LOCAL INTERACTIONS AND SPIN TRANSFER MECHANISMS IN THE
HEUSLER-TYPE ALLOYS $Pd_{1+x}MnSb$ AND $Pd_2MnSb_{0.9}Sn_{0.1}$

L. J. Swartzendruber
National Bureau of Standards, Washington, D.C. 20234

B. J. Evans
University of Michigan, Ann Arbor, Michigan 48104

ABSTRACT

The magnetic hyperfine fields at ^{121}Sb, $H_{eff}(Sb)$, in the
Heusler-type alloys $Pd_{1+x}MnSb$ are found to be strongly dependent on
x, varying from about 600 kG for x=1 to about 300 kG for x=0. As x
is decreased from unity, the single unique value observed in
Pd_2MnSb is replaced by a distribution in $H_{eff}(Sb)$, with an average
value which decreases in a regular manner with the number of Pd
vacancies. In $Pd_2MnSb_{0.9}Sn_{0.1}$, $H_{eff}(Sn)$ is found to be similar in
magnitude to $H_{eff}(Sn)$ in Pd_2MnSn. Both these results indicate that
local spin transfer mechanisms are important in determining the
magnitude and sign of H_{eff} at the Sb site in Heusler-type alloys.

INTRODUCTION

Ordered intermetallic compounds with the composition X_2MnZ
are generally referred to as Heusler alloys. The (often incomplete)
ordering is of the Cu_2MnAl type (L2$_1$) and, for example, X is Cu, Ni,
Pd, or Co and Z is Al, In, Sn or Sb. Most of these alloys are fer-
romagnetic, with exceptions such as Pd_2MnIn which is antiferromag-
netic.[1] A related series of compounds with the composition X MnZ
exhibit order of the MgAgAs (Cl_b) type and are also mostly ferro-
magnetic. The crystal structures are illustrated in Fig. 1. Mea-
sured magnetic moments range between 3.5 and 4.5 μ_B per formula unit
and are (with exceptions[2] when X is Co) localized on the Mn site[3].
In these alloys the Mn-Mn separations are large and indirect exchange
interactions are an important factor in determining their magnetic
properties[4].
        In a previous study[5] we have measured $H_{eff}(Sb)$ in $Ni_{1+x}MnSb$ for
$1 \geq x \geq 0$. These alloys exhibit a continuous transition between the
L2$_1$ and Cl_b structures[6]. The saturation value of $H_{eff}(Sb)$ is approx-
imately +300 kG, with a relatively small dependence on x. Here we
present results on the isoelectronic alloys $Pd_{1+x}MnSb$. In contrast
to the $Ni_{1+x}MnSb$ alloys, $H_{eff}(Sb)$ in $Pd_{1+x}MnSb$ has a considerable
dependence on x. The Sb and Sn hyperfine fields in $Pd_2MnSb_{0.9}Sn_{0.1}$
were also measured. While the presence of the Sn decreases the
average magnitude of the Sb hyperfine field, the average Sn field
has about the same magnitude as that found at the Sn site in Pd_2MnSn.

EXPERIMENTAL

Alloys of $Pd_{1+x}MnSb$ for x=1.00, 0.75, 0.50 and 0, and an alloy
of $Pd_2MnSb_{0.9}Sn_{0.1}$ were prepared by arc melting weighed quantities
in a gettered argon atmosphere. The ingots were homogenized at

920 K for four days and water quenched. A metallographic examination followed. Predominantly single phase alloys with less than 2% of unidentified second phases were revealed in each case. The ingots were crushed to a powder and transmission Mössbauer spectra obtained on samples containing approximately 350 mg of the powder embedded in a plastic disc 2.5 cm in diameter. Sources were $(^{121}Sn)BaSnO_3$ for the ^{121}Sb spectra and $(^{119*}Sn)BaSnO_3$ for the ^{119}Sn spectra. X-ray measurements, performed on the crushed powder, revealed no extraneous phases. The measured lattice constants are listed in Table I. Crystallographic order, as evidenced from the resolution of the α_1, α_2 doublet of the (224) x-ray peak, increased as x decreased.

