1].

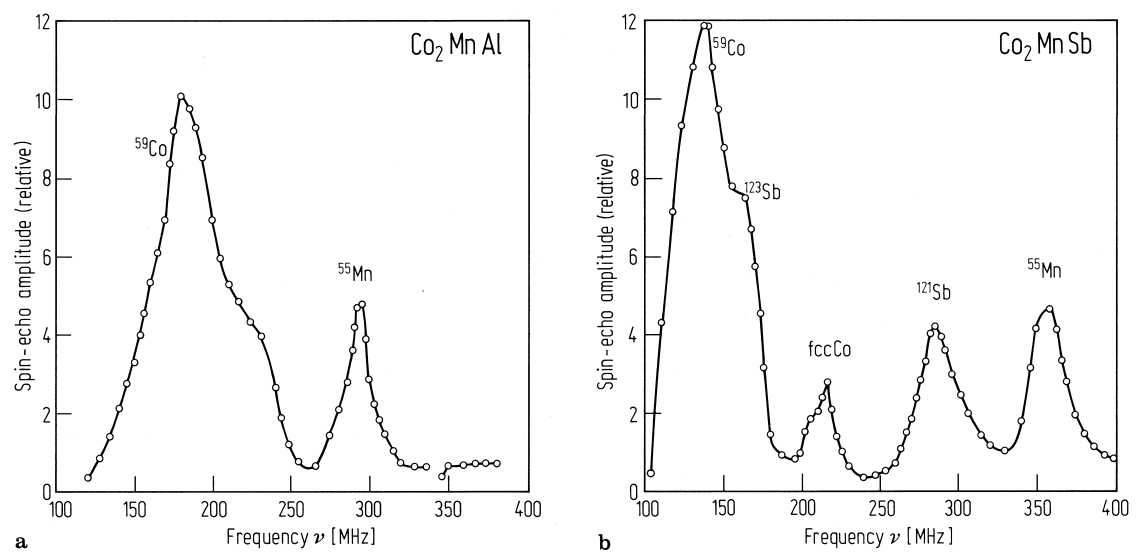


Fig. 370. Zero-field spin-echo amplitude of (a) Co_2MnAl and (b) Co_2MnSb at 4.2 K [89K1].

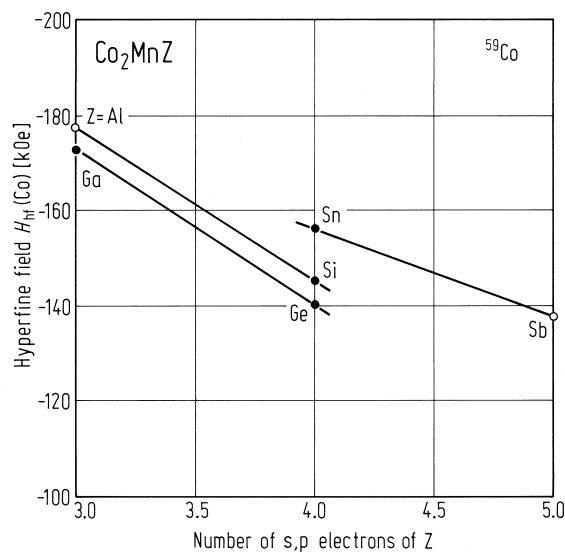


Fig. 371. Co hyperfine field $H_{\text{hyp}}(\text{Co})$ in Co_2MnZ as a function of s,p electrons on Z [89K1].

Quaternary systems Co_2Mn (Al, Si) and Co_2Mn (Ga, Si)

The effects of changing the conduction electron concentration has been investigated in the alloy system. The results show a linear decrease in the field at the Z site as it changes from a group 3B to a 4B element.

Table 78. Exchange interactions for some cobalt based Heusler alloys [88S1].

Alloy	J_{sf} [MeV]	Alloy	J_{sf} [MeV]
Co_2MnGa	− 59.2	$\text{Co}_2\text{MnGa}_{0.36}\text{Si}_{0.64}$	− 45.9
$\text{Co}_2\text{MnGa}_{0.77}\text{Si}_{0.23}$	− 47.4	$\text{Co}_2\text{MnGa}_{0.16}\text{Si}_{0.84}$	− 36.9
$\text{Co}_2\text{MnGa}_{0.6}\text{Si}_{0.4}$	− 39.7	Co_2MnSi	− 30.6

Table 79. A summary of structural and hyperfine field parameters for compounds in the series $\text{Co}_2\text{MnAl}_{0.98-x}\text{Si}_x\text{Sn}_{0.2}$ tabulated as a function of x [83D2]. Lattice parameter a , Sn hyperfine field H , Mössbauer linewidth (HWHM) Γ , isomer shift IS and Fermi vector k_F .

