Mössbauer-effect experiments on samples of $\text{Pd}_{1-x} \text{MnSb}_{1-x} \text{Sn}_x$ performed systematically as a function of heat treatment have revealed the existence of three $^{119}\text{Sn}$ magnetic field sites characterized by high-, intermediate-, and low-field values. A high-field site of $210 \pm 5$ kOe is identified with Sn replacing Sb in the ordered $L2_1$ structure of $\text{Pd}_3\text{MnSb}$. An intermediate-field site of about 100 kOe is identified with a defect Sn environment which probably consists of 4 Pd vacancies in the near-neighbor coordination of the regular high-field site. The identification of the intermediate-field site is suggested by a set of measurements performed as a function of Pd composition $x$ in $\text{Pd}_{1-x} \text{MnSb}_{1-x} \text{Sn}_{0.01}$ samples, which revealed the Sn field in the $C1_x$ structure of $\text{PdMnSb}$ to be 100 kOe. Finally, a low-field site ($\sim 0$ kOe) is observed on prolonged annealing $\text{Pd}_{1-x} \text{MnSb}_{1-x} \text{Sn}_{0.01}$ samples. This site is shown to be formed irreversibly due to the presence of oxygen contamination and represents a defect Sn site whose structure is less certain. The $^{119}\text{Sn}$ field results in $\text{PdMnSb}$ and $\text{Pd}_3\text{MnSb}$ hosts are compared with estimates of these fields based on the Jena-Geldart model.

I. INTRODUCTION

Although internal magnetic fields in Heusler alloys $X_2\text{MnY}$ have been measured for over a decade, it is clear that our present understanding of these data is far from complete. Attempts to gain a fundamental understanding of the origin of fields in these ternaries have come recently through the systemsatics of fields at $5sp$ impurities substituted at the Sb site in the well-characterized Heusler alloys $\text{Pd}_3\text{MnSb}$ and $\text{PdMnSb}$. A number of recent publications dwelling on the experimental and theoretical aspects of this problem have appeared and these seem to reinforce the expediency in pursuing this approach. Unfortunately, in some of these measurements, from an experimental point of view, important questions concerning the metallurgy of the $5sp$ impurity in question with the Heusler alloy host have not been clarified, leading to serious discrepancies in field measurements. The case of the impurity Sn in $\text{Pd}_3\text{MnSb}$ appears to be one such example.

A clearly resolved Sn magnetic hyperfine structure in ferromagnetic $\text{Pd}_3\text{MnSb}$ was first observed by us and more recently by others, suggesting a Sn field value of $210 \pm 5$ kOe at $4.2\,\text{K}$ in the indicated Heusler alloy. Previous study of the $^{119}\text{Sn}$ hyperfine interaction in $\text{Pd}_3\text{MnSb}$ was also reported by Campbell and Leiper, who observed a much smaller field of about 10 kOe. The large discrepancy between these field results has remained unexplained. In this paper, we show the existence of thermally induced structural and metallurgical effects in the Sn-doped $\text{Pd}_3\text{MnSb}$ samples. Induction melted samples of $\text{Pd}_3\text{MnSb}_{0.99}^{0.01}\text{Sn}$ were used as absorbers in these $^{119}\text{Sn}$ Mössbauer-effect (ME) experiments exhibit three distinct hyperfine field sites. The population of these sites is found to be sensitive to the heat treatment undergone by the alloy. In the present paper, we attempt to elucidate these heat treatment effects and to identify the magnetically inequivalent sites.

Of the few available $5sp$ Mössbauer-effect probes that can be utilized to investigate Heusler alloys, $^{119}\text{Sn}$ is in a sense unique. One can pursue room-temperature measurements in this spectroscopy and thus investigate the paramagnetic phase of $\text{Pd}_3\text{MnSb}$. Systematic changes in room-temperature isomer shift (IS) of $\text{Pd}_3\text{MnSb}_{0.99}^{0.01}\text{Sn}_{0.01}$ samples were observed as a function of thermal history undergone by the samples. A correlation of these IS's with the internal fields is made to elucidate the observed annealing effects in this system.

Two other types of experiments were also undertaken in this work. Measurements were performed as a function of Pd composition $x$ in $\text{Pd}_{1-x} \text{MnSb}_{0.99}^{0.01}\text{Sn}_{0.005}$ samples with the purpose of measuring the Sn field in the $C1_x$ structure of $\text{PdMnSb}$. Secondly, the compositional behavior of the Sn field in the $\text{Pd}_3\text{MnSb}_{1-x}\text{Sn}_x$ system was systematically studied. We show in this paper that these data reveal a smooth composition behavior, which is suggestive of miscibility of Sn and Sb at the $Y$ site in these alloys.

