Title
Superconductivity and magnetism in the Heusler alloys Pb (M=rare earth, Th, and U)

Permalink
https://escholarship.org/uc/item/1m83z4ct

Journal
Physical Review B - Condensed Matter and Materials Physics, 53(5)

ISSN
1098-0121

Authors
Seaman, C
Dilley, N
de Andrade, M
et al.

Publication Date
1996

DOI
10.1103/PhysRevB.53.2651

License
CC BY 4.0

Peer reviewed
Superconductivity and magnetism in the Heusler alloys MPd$_2$Pb ($M$=rare earth, Th, and U)

C. L. Seaman, N. R. Dilley, M. C. de Andrade, J. Herrmann, M. B. Maple, and Z. Fisk
Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093
(Received 27 September 1995)

We report on an investigation of superconductivity and magnetism in the series of compounds MPd$_2$Pb ($M$=rare earth, Th, U) through measurements of electrical resistivity, magnetic susceptibility, specific heat, and lattice parameters. Both single crystals and polycrystalline samples were studied. The compound UPd$_2$Pb was examined for possible heavy-fermion behavior, and found to exhibit antiferromagnetic order below $T=35$ K.

INTRODUCTION

Several Heusler alloys (cubic $L2_1$ structure) with the general chemical formula $RT_2X$ have been found to exhibit superconductivity, including YPd$_2$X ($X=$Sn, Pb, In, and Sb), YAu$_2$Sn, and RPd$_2$Sn ($R=$Sc, Y, Tm, Yb, and Lu), with critical temperatures as high as 4.76 K. Moreover, superconductivity and antiferromagnetism coexist in the compound YbPd$_2$Sn. Higher $T_c$ values among rare earth, Th, and U have been found to exhibit superconductivity, including YPd$_2$X, with critical temperatures as high as 4.76 K. For RPd$_2$Pb samples, we also expected the effects of magnetic pair breaking by the magnetic $R$ ions to be minimized because of the large lattice parameters, which could give rise to interesting effects due to the interaction and competition between superconductivity and magnetism. We report on an investigation of superconductivity and magnetism in the series of compounds MPd$_2$Pb ($M$=rare earth $R$, Th, and U), primarily through measurements of electrical resistivity and magnetic susceptibility. Both polycrystalline samples and single crystals were studied. We find that the magnetic rare-earth ions order antiferromagnetically at low temperatures with the lowest Néel temperature $T_N$ values among RPd$_2$X compounds. Bulk superconductivity is found for $R=$Sc, Y, Tm, Yb, and Lu, but with lower $T_c$ values than expected, probably associated with sample quality. Motivated by heavy-fermion behavior previously observed in UPd$_2$Sn, the compound UPd$_2$Pb was examined for possible heavy-fermion behavior, and found to exhibit antiferromagnetic order below $T=35$ K, inferred from a sharp cusp observed in the magnetic susceptibility. The large value of the linear coefficient of the specific heat $\gamma\approx 100$ meV/K$^2$, determined from data measured below 35 K, along with the temperature dependence of the electrical resistivity, suggest that this may be an antiferromagnetic low effective mass heavy-fermion compound.

EXPERIMENTAL DETAILS

Single crystals and polycrystalline samples of MPd$_2$Pb were fabricated by flux growth and by melting in sealed Ta tubes, respectively. Powder x-ray-diffraction measurements were subsequently made using a Rigaku rotating-anode diffractometer utilizing Cu $K\alpha$ radiation. Electrical-resistivity measurements were made on the polycrystalline samples from 1 to 300 K in a $^4$He cryostat using a self-balancing, four-wire ac resistance bridge operating at 16 Hz, with typical excitation current densities of $\sim 100$ $\mu$A/cm$^2$. Platinum electrical leads (50 $\mu$m diameter) were attached with silver epoxy. Static magnetic-susceptibility measurements were performed on single crystals using a Quantum Design superconducting quantum interference device (SQUID) magnetometer from 1.8 to 300 K in magnetic fields up to 7 T. Low-temperature ($0.2\leq T\leq 6$ K) ac magnetic-susceptibility measurements were performed in a $^3$He/$^4$He dilution refrigerator. Specific-heat measurements were made on a polycrystalline sample of UPd$_2$Pb from 0.5 to 20 K using a semiadiabatic heat-pulse calorimeter utilizing a $^3$He cryostat.