x	a [Å]	H [kOe]	Γ [mm s ⁻¹]	IS [mm s ⁻¹]	k_F [Å ⁻¹]
0.00	5.758 ± 0.003	40 ± 1	1.40 ± 0.05	1.51 ± 0.04	1.38
0.20	5.731 ± 0.003	19 ± 1	1.15 ± 0.05	1.44 ± 0.04	1.43
0.40	5.707 ± 0.003	8 ± 1	0.85 ± 0.05	1.45 ± 0.03	1.47
0.58	5.692 ± 0.003	-7 ± 1	0.80 ± 0.05	1.44 ± 0.02	1.52
0.78	5.674 ± 0.003	-11 ± 1	0.75 ± 0.05	1.44 ± 0.03	1.56
0.98	5.658 ± 0.003	-16 ± 1	0.55 ± 0.05	1.45 ± 0.04	1.60

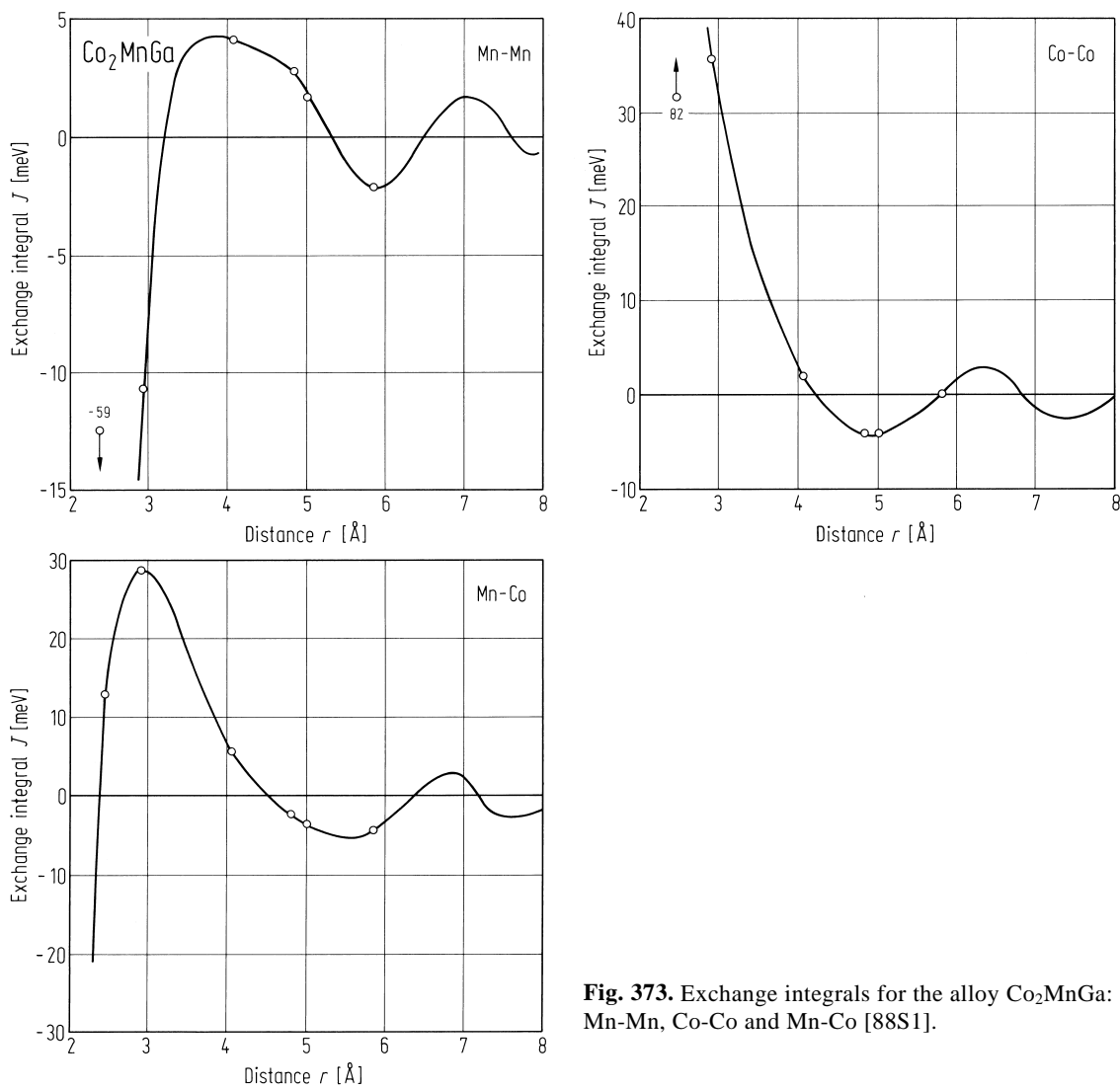


Fig. 373. Exchange integrals for the alloy Co_2MnGa : Mn-Mn, Co-Co and Mn-Co [88S1].