In conclusion, we compare the $^{119}\text{Sn}$ field result in $\text{PdMnSb}$ and $\text{Pd}_3\text{MnSb}$ hosts with estimates of these fields available from current theoretical models. The agreement between theory and experiment is excellent for the $\text{PdMnSb}$ host. It is proposed that the lack of as good an agreement
for the Pd₃MnSb host, on the other hand, may be a band-structure effect.

II. EXPERIMENTAL PROCEDURE

Samples of Pd₃MnSbₓSnₓ (x = 0.0075, 0.01, 0.10, 0.50, 1.0) and PdMnSb₀.₉₉₅Sn₀.₀₀₅ were prepared by induction melting stoichiometric amounts of the desired elements using a graphite boat in a quiescent argon atmosphere. Enriched ¹¹⁹SnO₂ obtained from Oak Ridge National Laboratory was reduced to metallic Sn by heating to 700 °C in a hydrogen atmosphere. A Mössbauer-effect spectrum of the reduced Sn samples showed no detectable trace of Sn⁺⁺, 99.99% pure Pd, Mn and 99.999% pure Sn from Speex Industries Metuchen, N. J., 99.999% pure Sb single crystal chips, and the enriched ¹¹⁹Sn were used as starting materials. The melts were retained at 1500 °C for 10 min. and 1300 °C for 20 min. at which point they were quenched by passing room-temperature argon gas rapidly through the sample chamber. The ingots so obtained were powdered, sealed in evacuated (<10⁻⁷ Torr) quartz ampules and annealed at 540 °C for varying time periods. X-ray patterns of both the virgin and annealed samples were taken and revealed the L₂₁ phase for these materials.

To investigate the role of thermal history on the induction melted samples, the experimental procedure consisted of systematically recording ME spectra of the Pd₃MnSb₀.₉₉₅Sn₀.₀₁ samples as a function of annealing time. Since the amount of absorber material typically used (400 mg) was rather small to uniformly pack a ¼-in. diameter lucite holder, we used MgO powder as a filler material. For heat treatment purposes the Heusler-alloy sample was physically separated from the MgO powder rather easily by cooling the mixture below 247 °K and extracting the sample by a magnet. For a given heat treatment, spectra were recorded both at 300 and 78 °K using a conventional constant acceleration drive and an exchange gas cryostat. ¹¹⁹Sn⁺⁺ in vanadium was used as a source of the 23.8-keV γ ray for all experiments.

As an alternative method of preparation, samples of Pd₃MnSb₀.₉₉₅Sn₀.₀₁ and PdMnSb₀.₉₉₅Sn₀.₀₀₅ were prepared by sintering appropriate amounts of the desired elements in carefully evacuated (<10⁻⁷ Torr) quartz ampules at 1000 and 800 °C, respectively. The materials were retained at these temperatures for a 72 h period followed by a quench to room temperature and annealing at 540 °C.

Samples of Pd₃MnSb₀.₉₉₅Sn₀.₀₀₅ were prepared by using Pd₃MnSb₀.₉₉₅Sn₀.₀₀₅ samples exhibiting a clear Sn magnetic field of 205 kOe, as the starting material and sintering these samples with appropriate amounts of Mn, Sb, and Sn at 900 °C.

III. RESULTS

A. Annealing results on Pd₃MnSb₀.₉₉₅Sn₀.₀₁

Spectra of Pd₃MnSb₀.₉₉₅Sn₀.₀₁ and Pd₂MnSn taken at 300 °K showed narrow single lines.³ This observation is consistent with the known cubic structure and Curie temperatures of Pd₃MnSb and Pd₂MnSn. On annealing the virgin samples of Pd₃MnSb₀.₉₉₅Sn₀.₀₁, systematic changes in both the room-temperature and liquid-nitrogen temperature spectra were observed. A least-squares fit analysis of the room temperature data to a single line is summarized in Table I. One notes that the isomer shift (IS) and size of the effect systematically increased, while the observed linewidth became somewhat narrower, as a function of annealing time. On an IS plot (see Fig. 1), one observes that the general domain of the measured IS's of the x = 0.01 samples fall in the neighborhood of Pd₂Sn and Pd₃MnSn, and further that these IS's are significantly different from those of α-Sn, β-Sn, or SnO₂. Pd₂MnSn, isomorphic to Pd₂MnSb,