SAMPLE PREPARATION

Single crystals of MPd$_2$Pb were successfully grown in Pb flux for $M=$Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, and Lu. Attempts to grow crystals with $M=$Yb and U were unsuccessful, even though polycrystalline samples could be prepared by arc melting. In addition, attempts to grow crystals consisting of the lighter rare-earth ions $M=$Ce, Pr, Nd, Sm, and Eu were unsuccessful, consistent with our inability to make polycrystalline samples, most likely due to the large size of the trivalent ions. The crystals were prepared in the following way.

Stoichiometric amounts of 99.9% pure $M$ and 99.99% pure Pd were placed in an alumina crucible with 99.999% pure Pb, which comprised 90 mol % of the mixture. Quartz wool was then placed inside the crucible, which was then sealed in a quartz tube and backfilled with 150 torr ultrahigh-purity (UHP) Ar. The sample was heated to 1200 °C, then slowly cooled (10 °C/h), allowing single crystals to nucleate. In our case, Pb from the flux was incorporated into the crystal structure. The sample was removed from the furnace at 800 °C and centrifuged immediately so that the molten flux spun through the quartz wool, leaving the crystals in the crucible. To etch away any remaining free Pb, the crystals were placed in a 1:1 solution of $H_2O_2$ (30%): glacial acetic acid for no more than 5 min. The crystals formed as cubes or clusters of cubes which appeared to grow in the (111) direction. Of these, crystals with $M=$Gd and Sc formed the largest-(~1 mm on a side) and smallest-sized cubes, respectively.

Subsequent x-ray powder diffraction of powdered crystals verified the single-phase $L2_1$ cubic Heusler structure for $R=$Lu, Tm, Er, Ho, Dy, Tb, Gd, Y, and Sc. No impurity

0163-1829/96/53(5)/2651(7)/$06.00$ 53

PHYSICAL REVIEW B 1 FEBRUARY 1996-IVOLUME 53, NUMBER 5

© 1996 The American Physical Society
peaks, including those of free Pb, were evident in the x-ray patterns. The intensity of the background noise level was only ~0.1% of the most intense peak corresponding to the (220) direction. The flux growths with Gd and Eu contained long, needle-shaped crystals (~5 mm length), but they exhibited multiple x-ray peaks which did not belong to the Heusler structure. The Gd flux growths also contained the cube-shaped crystals with the Heusler structure. ThPd$_2$Pb formed, though it contained several impurity phases, one of which was identified as ThPb. Attempts to grow single crystals of $R =$ Yb, Eu, Sm, Nd, Pr, Ce, and U were unsuccessful.

Polycrystalline samples were fabricated by melting in Ta tubes as follows. Stoichiometric amounts of each element were sealed in a 1-cm-diameter Ta tube, with 1 atm UHP Ar. The tube was then sealed in a quartz tube backfilled to 150 torr UHP Ar, heated to 1300 °C for 1 h, and subsequently quenched by placing the 1300 °C tube in water at room temperature. Samples with the Heusler structure were made for $R =$ Sc, Y, Tb, Dy, Ho, Tb, Yb, and U. X-ray powder-diffraction data revealed trace amounts of elemental Pb (a superconductor with $T_c =$ 7.2 K) in all samples, Pb$_2$Pd (a superconductor with $T_c =$ 3.0 K) for $R =$ Y, Dy, Ho, and Tb, and RPD$_2$ (not superconducting) for $R =$ Yb. This method was not successful for $R =$ Ce, Eu, Gd, Lu, or Th, although a minority Heusler phase was still discernible for Lu. The $R =$ Er sample was made by arc melting with excess Pb to compensate for loss due to its high vapor pressure. None of the samples were subsequently annealed.

It is interesting to note that the related compounds RPD$_2$Sn, with $R =$ Tb and Dy, exhibit structural transformations at ~250 and 50 K, respectively, which lowers the crystal symmetries. The transformations were not evident from magnetic susceptibility, and we cannot rule out similar transformations occurring in our RPD$_2$Pb samples.