RESULTS

For x=0 and x=1, satisfactory least squares fits could be obtained to the $Pd_{1+x}MnSb$ spectra using a single-valued magnetic hyperfine field pattern. For intermediate values of x, a hyperfine field distribution is evident. These spectra were fitted using two single-valued magnetic hyperfine field patterns. Such fits are probably not unique. However they give as satisfactory a representation of the distribution as is justified by the scatter in the data, and give accurate values for the average hyperfine field values. They can also be used to prove that, for intermediate values of x, the spectra are not simply the sum of the Pd_2MnSb and PdMnSb spectra. A similar fit was used to represent the ^{121}Sb spectrum from the $Pd_2MnSb_{0.9}Sn_{0.1}$. The ^{119}Sn spectrum from the same sample was fitted to a single valued hyperfine field pattern and thus only an average hyperfine field value was obtained. Table I lists results for the ^{121}Sb spectra. Table II compares average hyperfine fields for a number of Heusler-type alloys. Table II also lists Curie temperatures. (In all cases, the hyperfine field at 100K is within 10% of its value extrapolated to 0 K.) The ^{121}Sb spectra and least squares fits are shown in Fig. 1. Some of the least squares fits show a slight assymetry which is due to a quadrupole splitting used as a free parameter in the fitting procedure. In no case did the quadrupole splitting exceed 0.2 mm/sec.

DISCUSSION

The Sb hyperfine fields in Ni_2MnSb, NiMnSb and PdMnSb are all approximately 300 kG. In contrast, Sb in Pd_2MnSb has a hyperfine field nearly twice as large[9]. This large field value is confirmed here in another sample and has also been measured using the spin echo technique[10]. For intermediate values of x in $Pd_{1+x}MnSb$, the ^{121}Sb ME spectra are not simply superpositions of spectra for Pd_2MnSb and PdMnSb. The introduction of Pd vacancies into the Pd_2MnSb lattice, or the substitution of Sn for Sb, tends to decrease $H_{eff}(Sb)$.

It has recently been recognized[5,8,11,12] that the virtual bound state-spin polarization model of Caroli and Blandin[13] fails to give a complete description of the hyperfine fields in Heusler alloys. This failure is most evident for the positive hyperfine fields observed in a number of alloys, e.g. at Sn in Ni_2MnSn, for which the model predicts a negative hyperfine field.[2] Considering the Heusler alloys as β-phase electron compounds[14] with an electron-
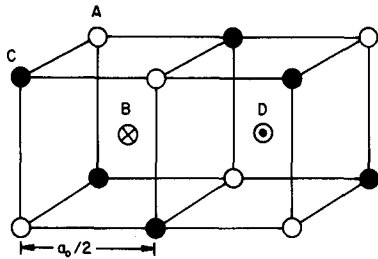
Composition	Structure	Site	Occupation
Pd_2MnSb	$L2_1$	A ○	Pd
		B ⊗	Mn
		C ●	Pd
		D ⊙	Sb
PdMnSb	$C1_b$	A ○	Pd
		B ⊗	Mn
		C ●	Empty
		D ⊙	Sb

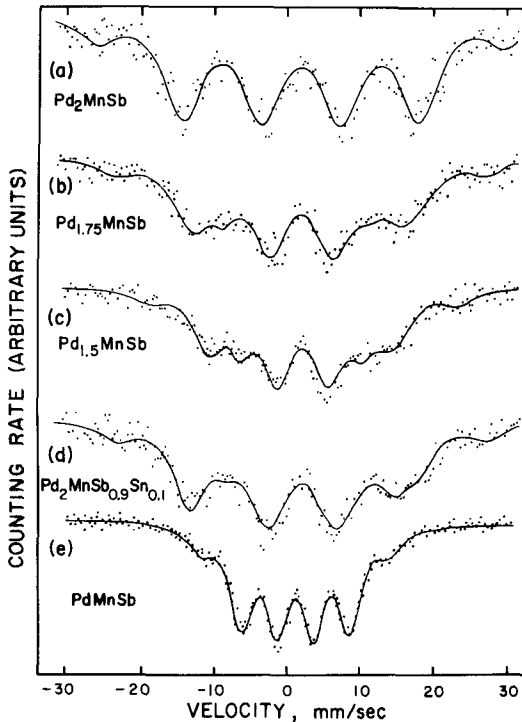FIGURE 1. Schematic illustration of the $Pd_2MnSb(L2_1)$ and $PdMnSb(C1b)$ structures.

FIGURE 2. ^{121}Sb Mössbauer effect spectra for several Heusler-type alloys at 100K. The solid line is a least square fit to the data points as described in the text.

to-atom ratio near 3/2, the Caroli-Blandin theory predicts (within the customary free-electron picture) a negative hyperfine field (for such atoms as Sn, Sb, and In) at the D-site for every alloy. The existence of positive hyperfine fields indicates that mechanisms other than the type of conduction electron polarization described by Caroli and Blandin must be contributing to the observed hyperfine field. The results obtained here on $Pd_{1+x}MnSb$ suggest that local interactions involving the Pd atoms play a considerable role in transferring the hyperfine field from a Mn to an Sb atom. These local interactions could be responsible for the very large hyperfine field found for Sb in Pd_2MnSb. The sign of $H_{eff}(Sb)$ in PdMnSb and Pd_2MnSb has not been determined, although the variation of $H_{eff}(Sb)$ with x in $Pd_{1+x}MnSb$ indicates that the sign is the same in PdMnSb and Pd_2MnSb.