<table>
<thead>
<tr>
<th>Table I. Analysis of room-temperature ¹¹⁹Sn Mössbauer spectra of Pd₃MnSb₁₋ₓSnₓ samples recorded as a function of heat treatment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₃MnSb₁₋ₓSnₓ Sample heat treatment</td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>x = 0.01 annealed 0 h</td>
</tr>
<tr>
<td>x = 0.01 annealed 12 h</td>
</tr>
<tr>
<td>x = 0.01 annealed 24 h</td>
</tr>
<tr>
<td>x = 0.01 annealed 36 h</td>
</tr>
<tr>
<td>x = 0.01 annealed ⁸⁻ h</td>
</tr>
<tr>
<td>x = 0.10 annealed 24 h</td>
</tr>
<tr>
<td>x = 0.50 annealed 24 h</td>
</tr>
<tr>
<td>x = 1.00 annealed 12 h</td>
</tr>
</tbody>
</table>

¹⁾ The IS are quoted relative to ¹¹⁹Sn in vanadium.
²⁾ Sample annealed with MgO powder.
represents a case where Sn replaces Sb in the Pd$_2$MnSb structure (Fig. 2). As we discuss later, we feel that these room-temperature data suggest that Sn is present in solid solution, replacing Sb in the Pd$_2$MnSb host.

At liquid-nitrogen temperatures ($T < T_c$), spectra of the Pd$_2$MnSb$_{10}$Sn$_{0.01}$ samples exhibited magnetic hyperfine splitting as expected. Spectra of the virgin samples showed evidence for two hyperfine field sites, a high-field site of $190 \pm 6$ kOe and an intermediate field of $101 \pm 6$ kOe. In Fig. 3, the smooth line fit to spectrum A represents a least squares analysis of the data to two sets of six lines, taking the $g_e/g_o$ ratio fixed at $0.2134^{12}$ and keeping the centroid, internal field values, and relative populations of the two sites variable. On annealing the virgin samples for a 12-h period, a noticeable change in the spectrum resulted (see spectrum B). The spectrum became more characteristic of a unique magnetic hyperfine interaction with the intensities of the outermost lines becoming larger than those of the innermost ones. The effect of annealing is to cause the population of the high-field site to increase at the expense of the intermediate field one (see Table II). On annealing the sample for a total of 24 h, the linewidth of the magnetic components reduced (see spectrum C of Fig. 3). Presumably, at this particular stage of annealing the internal field of the high-field site becomes more unique, although here it should be indicated that the linewidths of the magnetic components (2.1 mm/sec) are still substantially larger than the linewidths encountered in the paramagnetic phase (0.83 mm/sec).

FIG. 2. Crystal structure of Pd$_2$MnSb (L2$_1$) and PdMnSb (C1$_b$). In the L2$_1$ structure, the open and filled circles represent Pd atoms. In the C1$_b$ structure the filled circles represent Pd atoms while the open circles Pd vacancies.

FIG. 3. $^{119}$Sn Mössbauer spectra of Pd$_2$MnSb$_{10}$Sn$_{0.01}$ samples recorded as a function of heat treatment time $t$ at 540 °C. (A) virgin sample, $t = 0$ h; (B), $t = 12$ h; (C), $t = 24$ h; (D), $t = 36$ h; (E), $t = 48$ h. See text for other details. Table II summarizes internal field results from these spectra which were all recorded at 78 °K.
TABLE II. Internal field results on Pd$_2$MnSb$_{1-x}$Sn$_x$ samples, and Pd$_{1.4}$MnSb$_{0.99}$Sn$_{0.01}$ and PdMnSb$_{0.99}$Sn$_{0.01}$ samples, extracted from spectra shown in Figs. 3 and 6, respectively. The subscripts $h$, $i$, and $l$ refer to high-, intermediate-, and low-field sites.

<table>
<thead>
<tr>
<th>Sample heating treatment</th>
<th>Internal field</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_k$, $I_k$, $I_l$</td>
<td></td>
</tr>
<tr>
<td>$x = 0.01$ annealed 0 h</td>
<td>A 106(6) 101(6) 44 54 46 0</td>
<td></td>
</tr>
<tr>
<td>$x = 0.01$ annealed 12 h</td>
<td>B 205(6) 104(6) 77 23 0 0</td>
<td></td>
</tr>
<tr>
<td>$x = 0.01$ annealed 24 h</td>
<td>C 206(6) 206(6) 77 23 0 0</td>
<td></td>
</tr>
<tr>
<td>$x = 0.01$ annealed 36 h</td>
<td>D 205(6) 205(6) 77 23 0 0</td>
<td></td>
</tr>
<tr>
<td>$x = 0.01$ annealed 84 h</td>
<td>E 205(6) 205(6) 77 23 0 0</td>
<td></td>
</tr>
</tbody>
</table>

Pd$_{1.4}$MnSb$_{0.99}$Sn$_{0.01}$
Annealed 48 h
Fig. 6 208(4) 98(8) 33 93 7 100

PdMnSb$_{0.99}$Sn$_{0.01}$
Annealed 12 h
Fig. 6 103(10) 33 100

*Sample annealed with MgO powder.