RESULTS AND DISCUSSION

RPd$_2$Pb ($R =$ rare earth: Sc, Y, Gd, Tb, Dy, Ho, Tb, Yb, Lu)

Electrical resistivity

Shown in Fig. 1 is the temperature dependence of the normal-state electrical resistivity $\rho(T)$, normalized to its room-temperature value, of RPD$_2$Pb compounds in which the 4$f$ electron shell of the $R$ ion is (a) empty or filled and (b) partially filled. Except for $R =$ Gd, for which a single crystal was used, polycrystalline samples were measured because of the difficulty of attaching electrical leads to the extremely small crystals. All samples exhibit metallic behavior with positive temperature coefficient of resistance at all temperatures below 295 K. The data display downward curvature except at the lowest temperatures where phonon scattering freezes out and the data eventually saturate towards the zero-temperature value due to scattering by defects and impurities. Although the degree of curvature varies among the RPD$_2$Pb samples, it does not appear to depend in a systematic way on the $R$ ion. In particular, temperature-dependent magnetic scattering due to splitting of the ground-state multiplet by the crystalline electric field (CEF) is not obvious. The resistance ratio $R/R_e$($T$) also varies a lot among samples, attesting to varying amounts of impurity scattering.

FIG. 1. Normal-state electrical resistivity normalized to its room-temperature value, $\rho(T)/\rho(295 \text{ K})$, vs temperature $T$ for RPD$_2$Pb polycrystalline samples in which the 4$f$ electron shell of the $R$ ion is (a) empty or filled and (b) partially filled. Data for $R =$ Gd are for a single crystal. Resistivity drops at $T =$ 7 K are due to Pb inclusions.

Qualitatively speaking, those samples with the largest-moment $R$ ions, namely, $R =$ Gd, Ho, and Dy, exhibit the smallest RR’s.

All of the polycrystalline samples have elemental Pb impurities, which causes $\rho(T)$ to drop below $T =$ 7 K owing to the superconductivity of Pb. For those samples in which $\rho(T)$ does not drop to zero by then, an additional drop is observed below $T =$ 3 K due to the presence of a Pb$_2$Pd impurity phase, which is superconducting with $T_c =$ 3.0 K. No such resistive drops are observed for the relatively impurity-free single-crystal specimen of GdPd$_2$Pb, allowing a small anomaly in $\rho(T)$, shown in the inset of Fig. 1(b), to be observed near $T =$ 4.5 K. This anomaly is due to antiferromagnetic ordering of the Gd moments, as inferred from the magnetic susceptibility discussed below.

Magnetic susceptibility

Shown in Fig. 2 is the inverse magnetic susceptibility $\chi^{-1}$ as a function of temperature $T$ for the RPD$_2$Pb compounds with magnetic rare-earth ions $R$. The $\chi(T)$ data were acquired for many clusters of single crystals with random orientations with respect to the magnetic-field direction, except for $R =$ Er for which a polycrystalline sample was measured. Over a wide temperature range (10 K $<$ $T$ $<$ 300 K), the data for all of these samples are well described by the Curie-Weiss law $\chi(T) = N\mu_g^2/3k_B(T - \theta_{cw})$, where $N$ is the number of rare-earth ions, $\mu_e$ is the effective magnetic moment, and $\theta_{cw}$ is the Curie-Weiss temperature. The solid lines in Fig. 2 represent least-squares linear fits of the data, which yield
values for \( \mu_{\text{eff}} \) and \( \theta_{\text{CW}} \) listed in Table I. The values of \( \mu_{\text{eff}} \) are close to the theoretical Hund’s rules ground-state values for free trivalent rare-earth ions as illustrated in Fig. 3 and do not deviate much from the Curie-Weiss fits above the antiferromagnetic ordering temperatures, suggesting that the CEF energy level splittings \( \Delta_{\text{CEF}} \) of the Hund’s rules ground-state multiplets are small (\( \Delta_{\text{CEF}} < 10 \text{ K} \approx 1 \text{ meV} \) in these compounds.

The Curie-Weiss temperatures \( \theta_{\text{CW}} \) are all negative, indicative of antiferromagnetic (AFM) exchange interactions. These interactions give rise to AFM order at low temperatures, revealed as a peak in the magnetic susceptibility for some of these samples at the Néel temperature \( T_{N} \), as shown in Fig. 4 and listed in Table I. Data for \( R = \text{Gd, Tb, and Dy} \) represent \( \chi_{\text{dc}} \) from static (dc) magnetization measurements taken in a field of 10 Oe (100 Oe for \( R = \text{Gd} \)) after zero-field cooling (ZFC) and during field cooling (FC). Data for \( R = \text{Ho and Er} \) are from low-temperature ac magnetic-susceptibility \( \chi_{\text{ac}} \) measurements.