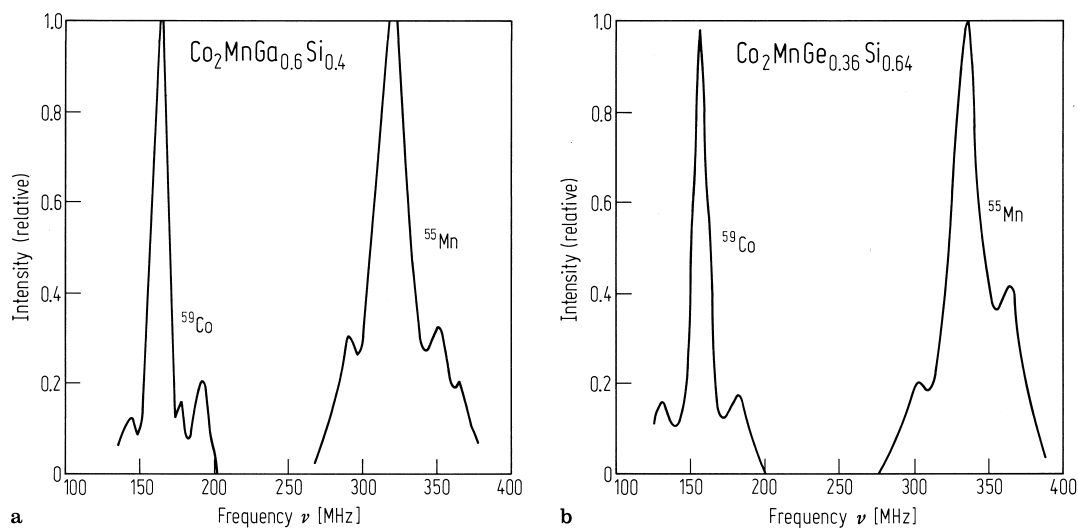


Fig. 372. Spin-echo spectra at 4.2 K in (a) $\text{Co}_2\text{MnGa}_{0.6}\text{Si}_{0.4}$ and (b) $\text{Co}_2\text{MnGe}_{0.36}\text{Si}_{0.64}$ [88S1].