Annealing the samples further for an additional 12 h, introduced a new feature in the spectrum, the appearance of a seventh line in the vicinity of zero velocity (see spectrum D of Fig. 3). The following comments are in order on this additional line, hence labeled as the third site. Its IS is +0.59(10) mm/sec, which agrees with neither metallic Sn ($\alpha$ or $\beta$), nor Pd$_2$MnSn (see Fig. 1), and further its linewidth is 2.1 mm/sec. We believe that the third site in spectrum D is not intrinsic to the annealing process of the HA but instead is a result of annealing the sample after stage C in a vacuum which was probably worse than $10^{-7}$ Torr. The third site can be totally avoided by sealing the samples in a vacuum better than $10^{-5}$ Torr before annealing. The finalized piece of experimental information is contained in spectrum E which represents the spectrum of a sample annealed beyond stage D differently. In going from stage D to E, we did not physically separate the HA sample from the MgO filler material and proceeded to seal the mixture in an evacuated quartz ampule. On annealing the sample thus at 540 °C for 48 h a rather dramatic change in the ME spectrum was observed. The high-field site converted totally to the third site.

As we discuss further, we believe that the third site observed in spectra D and E results from oxygen contamination of the Pd$_{1.4}$MnSb$_{0.99}$Sn$_{0.01}$ samples. This result was checked independently by observing an enhancement of the third site at the expense of the high-field one on annealing a sample exhibiting a clear magnetic splitting (such as in spectrum C of Fig. 3) in a vacuum of worse than $10^{-5}$ Torr. Our attempts to decontaminate samples exhibiting the third site by heating to 600 °C while pumping on these with a trapped diffusion pump were unsuccessful. This leads us to believe that the third site is formed irreversibly.

Spectra of Pd$_2$MnSb$_{0.99}$Sn$_{0.01}$ samples prepared by sintering the materials in a quartz tubing at 1000 °C followed by a quench to room temperature were similar to spectrum A in Fig. 3. On annealing these samples for a 24-h period at 600 °C, a clear magnetic hyperfine structure characteristic of the high-field site (spectrum C in Fig. 3) was observed.

B. $^{119}$Sn fields in Pd$_2$MnSb$_{1-x}$Sn$_x$

The magnitude and sign of the Sn field in Pd$_2$MnSn was measured by Geldart et al.\textsuperscript{19} to be $-35 \pm 2$ kOe. The magnitude and sign of the field at a dilute Sn impurity in Pd$_2$MnSb has been established by our previous work\textsuperscript{4} to be $+210 \pm 5$ kOe. In the present work we have attempted to establish the compositional behavior of the Sn field between these two extremum ($x \approx 0$, and 1) compositions. Spectra of induction melted Pd$_2$MnSb$_{1-x}$Sn$_x$ samples taken at a few compositions are reproduced in Fig. 4. These spectra are indicative of a reasonably well-defined magnetic interaction and were fit to a six-line magnetic spectrum. In Table III, a summary of the Sn fields extracted from these spectra are presented. Price et al.\textsuperscript{5} have also investigated this Heusler alloy system and the present results on the $^{119}$Sn field systematics are in general agreement with their results. A point of some difference between the present data and the data of Price et al.\textsuperscript{5} can be traced to the spectrum at the composition $x = 0.10$. A spectrum of a sample taken at this composition (Fig. 4) in the present work exhibited a fairly well-defined Sn field. This spectrum does not
exhibit the nonhomogeneous field distribution seen by Price et al. and leads us to believe that the sample used in the present work by virtue of its preparation, could conceivably have been more homogeneous.