TABLE I

Parameters obtained in least squares fits to the 100 K ^{121}Sb Mössbauer Spectra of several Pd-based Heusler-type alloys. Two magnetic hyperfine field patterns with identical linewidths and isomer shifts were assumed. Isomer shift is with respect to an InSb absorber at 100 K. Lattice constants determined by x-ray analysis are also listed.

	Ha kG (±5)	Hb kG (±5)	Area Fraction of pattern b (±0.05)	FWHM mm/sec (±0.2)	Isomer Shift mm/sec (±0.2)	χ^2 per point	Lattice Constant nm
Pd_2MnSb	585	–	0	4.9	1.2	1.26	0.6428
$Pd_{1.75}MnSb$	526	367	0.42	4.3	1.1	1.11	0.6381
$Pd_{1.5}MnSb$	443	299	0.49	3.6	0.9	1.19	0.6338
$PdMnSb$	–	307	1.0	3.5	0.7	1.14	0.6231
$Pd_2MnSb_{0.9}Sn_{0.1}$	526	336	0.29	4.4	1.2	1.06	0.6416

TABLE II

Average Z-ion hyperfine fields, H_{eff}^{avg}, at 100 K in several X_2MnZ and XMnZ Heusler-type alloys. Signs of the fields and Curie temperatures are indicated where known.

Alloy	H_{eff}^{avg} kG(±5)	Reference	T_c K	Reference
Pd_2MnSb	585	[7]	247	[1]
$PdMnSb$	305	[7]	500	[15]
$NiMnSb$	+307	[5]	720	[16]
Ni_2MnSb	+291	[5]	360	[17]
Ni_2MnSn	+ 87	[8]	344	[17]
Pd_2MnSn	– 35	[8]	189	[1]
$Pd_2MnSb_{0.9}Sn_{0.1}$	471(Sb) 37(Sn)	[7]		

REFERENCES

1. P. J. Webster and R. S. Tebble, Phil. Mag. 16, 347 (1967).
2. J. P. Felcher, J. W. Cable and M. K. Wilkinson, J. Phys. Chem. Solids 24, 1663 (1963); P. J. Webster, Phil. Mag. 16, 347 (1967).
3. P. J. Webster, J. Phys. Chem. Solids 32, 1221 (1971).
4. C. Zener and R. R. Heikes, Rev. Mod. Phys. 25, 191 (1953).
5. L. J. Swartzendruber and B. J. Evans, AIP Conf. Proc. 5, 539 (1972).
6. L. Castelliz, Mh. Chem. 82, 1059 (1951).
7. This work. Figures represent the average hyperfine field.
8. D. J. W. Geldart, C. C. M. Campbell, P. J. Pothier and W. Leiper, Can. J. Phys. 50, 206 (1972).
9. L. J. Swartzendruber and B. J. Evans, Phys. Letters 38A, 511 (1972).
10. S. K. Malik, R. Vijayaraghavan, Le Dang Khoi and P. Veillet, Phys. Letters 40A, 161 (1972). Structure is apparent in the spin echo spectrum due to Pd-Sb disorder. However, H_{eff}(Sb) is nearly the same on either site, resulting in only a slight broadening of the ME spectrum. The slight differences between the present value for H_{eff}(Sb), the average spin-echo frequency, and previous ME results [ref. 9], probably reflects small differences in the amount of disorder in different samples.
11. J. M. Williams, J. de Physique 32, C1-790 (1971).
12. R. Segnan, W. A. Ferrando, D. Sweger, and P. J. Webster, J. de Physique 32, C1-792 (1971).
13. B. Caroli and A. Blandin, J. Phys. Chem. Solids 27, 503 (1966).
14. B. R. Coles, W. Hume-Rothery and H. P. Myers, Proc. Roy. Soc. (London) 196A, 125 (1949).
15. K. Endo, J. Phys. Soc. Japan 29, 643 (1970).
16. L. Castelliz, Mh. Chem. 82, 1059 (1951).
17. P. J. Webster, Contemp. Phys. 10, 559 (1969).