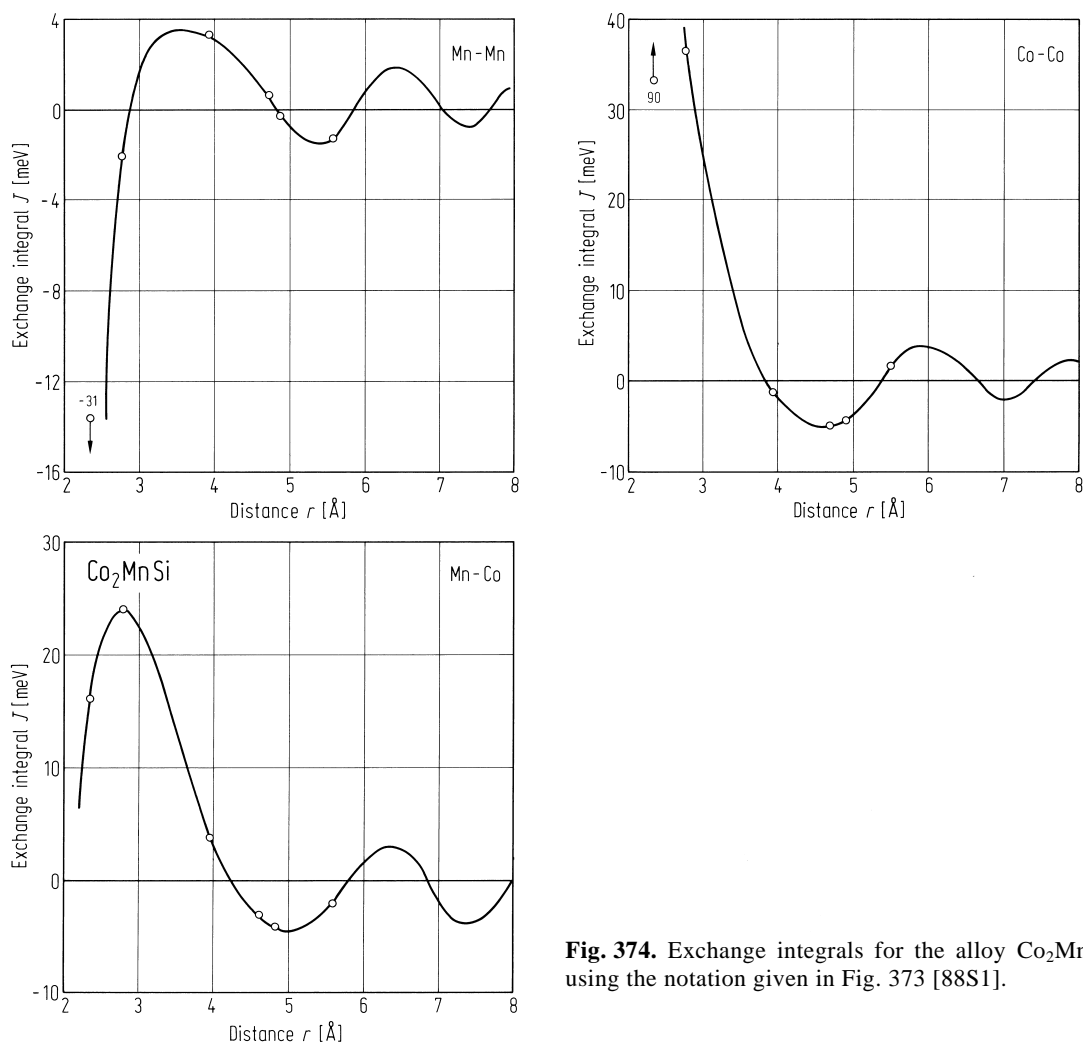


Fig. 374. Exchange integrals for the alloy Co_2MnSi using the notation given in Fig. 373 [88S1].

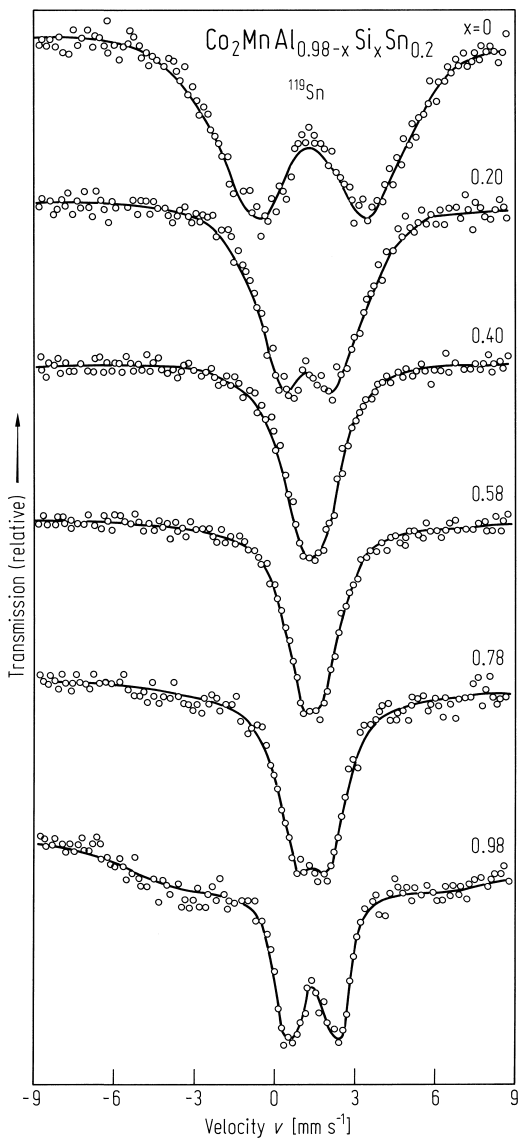


Fig. 375. ^{119}Sn Mössbauer spectra at 77 K of $\text{Co}_2\text{MnAl}_{0.98-x}\text{Si}_x\text{Sn}_{0.2}$ alloys. The solid lines represent a least squares fit to the data [83D2].

Pressure effects

Table 80. The resonance frequency at 4.2 K, $\nu_{4.2\text{K}}$, the corresponding hyperfine field H_{hf} , the pressure dependence of the resonance frequency $(1/\nu)(\partial\nu/\partial p)$ for ^{55}Mn and ^{59}Co and Curie temperature in Co_2MnZ alloys [87K2].

(a) ^{55}Mn resonance.

Co_2MnZ	T_{C} [K]	$\nu_{4.2\text{K}}$ [MHz]	H_{hf} [kOe]	$(1/\nu)(\partial\nu/\partial p)$ [10^{-3} GPa^{-1}]
Co_2MnSi	985	354.5 ± 0.3	-335.9	-1.61 ± 0.04
Co_2MnGe	905	358.2 ± 0.3	-339.4	-1.20 ± 0.06
Co_2MnSn	829	363.1 ± 0.3	-344.1	-1.19 ± 0.03
Co_2MnGa	694	295.5 ± 0.4	-280.0	$+1.86 \pm 0.03$

(b) ^{59}Co resonance.