In Fig. 5 we have summarized the $^{119}\text{Sn}$ field systematics in Pd$_3$MnSb$_{1-x}$Sn$_x$ from the present work and the work of Price et al. Two interesting features of these field systematics are to be noted. First, there is a sharp drop in the Sn fields in the composition range $0.01 \leq x \leq 0.10$. And second, one observes a fairly continuous change in the fields from +205 kOe to -35 kOe between the two extreme compositions. We believe that $^{119}\text{Sn}$ magnetic interactions in these Heusler alloys in the composition range $0 < x < 0.10$ are unusually sensitive to local fluctuations in Sn concentrations in the samples because of a very strong dependence of the $^{119}\text{Sn}$ field on the Sn concentration in this range. The latter physical effect as we discuss further in Sec. IV B, is probably due to a band-structure effect. No attempts were made to clarify the role of sample preparation on the resulting field distribution that were observed at $x = 0.02$. This represents an area that merits careful future investigations. Mössbauer spectra of Pd$_3$MnSb$_{1-x}$Sn$_x$ samples taken in the paramagnetic phase exhibited narrow single lines having IS ranging from +0.10(2) to 0.14(1) mm/sec over the entire composition range $0 < x < 1$.

**TABLE III** Analysis of Mössbauer spectra of Pd$_3$MnSb$_{1-x}$Sn$_x$ samples recorded at 78 K (see Fig. 4). The sign of fields at $x = 0.10$ and 0.50 are assigned based on systematics shown in Fig. 5.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Gamma$(mm/sec)</th>
<th>IS (mm/sec)</th>
<th>$H$ (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0075</td>
<td>2.78(20)</td>
<td>+0.17(9)</td>
<td>+208(6)</td>
</tr>
<tr>
<td>0.01</td>
<td>2.23(5)</td>
<td>+0.18(9)</td>
<td>+205(5)</td>
</tr>
<tr>
<td>0.10</td>
<td>3.79(26)</td>
<td>+0.27(8)</td>
<td>+68(7)</td>
</tr>
<tr>
<td>0.50</td>
<td>2.18(8)</td>
<td>+0.13(4)</td>
<td>-14(6)</td>
</tr>
<tr>
<td>1.00</td>
<td>2.80(20)</td>
<td>+0.15(2)</td>
<td>-39(4)</td>
</tr>
</tbody>
</table>
FIG. 6. $^{119}$Sn Mössbauer spectra of indicated samples recorded at 78 °K.

and are thus suggestive of a broad field distribution. The IS of the magnetic component was found to be $+0.04 \pm 0.06$ mm/sec and this shift much like the IS in Pd$_2$MnSb is indicative of a Sn site located at the Sb site. The single line in these spectra is characterized by the following parameters: IS of $+0.74 \pm 0.03$ mm/sec and $\Gamma = 0.92 \pm 0.03$ mm/sec. This IS rules out the possibility that it represents $\alpha$- or $\beta$-Sn.

Some additional confidence in the above quoted value for the Sn field in PdMnSb follows from the spectrum of $z = \frac{1}{2}$ sample in Fig. 6. The spectrum was fit to two Sn field sites keeping the high field site fixed at 208 kOe. The low-field site, which is predominant in this spectrum, gave a field value of $98 \pm 8$ kOe. The linewidth of the magnetic components was found to be 3.8 mm/sec. An interpretation of this data is given in Sec. IV B.

IV. DISCUSSION

A. Heat treatment effects

The present work illustrates the diverse and important metallurgical effects of Sn in the Heusler alloy system Pd$_{1-x}$MnSb$_{0.96}$Sn$_{0.04}$ that have been studied somewhat uniquely with the use of $^{119}$Sn Mössbauer spectroscopy. Perhaps the most striking experimental results bear on the annealing effects observed on Pd$_{2.8}$MnSb$_{0.96}$Sn$_{0.04}$ samples. Melts of Pd$_{2.8}$MnSb$_{0.96}$Sn$_{0.04}$, when quenched to room temperature yield a defective structure. Existence of structural disorder in Pd$_3$MnSb host was documented by Webster$^{14}$ in some of the earliest structure work on this material. We believe that by cooling the indicated melt, one quenches a large number of Pd vacancies in the $L_2_1$ structure. Sn sites having eight Pd near neighbors experience the high-field value of 210 kOe while those Sn sites having an average four Pd near neighbors experience the intermediate field. This interpretation is suggested by the identity of the intermediate field value of 101 kOe with the Sn field in PdMnSb. Annealing Pd$_{2.8}$MnSb$_{0.96}$Sn$_{0.01}$ samples at 540 °C for 24 h promotes structural order which was in fact observed directly for the host material in x-ray diffraction patterns as a narrowing of the x-ray lines. On annealing the samples, Pd vacancies become thermally activated and annihilate with Pd interstitials. Consequently one observes in the spectra an enhancement of the high-field site at the expense of the intermediate field one. Closely similar annealing effects have been observed on the Pd$_3$MnSb host materials by Langouche et al.$^{1,15}$ in $^{119}$Sn Mössbauer spectroscopy. In these experiments, samples obtained by cooling Pd$_3$MnSb melts exhibited two hyperfine fields, a high-field Sb site characteristic of Pd$_3$MnSb and a low field one characteristic of PdMnSb. On annealing these samples the low-field site disappeared, and only the high-field site remained.$^4$