Two interesting aspects of the magnetic-susceptibility data are (1) there is only a small decrease in \( \chi(T) \) below \( T_{N} \) as \( T \rightarrow 0 \) [the ratio \( \chi(0)/\chi(T_{N}) \) is much larger than the theoretical value of 2/3 for an isotropic, uniaxial AFM powder specimen] and (2) irreversibility in \( \chi_{\text{dc}} \) appears below an onset temperature \( T_{\text{irr}} \), reminiscent of spin-glass freezing. The large \( \chi(0)/\chi(T_{N}) \) ratio is characteristic of spin glasses, but can also occur for an antiferromagnetically ordered fcc lattice due to low anisotropy energy. In the latter case, the measured susceptibility below \( T_{N} \) approaches \( \chi_{0} \) (in which the antiparallel moments are perpendicular to the applied magnetic field \( H \)), which is more energetically favorable than \( \chi_{\text{dc}} \) (moments parallel to \( H \)). Paramagnetic impurities could also increase the measured value of \( \chi(0)/\chi(T_{N}) \). The irreversible \( \chi_{\text{dc}}(T) \) for GdPd\(_{2}\)Pb was measured with \( H = 1, 10, 100 \), and 200 Oe, with little change in \( \chi(T) \) or \( T_{N} \). This observation, as well as the observed scaling of \( T_{N} \) with the de Gennes factor (described below), and the electrical-resistivity results (described above) eliminate the possibility that these anomalies are due to superconductivity. The irreversibility in the magnetization might be due to structural disorder (defects) in the samples, which could give rise to

![Image of Fig. 2](image2.png)

**Fig. 2.** Inverse magnetic susceptibility \( \chi^{-1} \) vs temperature \( T \) for RPD\(_{2}\)Pb single crystals, where \( R \) has a partially filled \( 4f \) electron shell. The measurements were made in a field of 1 T for \( 1.8 \leq T \leq 300 \text{ K} \).

![Image of Fig. 3](image3.png)

**Fig. 3.** Effective magnetic moments \( \mu_{\text{eff}} \) of the rare-earth ions \( R \) in RPD\(_{2}\)Pb (solid circles), derived from Curie-Weiss fits to the magnetic susceptibility, compared to the theoretical free-ion values (open circles).

![Image of Fig. 4](image4.png)

**Fig. 4.** Low-temperature magnetic susceptibility \( \chi \) vs temperature \( T \) of RPD\(_{2}\)Pb single crystals, revealing antiferromagnetic order below the Néel temperature \( T_{N} \), determined from the cusp in the data. The data for \( R = \text{Gd, Tb, and Dy} \) are from dc measurements taken in fields of 100, 10, and 1 Oe, respectively, upon zero-field cooling (ZFC) and field cooling (FC). The data for \( R = \text{Ho and Er} \) are from ac susceptibility measurements as described in the text.

**Table I.** Physical parameters for MPd\(_{2}\)Pb. A dash indicates that the entry is not applicable to nonmagnetic \( M \) ions. * indicates not detected above 0.1 K.