Co_2MnZ	T_{C} [K]	$\nu_{4.2\text{K}}$ [MHz]	H_{hf} [kOe]	$(1/\nu) (\partial\nu/\partial p)$ [10^{-3} GPa^{-1}]
Co_2MnSi	985	146.5 ± 0.2	-145.0	-4.26 ± 0.14
Co_2MnGe	905	141.6 ± 0.2	-140.2	-3.94 ± 0.07
Co_2MnSn	829	157.6 ± 0.3	-156.0	-1.82 ± 0.07
Co_2MnGa	694	173.6 ± 0.4	-171.8	$+0.52 \pm 0.06$

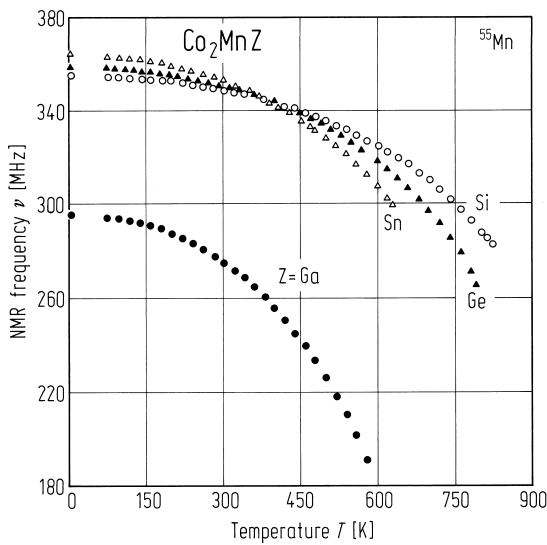


Fig. 376. ^{55}Mn NMR frequency ν vs. temperature T in Co_2MnZ alloys with $Z = \text{Si, Ge, Sn, Ga}$ [87K2].

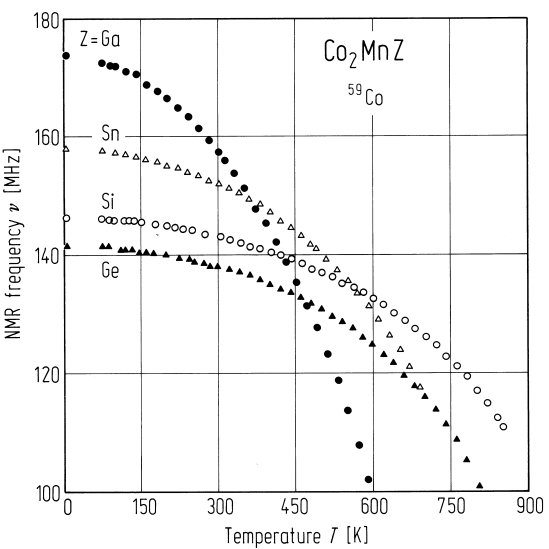


Fig. 377. ^{59}Co NMR frequency ν as a function of temperature T in Co_2MnZ alloys with $Z = \text{Si, Ge, Sn, Ga}$ [87K2].

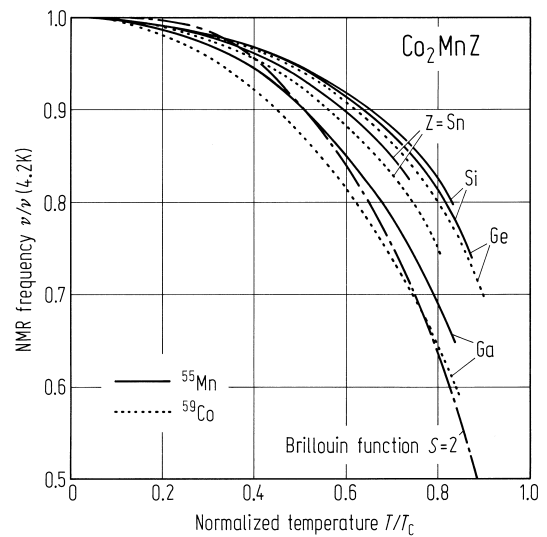


Fig. 378. Normalised frequency $\nu/\nu_{4.2\text{K}}$ vs. reduced temperature T/T_{C} for Co_2MnZ alloys ($Z = \text{Si, Ge, Sn, Ga}$). The solid lines are for ^{55}Mn and the dotted lines are for ^{59}Co . The ^{59}Co line for $Z = \text{Si}$ and the ^{55}Mn line for $Z = \text{Ge}$ almost overlap. The broken curve represents the variation of a Brillouin function for $S = 2$ [87K2].

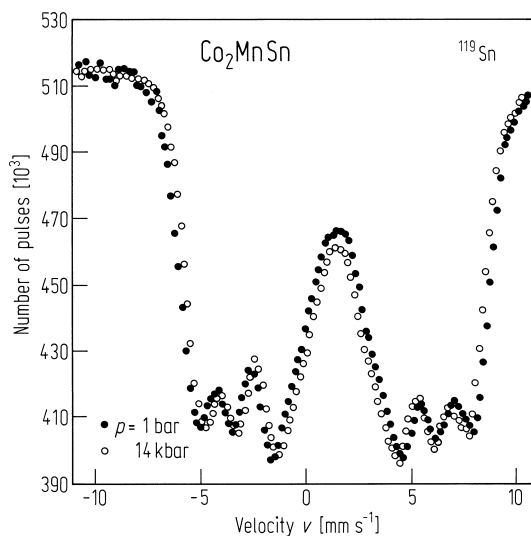


Fig. 379. Mössbauer spectra of the ^{119}Sn nuclei in Co_2MnSn for two different applied pressures of 1 bar and 14 kbar [75N1].