Room temperature ME parameters on Pd$_{2.8}$MnSb$_{0.96}$Sn$_{0.01}$ samples obtained as a function of annealing time at 540 °C exhibit a systematic correlation with the internal field data obtained at 78 °K. Going back to the results described in Sec. IIIA, perhaps the most significant correlation emerges in going from the virgin samples to a sample annealed for 12 h (spectrum B to spectrum A of Fig. 3). We believe that the single-resonance line observed in the room-temperature spectra of virgin samples is really a composite of two single lines of nearly equal intensity and having slightly different IS’s ($<0.02$ mm/sec). The single line having the more positive IS of the two lines is ascribed to Sn associated with the high-field site. The consequent reduction in observed linewidths, increase in percent absorption and more positive IS’s on annealing that are documented in Table I can then be understood as resulting due to an increase in population of the high-field site at the expense of the intermediate field site.

We believe that appearance of the broad single line near zero velocity in spectra D and E of Fig. 3 results from oxygen contamination of the Pd$_{2.8}$MnSb$_{0.96}$Sn$_{0.01}$ samples on progressive annealing and that this feature is not intrinsic to Pd$_3$MnSb. We suggest that Sn acts as an effective trap of oxygen in a Pd$_3$MnSb host. Since our attempts to decontaminate such samples by heating to 600 °C in a hard vacuum were unsuccessful, we are lead to believe that the Sn defect site is formed.
irreversibly and is a stable entity. The only significant change observed in the spectra, following the above heat treatment to decontaminate the samples, was to narrow the linewidth of the single line from 2.1 to 1.2 mm/sec and this result then leads us to conclude that the low-field site is really a zero-field site. One can speculate on the possible structure of this “defect site” based on its IS of 0.59(10) mm/sec. This IS is larger than the IS of a Sn site substituting Sb in Pd₄MnSB and, further, it lies in the domain of the Sn IS in its divalent state as in SnO (isomer shift 5 = +1.03 mm/sec). Such a result could be due to the presence of oxygen in the first coordination sphere causing localization of some of the 5s and 5p—like charge density on Sn relative to the substitutional high-field Sn site.

B. Compositional effects

¹¹⁰Sn field measurements on the Pd₄MnSBₓ⁺ₓSnₓ system reported in the present work are in general agreement with the earlier results of Price et al.⁵ On combining the present data with those in Ref. 5, one can clearly observe a smooth compositional variation of the ¹¹⁰Sn field from +210 kOe at x = 0.10 to -35 kOe at x = 1.00 as shown in Fig. 5. From the room-temperature data, the measured IS’s for this system are situated in a narrow range containing the IS’s of Pd₄MnSn and 24-h annealed Pd₄MnSb₀.⁶8Sn₀.₃₂ both of which represent a case in which Sn has eight Pd near neighbors. This trend coupled with the smooth compositional dependence of the IS field in Pd₄MnSBₓ⁺ₓSnₓ system, reflects in our view, the random substitution of Sn and Sb at the Y site in this Heusler alloy (X₂MnY) system. These observations are consistent with what is already known about the magnetic properties and crystal structure of the end-point members. Pd₄MnSb and Pd₄MnSn are known to be ferromagnetic with Curie points²⁹ of 247 and 189 °K, and further both Heusler alloys crystallize in the cubic L₂₁ structure with lattice parameters²⁹ of 6.424 and 6.380 Å, respectively. Recently Webster and Ramadan²³ have reported observing a smooth compositional dependence of Tc and α₀ in this system. In contrasting the compositional variation of Hₘ with that of Tc, one is struck by the similarity in behaviour and in particular by the sharp compositional dependence that occurs in the composition range 0 < x < 0.10 for both physical parameters.