<table>
<thead>
<tr>
<th>( M )</th>
<th>( a ) (Å)</th>
<th>( \mu_{\text{eff}} ) (( \mu_{B} ))</th>
<th>( \theta_{\text{CW}} ) (K)</th>
<th>( T_{c} ) (K)(^a)</th>
<th>( T_{N} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>6.63</td>
<td>0</td>
<td>–</td>
<td>2.4</td>
<td>–</td>
</tr>
<tr>
<td>Y</td>
<td>6.74</td>
<td>0</td>
<td>–</td>
<td>2.3</td>
<td>–</td>
</tr>
<tr>
<td>Gd</td>
<td>6.81</td>
<td>8.51</td>
<td>–17.3</td>
<td>*</td>
<td>4.5</td>
</tr>
<tr>
<td>Tb</td>
<td>6.79</td>
<td>10.17</td>
<td>–16.9</td>
<td>*</td>
<td>2.8</td>
</tr>
<tr>
<td>Dy</td>
<td>6.76</td>
<td>11.13</td>
<td>–9.8</td>
<td>*</td>
<td>2.4</td>
</tr>
<tr>
<td>Ho</td>
<td>6.75</td>
<td>11.10</td>
<td>–6.5</td>
<td>*</td>
<td>0.8</td>
</tr>
<tr>
<td>Er</td>
<td>6.76</td>
<td>9.77</td>
<td>–5.2</td>
<td>*</td>
<td>0.6</td>
</tr>
<tr>
<td>Tm</td>
<td>6.72</td>
<td>7.85</td>
<td>–2.7</td>
<td>2.1</td>
<td>*</td>
</tr>
<tr>
<td>Yb</td>
<td>6.73</td>
<td>4.15</td>
<td>–3.6</td>
<td>2.8</td>
<td>*</td>
</tr>
<tr>
<td>Lu</td>
<td>6.73</td>
<td>0</td>
<td>–</td>
<td>2.4</td>
<td>–</td>
</tr>
<tr>
<td>Th</td>
<td>6.88</td>
<td>0</td>
<td>–</td>
<td>*</td>
<td>–</td>
</tr>
<tr>
<td>U</td>
<td>6.85</td>
<td>2.8</td>
<td>–51</td>
<td>*</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^a\)Onset temperature of superconducting diamagnetic transition in static magnetic susceptibility.
The susceptibility measurements, taken upon both ZFC and FC in
samples of YPd$_2$Pb yielded higher values among the heavy magnetic rare earths. The
attribute to flux pinning. A significant diamagnetic response,
cally 50% of the ZFC values for each sample, which we
osity of states. It is not clear what value of
highly sensitive to the stoichiometry in these Heusler sys-
ions. R were corrected for the magnetic background contribution of the R
ions.

spin-glass-like behavior, or possibly geometrical frustration
of the ordered moments on the fcc lattice.

The existence of bulk superconductivity was confirmed
for some of the RPD$_3$Pb samples from dc magnetic-
susceptibility measurements, taken upon both ZFC and FC in
a magnetic field $H=10$ Oe. ZFC data are shown in Fig. 5. The
($T$) data were irreversible with the FC data being typi-
50% of the ZFC values for each sample, which we
tribute to flux pinning. A significant diamagnetic response,
ide of bulk superconductivity, is observed for RPD$_3$Pb
compounds in which R is a nonmagnetic trivalent ion, in-
cluding R=Sc, Y, and Lu. Evidently, superconductivity is the
ground state of this system in the absence of magnetic pair
breaking by magnetic R ions. The d electrons of the Pd ions
are believed to be mainly responsible for superconductivity
in these compounds. Curiously, superconductivity was not
observed down to 1.8 K for ThPD$_3$Pb, Th being a nonmag-
netic tetravalent ion. Superconductivity was also observed for
R=Tm and Yb, which are trivalent magnetic ions with the
smaller values of the de Gennes factor $(g-1)^2J(J+1)$
among the heavy magnetic rare earths. The $\Delta T$ data shown in
Fig. 5 for R=Tm and Yb were obtained by subtracting the
magnetic contribution of the Tm and Yb ions, respectively.
As shown in Fig. 5, the diamagnetic shielding fractions, esti-
mated from the ZFC measurements, vary from $\sim$10% to
$\sim$60% for single-crystal specimens, and are as high as 140%
for polycrystalline YPd$_3$Pb. These values should be multi-
plied by a factor of $\sim2/3$ to account for the demagnetization
correction if one approximates the cube-shaped crystals as
pheres.

The superconducting transitions are rather broad, with on-
set temperatures ranging from 2.1 to 2.8 K (see Table 1).
Previous measurements of $T_c$ for arc-melted polycrystalline
samples of YPd$_3$Pb yielded higher values of $T_c=4.76$
(Ref. 1) and 4.05 K. The precise value of $T_c$ is known to be
highly sensitive to the stoichiometry in these Heusler sys-
tems, with a possible correlation with lattice parameter,
which could be due to a sharp feature in the electronic den-
sity of states. It is not clear what value of $T_c$ represents that
of the stoichiometric compound YPd$_3$Pb. We note, however,
that one must be very careful to account for the effects of any
superconducting impurities including Pb ($T_c=7.2$ K) and
Pb-Pd ($T_c=3.0$ K).