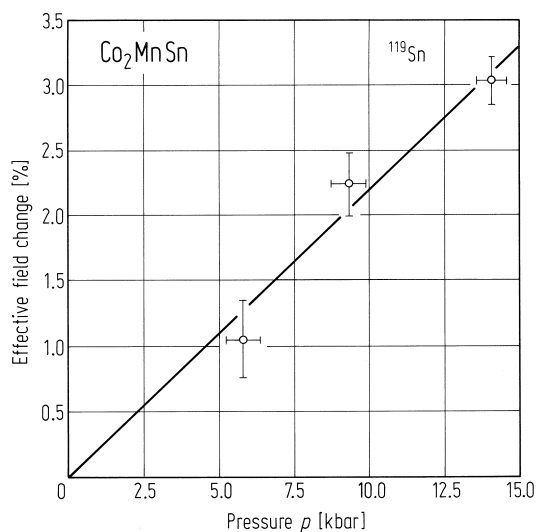


Fig. 380. Relative change in the effective field at the ^{119}Sn nuclei in Co_2MnSn as a function of applied pressure [75N1].

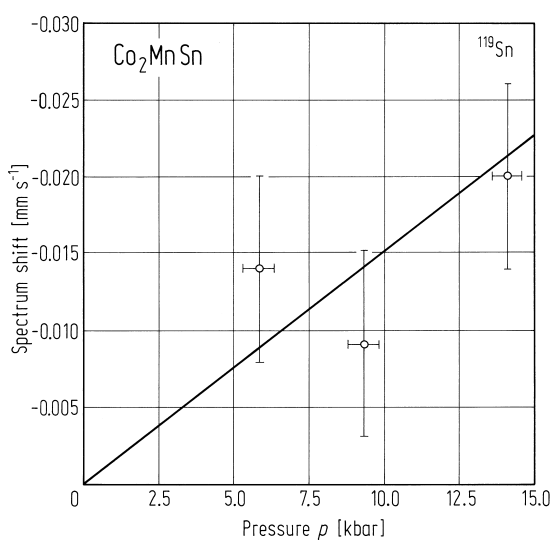


Fig. 381. Change in the position of the centre of gravity of the spectrum of the ^{119}Sn nuclei in Co_2MnSn as a function of applied pressure [75N1].

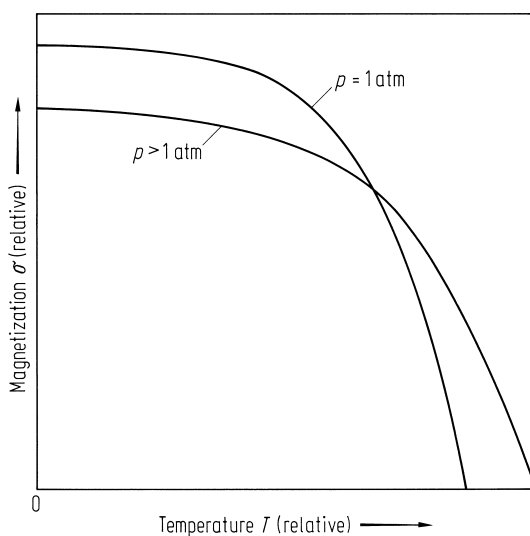


Fig. 382. Schematic temperature variation of the magnetisation for (1) $p = 1 \text{ atm}$ and (2) $p > 1 \text{ atm}$ [75N1].

X₂YZ **X = 3d, Y = 3d**

X = 7A: Mn

Y = 8A: Co, Ni

Z = 4B: Sn

Mn₂YSn

The compounds which are ferromagnetic are of particular interest since the Mn atoms occupy the tetrahedral sites.

Table 81. A summary of the structural and magnetic properties of several Heusler alloys [90S3].

Alloy	t_a [h]	T_a [°C]	a [Å]	p_{00} [μ _B]	T [K]
Mn ₂ CoSn	170	800	6.056 + 0.005	2.66 + 0.05	580 + 5
Mn ₂ NiSn	170	800	6.096 + 0.005	2.02 + 0.05	533 + 5
Ni ₂ MnSn	170	850	6.054 + 0.005	4.02 + 0.05	353 + 5
Co ₂ MnSn	24	720	6.00	5.08 + 0.05	329 + 4