The systematics of ¹¹⁰Sn field in Pd₄MnSBₓ⁺ₓSnₓ summarized in Fig. 5 can be broadly divided into two parts: (a) a sharply varying component in the range 0 < x ≤ 0.10; and (b) a slowly varying component in the range 0.10 < x < 1.0. The reduction in Sn fields observed on replacing the pentavalent Sb by the tetravalent Sn in Pd₄MnSBₓ⁺ₓ can be understood in terms of the Jena-Geldart¹⁰ or Blandin-Campbell¹⁰ model, as arising due to a decrease in the induced spin polarization because of a smaller conduction-electron density (nₑ).

We believe that feature (b) of the ¹¹⁰Sn field systematics is a manifestation of such an effect and can be qualitatively understood.

In Fig. 5, we project the field systematics as a function of Sn concentration x, based on the Jena-Geldart model. The lack of agreement between theory and experiment in the composition range 0.01 < x < 0.10 is particularly significant in this case. In contrast one may indicate that a similar comparison between theory and experiment for the Cu₃MnInₓ⁺ₓSnₓ system¹⁵ works reasonably well over the whole composition range 0 < x < 1 (see Fig. 7). The lack of a sharp field dependence on the Sn concentration observed in the Cu₃MnInₓ⁺ₓSnₓ system¹⁵ may be suggestive of the fact that feature (a) of the present systematics is peculiar to the presence of Pd in the present Heusler alloy system.

C. ¹¹⁹Sn magnetic field in PdMnSB

The broad linewidths of the magnetic components for the ¹¹⁰Sn interaction in PdMnSB₀.⁶₈Sn₀.₃₂ suggest a homogeneously broadened magnetic interaction. Such a result could arise in our view, due to some degree of structural disorder around Sn in the defect structure (C1₅) of PdMnSB host. To our knowledge, PdMnSn isomorphic to PdMnSB is not known to exist, and this could point towards the difficulty of substituting the Sb site in
PdMnSb by a Sn atom. On addition of Pd to Pd_{1-x} MnSb_{x}, two significant effects occur; the solubility of Sn in the Heusler alloy phase increases (see spectrum of z = 1/2 sample in Fig. 6) as the narrow single line around zero velocity in a z = 0 sample associated with a Sn-rich phase totally disappears. The noticeable reduction in observed linewidths of the magnetic components from 5 to 3.8 mm/sec in going from z = 0 to z = 1/2 further suggests that the Sn-doped PdMnSb phase seems to stabilize in the presence of excess Pd. Conceivably, such a result could be due to an increase in lattice size on addition of Pd, making it more feasible for the larger sized Sn to replace Sb.

These hyperfine field data at a dilute Sn impurity in Pd_{1-x} MnSb for the three compositions z = 0, 1/2, 1 examined in the present work, follow a trend which is closely similar to the one reported earlier for the 121\text{b} field systematics in the Pd_{1-x} MnSb host. In the work of Price et al., 121\text{b} spectra of Pd_{1-x} MnSb samples were analyzed in terms of hyperfine field probability distributions. The results generally showed a two-peak distribution. One of the peaks was centered around 650 kOe and the other at about 300 kOe over the whole composition range 0 < z < 1. This result was also obtained by Swartzendruber et al. and shows that for a mixed composition such as z = 1/2 for, e.g., Sb nuclei do not experience a unique field but instead choose two types of fields, a high field almost characteristic of Sb sites in Pd_{2}MnSb type of surroundings, and a low-field site nearly characteristic of Sb sites in Pd_{x}MnSb type of surroundings. It is therefore anticipated by analogy, that the low field observed in the present Sn experiments on Pd_{1-x} MnSb_{s,0.99}Sb_{0.01} samples represents the field in PdMnSb. Finally, the substantially smaller solubility of Sn in PdMnSb host compared to Pd_{x}MnSb host, is much like the case of the Te impurity which we have recently examined in \text{128}Te and \text{129}I ME experiments.\text{17}

![FIG. 8. Hyperfine field observed (open and filled circles) at 5sp elements in Pd_{x}MnSb and PdMnSb hosts as a function of impurity valence \text{Z}_{p}. The thin continuous and dashed lines are estimates of these fields based on the Jena-Geldart model.](image)

These results are most likely the consequence of a smaller unit cell dimensions of the PdMnSb host.

D. Interpretation of 119Sn fields in Pd_{x} MnSb and PdMnSb

The 119Sn field in Pd_{x} MnSb and PdMnSb forms part of a general trend of fields that have been observed at other 5sp impurities when these substitute the Sb site in this Heusler alloy. Figure 8 summarizes these field systematics as a function of atomic valence of the sp impurity. The experimental results of the fields in PdMnSb are taken from the work of a number of investigators, and these are summarized in Table IV.