Magnetic interactions in a metal with rare-earth ions are
governed by the $sf$ exchange interaction between the con-
duction electron spins $s$ and the total angular momentum $J$ of
the local 4f states, given by the Hamiltonian
$\mathcal{H}_{sf}=-2J_{sf}(g_J-1)J\cdot s$, where $J_{sf}$ is the exchange
coupling parameter and $g_J$ is the Landé $g$ factor of the rare-earth
ion. The factor $(g_J-1)$ results from replacing the total spin $S$ with its projection onto the total $J$ for rare earths with finite
orbital angular momentum $L$. For superconducting metals,
this interaction leads to magnetic pair breaking as described,
for example, by the Abrikosov-Gorkov theory. For a lattice
of rare-earth ions, this interaction leads to the RKKY indirect
exchange interaction between rare-earth ions, with Hamiltonian
$\mathcal{H}_{RKKY}=-2\sum_i\epsilon_i J_i\cdot J_j$, where $\epsilon_i$ and $\mathcal{H}_{RKKY}$ are the square of the component of the total spin $S$ in the total J
direction, $\langle S\cdot J \rangle^2$.

Figure 6 summarizes the results of the magnetic-
susceptibility measurements on the RPD$_3$Pb compounds,
showing $\theta_{CW}$, $T_N$, and $T_c$ for the heavy rare-earth R ions.
Both $\theta_{CW}$ and $T_N$ scale approximately with the de Gennes
factor $(g_J-1)^2J(J+1)$, represented by the solid line in Fig.
6 (normalized to the values for $R=Gd$). Crystalline electric
field effects could be responsible for deviations from this
scaling. It is interesting to note that the values of $T_N$ and $\theta_{CW}$
are very small compared to other rare-earth intermetallic
compounds, implying small exchange interactions. Of par-
ticular interest is the existence of superconductivity for
$R=Tm$ and Yb. Apparently, because of the small de Gennes
factors, the magnetic pair breaking due to the magnetic Tm
and Yb ions is not sufficiently strong to destroy supercon-
ductivity. In addition, since Tm is a non-Kramer’s ion, it is
possible for it to have a nonmagnetic CEF ground state,
which might also reduce magnetic pair breaking. Supercon-

![Figure 5](image1.png)

**FIG. 5.** Superconducting contribution to the magnetic susceptibility $\Delta T$, after zero-field cooling (ZFC) and then applying a 10 Oe
field, for single-crystal specimens of the RPD$_3$Pb compounds which
were found to be superconducting. The data for $R=Tm$ and Yb
were corrected for the magnetic background contribution of the R
ions.

![Figure 6](image2.png)

**FIG. 6.** Curie-Weiss temperatures $\theta_{CW}$ (solid circles), Néel temperatures $T_N$ (open circles), and onset superconducting critical tem-
peratures $T_c$ (open squares) of the RPD$_3$Pb compounds, derived
from magnetic-susceptibility measurements. The values $\theta_{CW}$ and
$T_N$ are compared to the de Gennes factor $(g_J-1)^2J(J+1)$, rep-
bresented by the solid line, and normalized to the values for $R=Gd$. 

![Image](image3.png)

![Image](image4.png)

![Image](image5.png)

![Image](image6.png)

![Image](image7.png)

![Image](image8.png)
Superconductivity and magnetism in the Heusler... 53

Superconductivity was previously observed in TmPd2Sn and YbPd2Sn with \( T_c \) values of 2.8 and 2 K, respectively, and YbPd2Sn was discovered to exhibit coexistence of superconductivity and antiferromagnetic order of the Yb ions below \( T_N = 0.23 \) K. This coexistence has been attributed to the small de Gennes factor of Yb. The TmPd2Sn compound was postulated to have a nonmagnetic CEF ground state. There does not appear to be any sign of magnetic order for TmPd2Pb or YbPd2Pb down to 1.8 K from our magnetic-susceptibility measurements.