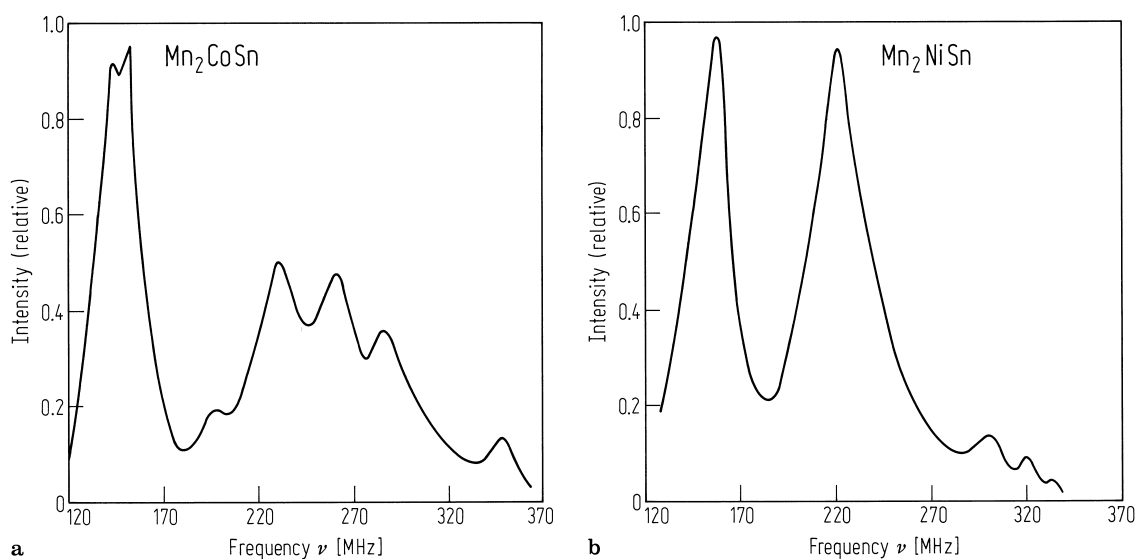


Fig. 383. Nuclear spin echo spectra of the Heusler alloys (a) Mn₂CoSn and (b) Mn₂NiSn at $T = 1.4$ K in zero external field [90S3].

X₂YZ **X = 3d, Y = 3d, Z = 4B**

X = 8A: Fe

Y = 7A: Mn

Z = 4B: Si

Fe₂Mn Si

The compound orders ferromagnetically below 214 K but undergoes a phase transition to a canted structure at 69 K. The effects of the atomic environment on the magnetic properties has been investigated using the hyperfine field on ⁵⁷Fe.

Table 82. $N(n)$ is the relative number of iron atoms on the B and D sites with n nearest neighbour iron atoms. x is the concentration of iron atoms on the C sites. IP is the relative integrated intensity under each peak in the $P(H)$. H_i is the magnetic hyperfine field at each peak in the $P(H)$ [91G1].

Fe ₂ MnSi ($x = 0.1$)				Fe _{1.5} Mn _{1.5} Si ($x = 0.01$)			
n	$N(n)$ [%]	IP [%]	H_i [kOe]	n	$N(n)$ [%]	IP [%]	H_i [kOe]
0	62.3	61	64	0	95.4	95	63
1	27.2	29	116	1	3.8	4	115
2	4.6	5	158	2	0.1		
c site	5.0	5	287	c site	0.7		

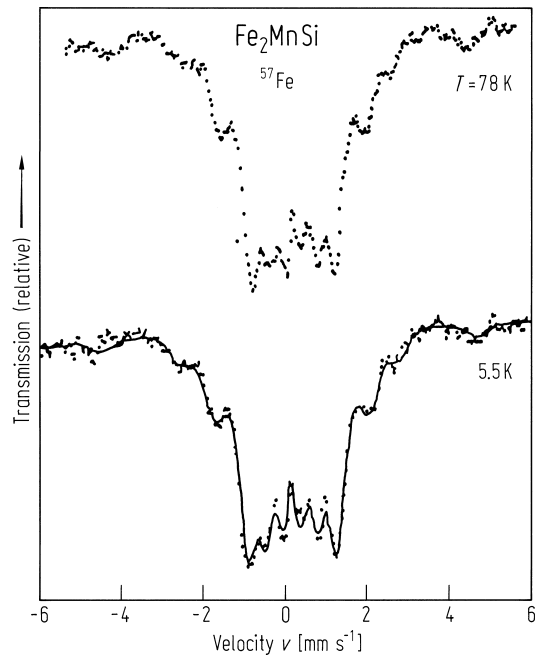


Fig. 384. ^{57}Fe Mössbauer spectra of Fe_2MnSi at 78 and 5.5 K. The solid curve is a theoretical simulation [91G1].