The 131Sn field of 329 ± 5 kOe in PdMnSb is based on the spectrum shown in Fig. 9. In the fitting routine, the magnetic moment ratio \( \mu_{f} / \mu_{i} \) was taken to be 0.748(20) from the work of Langouche et al.\text{4} and the use of this new moment ratio probably accounts for the difference between the field quoted above and a somewhat lower field of 302 ± 5 kOe reported earlier by Swartzendruber et al.\text{2} The positive sign of the field derives from the work of Price et al.\text{5} who have observed a

<table>
<thead>
<tr>
<th>Element</th>
<th>5s p value</th>
<th>H (kOe) Experiment</th>
<th>H (kOe) Theoretical</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>255 ± 10</td>
<td>90 ± 4</td>
<td>-273</td>
<td>Walus et al., Ref. 18</td>
</tr>
<tr>
<td>In</td>
<td>103 ± 10</td>
<td>78</td>
<td>+126</td>
<td>Present work</td>
</tr>
<tr>
<td>Sn</td>
<td>329 ± 5</td>
<td>78</td>
<td>+330</td>
<td>Swartzendruber et al., Ref. 2</td>
</tr>
<tr>
<td>Te</td>
<td>572 ± 10</td>
<td>4.2</td>
<td>+467</td>
<td>Boolchand et al., Ref. 7</td>
</tr>
<tr>
<td>I</td>
<td>681 ± 6</td>
<td>4.2</td>
<td>+494</td>
<td>Boolchand, et al., Ref. 17</td>
</tr>
<tr>
<td>Xe</td>
<td></td>
<td></td>
<td>+294</td>
<td></td>
</tr>
</tbody>
</table>
net increase in the Sb field on application of an external field to PdMnSb.

Price et al. have, in a recent review, compared various theoretical models that have been proposed to explain hyperfine fields in Heusler alloys and the reader is referred to their paper. Two models that appear to qualitatively reproduce the observed field systematics shown in Fig. 8 are due to Jena-Geldart, and the other is due to Blandin-Campbell. In what follows, we compare the experimental field results with the theoretical calculations of these fields based on the Jena-Geldart model. The results of these calculations for various 5p impurities are summarized in Table IV. The Jena-Geldart model is an adaptation of the Daniel-Friedel model for the case of Heusler alloys. In this model one calculates the internal field $H_{int}$ by obtaining the spin polarization $P(0)$ induced at the nonmagnetic sp impurity due to the spin-polarized conduction electrons taking into account the charge screening of the impurity. The model assumes the conduction band to be “free-electron” like and includes effects of coherent scattering, exchange and hybridization through a parameter $\alpha^2$, Bloch wave enhancement factors, that is determined from first principles for each impurity.

$$H_{int} = -\frac{1}{3} \gamma \mu_B \alpha^2 P(0).$$

The existing calculations are normalized for the Sb field in PdMnSb. The excellent agreement in the magnitude of the field for the case of Sn between experiment ($103 \pm 10$ kOe) and theory (111 kOe) is actually also reflected generally for other 5p impurities where measurements are available (see Table IV). In cases where the sign of the fields have been explicitly measured, such as for Sb and Te, these calculations indeed give the correct sign. The above comparison shows that the Jena-Geldart model works rather well for the PdMnSb host.

The substantial enhancement in the Sn, Sb, and Te fields observed in going from PdMnSb host to Pd$_x$MnSb host are results that cannot be understood based on the Jena-Geldart model. Further the difficulty in understanding the compositional behaviour of Sn fields in the Pd$_x$MnSb$_{1-x}$Sn$_x$ system (Sec. IV B) based on this model, are indications of the limitations of this rigid-band approach. It appears that these internal field data on a Pd-rich Heusler alloy may be exhibiting band-structure effects arising due to the presence of a sharp d density of states of Pd at the Fermi level. A large enhancement in the density of states at the Fermi level probably occurs as one adds Pd to PdMnSb causing a significant effect on the internal field values. Elaborate band-structure calculations on Pd$_x$MnSb are now clearly needed to clarify the situation.

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119 Sn MOÖSSBAUER-EFFECT STUDIES IN HEUSLER ALLOYS...

12The value of $g_e/g_b = -0.2134$ is taken from an average of number of measurements summarized by N. N. Greenwood and T. C. Gibbs, in Mössbauer Spectroscopy (Chapman and Hall, London, 1971), p. 380.
15G. Langouche (private communication of unpublished results).