From magnetic-susceptibility and \(^{119}\)Sn Mössbauer measurements on TmPd2Sn, Malik, Umarji, and Shenoy\(^{10}\) deduced that the Tm\(^{3+}\) ions have a \( \Gamma_3 \) nonmagnetic ground state with a first excited triplet state \(~1\) meV \((~10\) K) above the ground state. Shown in Fig. 7 are magnetization \( M(H) \) data for TmPd2Pb single crystals at 1.8 K, measured in fields \( H \) up to 7 T. The \( M(H) \) data are nonlinear and consist of a contribution that appears to saturate like a Brillouin function in high fields and a linear term with a slope \( \chi_0 = 0.07 \) emu/mol, represented by the dashed line. A straight line could be a second-order van Vleck susceptibility term. Extrapolation of the linear term to zero yields the saturation magnetization of \(~19\times10^3 \) emu/mol, corresponding to \( g_{\rho f} = 3.4 \mu_B \), which is less than the saturation moment of \( 7 \mu_B \) for the full Tm\(^{3+}\) multiplet. This reduced value could be due to the cubic CEF which splits the multiplet such that the \( \Gamma_3^{(2)} \) triplet, which has the magnetic moment \( g_{\rho f}(\Gamma_3^{(2)}|\mu|\Gamma_3^{(2)}) = 3.13 \mu_B \), lies lowest.\(^{11}\) A nonmagnetic ground state appears to rule out the CEF splittings of the 5f electrons, which is very small compared to 1.8 K.

Shown in the inset is a plot of the temperature dependence of the inverse magnetic susceptibility from 1.8 to 10 K as measured in a low field of 1 kOe where \( M(H) \) is approximately linear down to 1.8 K. The dashed line in the inset represents a fit to a Curie-Weiss law in this temperature range, which has nearly the same \( \mu_{\text{eff}} \) and \( \theta_{\text{CW}} \) as the high-temperature fits, again suggesting that the CEF splitting is very small, or that the \( \Gamma_3^{(2)} \) triplet lies lowest in energy. In either case, it is surprising that superconductivity exists in TmPd2Pb despite the highly magnetic character of the Tm ions even at low temperatures \( T \sim T_c \).

**UPd2Pb**

In a previous study of uranium-based ternary compounds with the chemical formula \( UT_x \) with \( T = \text{Pd, Au and } X = \text{In, Si, Ge, Sn, Sb} \), it was found that only those with \( M = \text{In} \) formed the cubic Heusler structure.\(^4\) The others revealed a more complicated structure in the x-ray-diffraction patterns, believed to be orthorhombic. None of those materials studied were superconducting down to 80 mK. The compound UPd2Sn, however, displayed characteristics of valence fluctuation or Kondo lattice phenomena below a characteristic temperature \(~10\) K, and is considered\(^4\) to be a nonmagnetic, nonsuperconducting heavy-electron material. In particular, the electronic specific-heat coefficient \( \gamma = C_{\text{eff}}/T \) was found to be strongly temperature dependent with a maximum value of \(~270 \) mJ/mol K\(^2\) at 9.7 K and an extrapolated value of \(~70 \) mJ/mol K\(^2\) at \( T=0 \) K.

We have synthesized polycrystalline samples of UPd2Pb and found that it forms the cubic \( L_2 \) Heusler structure. The cubic lattice parameter \( a = 6.85 \pm 0.01 \) Å is the largest of all the \( MPd_2X \) \( L_2 \) Heusler compounds (see Table I), except perhaps for a mixed-phase ThPd2Pb sample which had a comparable value \( a = 6.88 \pm 0.05 \) Å. It is interesting that this compound forms while \( MPd_2X \) compounds with \( M = \text{Sm and Eu} \), which would have smaller or comparable lattice parameters, do not. It is possible that the hybridization of the \( 5f \) electrons with the conduction-band states stabilizes this...
crystal structure. We subsequently measured $\rho(T)$, $\chi(T)$, and $C(T)$ in order to characterize it for possible heavy-fermion behavior.

The temperature dependences of the normalized electrical resistivity and magnetic susceptibility of UPd$_2$Pb are shown in Figs. 8(a) and 8(b), respectively. The electrical resistivity $\rho(T)$ increases by only a few percent with decreasing temperature down to $\sim$100 K, below which $\rho(T)$ decreases. The negative temperature coefficient of resistance above 100 K is indicative of Kondo-like magnetic scattering and is a typical feature of heavy-fermion materials, as is the subsequent drop below 100 K. A small kink in the $\rho(T)$ data is observed at $T$=35 K, which we attribute to antiferromagnetic ordering of the U ions, inferred from the magnetic-susceptibility data in Fig. 8(b). Like the other MPd$_2$Pb polycrystalline samples, $\rho(T)$ drops suddenly below 7.2 K due to Pb inclusions. The low-temperature resistivity of MPd$_2$Pb could be studied by applying a magnetic field sufficient to destroy the superconductivity of Pb and Pb,Pd impurity phases.