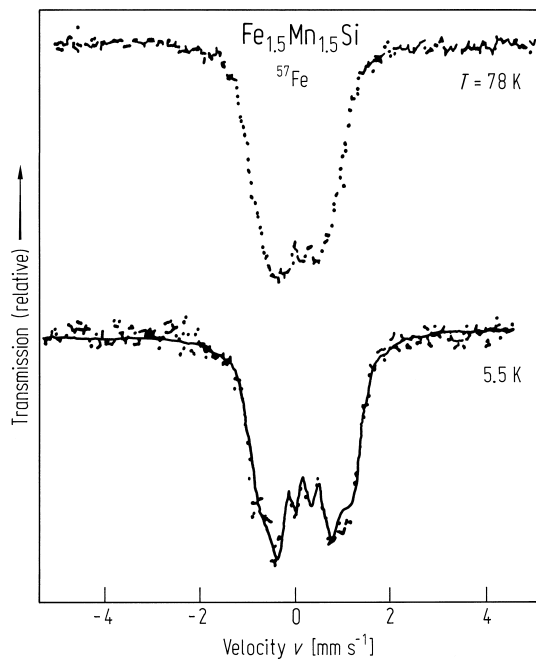


Fig. 385. ^{57}Fe Mössbauer spectra of $\text{Fe}_{1.5}\text{Mn}_{1.5}\text{Si}$ at 78 and 5.5 K. The solid curve is a theoretical simulation [91G1].

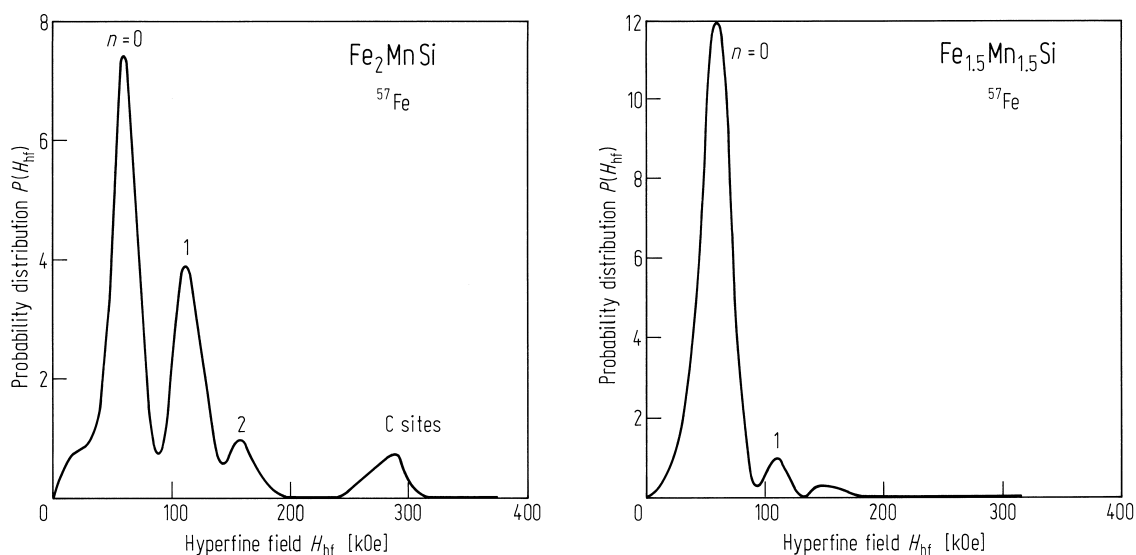


Fig. 386. Distributions of hyperfine field $P(H)$ for the spectra of Fe_2MnSi and $\text{Fe}_{1.5}\text{Mn}_{1.5}\text{Si}$ at 5.5 K. Each peak corresponds to the number n of nearest neigh-

bour iron atoms around an iron atom of the B or D sites (see Figs. 384 and 385) [91G1].

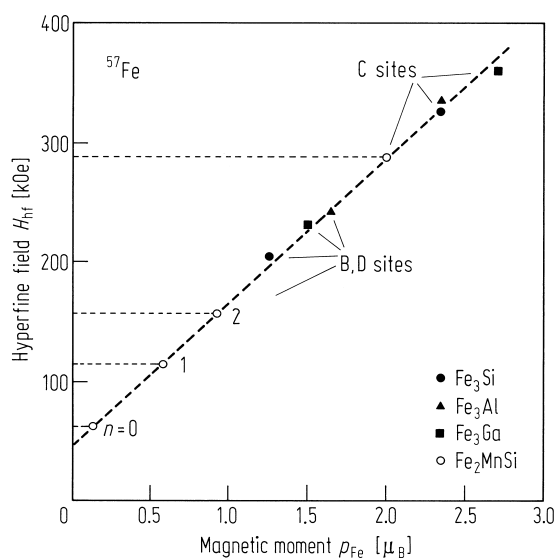


Fig. 387. Relation between ^{57}Fe hyperfine field and magnetic moment of iron atom in several D0_3 type alloys. The dotted line indicates the Wertheim relation for $p_{\text{Fe}} = 1.5 \mu_B$. For Fe_2MnSi n is the number of nearest neighbour iron atoms around an iron atom on the B or D sites [91G1].

X₂YZ X = 3d, 4d, Y = 3d, Z = 3B

X = 8A: Ni, Pd

Y = 7A: Mn

Z = 3B: Ga; 4B: Sn

Ni₂MnGa

The compound orders ferromagnetically with a moment of approximately $4 \mu_B$ confined to the Mn atom. At approximately 220 K the compound transforms to a tetragonal structure.