The magnetic susceptibility of UPd$_2$Pb is shown in Fig. 8(b). A sharp cusp is observed at $T$=35 K, which we attribute to AFM order of the U ions. In contrast to the RPD$_2$Pb compounds which exhibit AFM order, the ratio $\chi(0)/\chi(T_{N})$=0.75 for UPd$_2$Pb, which is only slightly larger than the theoretical value of 2/3 for an isotropic, uniaxial AFM powder specimen. At higher temperatures, the $\chi(T)$ data can be described by a Curie-Weiss law plus a constant $\chi_0$, $\chi(T) = N\mu^2_{eff}/3k_B(T-\theta_{CW}) + \chi_0$, represented by the solid line, with $\mu_{eff}=2.77\mu_B$, $\theta_{CW}=-50$ K, and $\chi_0=6.2\times10^{-4}$ emu/mol. The effective moment is somewhat smaller than the free-ion values for trivalent ($3.62\mu_B$) and tetravalent ($3.58\mu_B$) U ions. The paramagnetic constant $\chi_0$ could be due to an enhanced Pauli susceptibility for a heavy-fermion compound. Significant CEF splitting ($\Delta_{CEF}$$\sim$100 K) might also give rise to the observed deviation from free-ion behavior. Not shown in Fig. 8(b), the $\chi(T)$ data reveal slightly irreversible behavior at temperatures below $T_N$.

Shown in Fig. 9 are low-temperature specific-heat data for UPd$_2$Pb, plotted as $C/T$ vs $T^2$, for 0.5$\leq$T$\leq$10 K. The solid line represents a least-squares fit of the data to the equation $C(T) = \gamma T + \beta T^2$, with $\gamma=98$ mJ/mol K$^2$ and $\beta=3.8$ mJ/mol K$^4$. The value of the Sommerfeld coefficient $\gamma$ is at least an order of magnitude larger than that of a normal metal, although it is small compared to prototypical heavy-fermion compounds for which 0.25$\leq$$\gamma$$\leq$1 J/mol K$^2$. However, the U ions are antiferromagnetically ordered at these temperatures, which might be responsible for the observed values of the coefficients $\gamma$ and $\beta$. Measurements of $C(T)$ to higher temperatures will give information about the ordering, as well as a measure of $\gamma$ above $T_N$.

### CONCLUSION

Single crystals of RPD$_2$Pb with very small amounts of impurity phases were fabricated. Measurements of magnetic susceptibility revealed bulk superconductivity for $R$=Sc, Y, Tm, Yb, and Lu, with $T_c$$\sim$2–3 K. These values are lower than expected; a $T_c$ value as high as 4.76 K was previously reported for YPD$_2$Pb. The discrepancy is most likely due to differences in sample composition and/or quality. In particular, the $T_c$'s of these Heusler compounds are known to be sensitive to exact stoichiometry; off-stoichiometric polycrystalline samples might yield higher $T_c$ values. The magnetic rare-earth ions order antiferromagnetically with very low Néel temperatures $T_N$$\leq$4.5 K. Both $T_N$ and $\theta_{CW}$ scale approximately with the de Gennes factor. It is unlikely that the Tm ions in TmPD$_2$Pb have a nonmagnetic ground state, making it more surprising that it is superconducting. ThPD$_2$Pb was not superconducting above 1.8 K. The Heusler compound UPd$_2$Pb orders antiferromagnetically below 35 K, and displays many characteristics of a low effective mass heavy-fermion material.

### ACKNOWLEDGMENTS

This research was supported by NSF Grant No. DMR 91-07698. J.H. acknowledges support from DAAD. Some of the equipment used in this research was part of the UCSD Center for Interface and Materials Sciences, provided by a grant from the Keck Foundation.

---


---

8. Present address: Energy Science Laboratories, 6888 Nancy Ridge Dr., San Diego, CA 92121-2232.
9. Present address: National High Magnetic Field Laboratory, 1800 East Paul Dirac Dr., Tallahassee, FL 32306-4005.