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Citation: Journal of Applied Physics 115, 213903 (2014); doi: 10.1063/1.4881278
View online: http://dx.doi.org/10.1063/1.4881278
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Robust superconductivity with large upper critical field in Nb$_2$PdS$_5$

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(Received 25 April 2014; accepted 21 May 2014; published online 3 June 2014)

We report synthesis, structural details, and complete superconducting characterization of very recently discovered [Q. Zhang, Sci. Rep. 3, 1446 (2013)] Nb$_2$PdS$_5$ new superconductor. The synthesized compound is crystallized in monoclinic structure with C2/m (#12) space group. Bulk superconductivity is seen in both ac/dc magnetic susceptibility and electrical resistivity measurements with superconducting transition temperature ($T_c$) at 6 K. The upper critical field ($H_{c2}(0)$) is clearly above the Pauli paramagnetic limit of $\sim 1.84T_c$. Heat capacity ($C_p$) measurements show clear transition with well defined peak at $T_c$, but with lower jump than as expected for a Bardeen–Cooper–Schrieffer type superconductor. The Sommerfeld constant ($\gamma$) and Debye temperature ($\Theta_D$) as determined from low temperature fitting of $C_p(T)$ data are 32 ml/mole-K$^2$ and 263 K, respectively. Hall coefficients and resistivity in conjugation with electronic heat capacity indicates multiple gap superconductivity signatures in Nb$_2$PdS$_5$. We also studied the impact of hydrostatic pressure (0–1.97 Gpa) on superconductivity of Nb$_2$PdS$_5$ and found nearly no change in $T_c$ for the given pressure range. © 2014 AIP Publishing LLC.

INTRODUCTION

Very recently discovered superconductivity in layered Nb$_2$PdS$_5$ along with superconductivity of Fe based oxy-pnictides i.e., REFeAsO/F has attracted huge attention of scientific community.$^{1,2}$ In fact, seemingly it was like second revolution after the invention of high $T_c$ cuprates superconductors like famous MgB$_2$ keep on adding, but it is only the Fe pnictides that search for new superconductors in past, but also the presence of S in its layered structure calls for the attention of famous high upper critical field $S$ containing Chevrel phase compounds.$^{21}$ Keeping in view the importance of Nb and the utility of S in new layered structure of the recent compound Nb$_2$PdS$_5$, we present here an easy and clear route of synthesis of this new superconductor. Further full superconducting characterization in terms of high field (140 kOe) and low temperature (down to 2 K), electrical, magnetic, and thermal characterizations are presented in current communication.

EXPERIMENT

Polycrystalline bulk Nb$_2$PdS$_5$ is synthesized via solid state reaction route by quartz vacuum encapsulation technique at 850 °C. The high purity (4N) ingredients, i.e., Nb, Pd, and S are weighed in stoichiometric ratio and mixed thoroughly in a glove box in Ar atmosphere. The mixed powder is pelletized, sealed in an evacuated quartz tube, and put immediately in box furnace. The sample is heated to 850 °C with heating rate of 3 min and hold at same temperature for 24 h. Subsequently, the furnace is switched off and allowed to cool to room temperature over a span of 6 h. Thus, obtained sample is once again pulverized, pelletized, sealed in encapsulated

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In a very recent electronic structure determination theoretical article,\textsuperscript{12,23} slightly different configuration is used, i.e., two different Pd-S chains/sheets, the superconducting upper critical field is highly directional dependent in these compounds.\textsuperscript{1,22,23} In a more recent communication,\textsuperscript{24} the \( \text{Nb}_2\text{Pd}_x\text{S}_{5-y} \) fiber exhibited slightly modified superconducting parameters including higher \( T_c \) of 7.14 K. The role of off stoichiometry and directional alignment could lead to changed superconducting characteristics. Here, we stick to stoichiometric \( \text{Nb}_2\text{Pd}_5 \) bulk polycrystalline compound to minimize the complications.

AC susceptibility versus temperature \( \chi(T) \) behavior of the \( \text{Nb}_2\text{Pd}_5 \) sample is depicted in Figure 2. AC susceptibility measurements are done at 33 Hz and 10 Oe AC drive field. DC applied field is kept zero to check the superconducting transition temperature \( T_c \). Both the real \( \chi' \) and imaginary \( \chi'' \) part of \( \chi(T) \) are measured. Real part \( \chi' \) susceptibility shows transition to diamagnetism at around 5.8 K, confirming bulk superconductivity. The imaginary part on the other hand exhibits a single sharp peak in positive susceptibility at around the same temperature. Presence of single sharp peak in \( \chi'' \) is reminiscent of better superconducting grains coupling in studied \( \text{Nb}_2\text{Pd}_5 \) superconductor. We also measured the AC susceptibility of the compound in applied dc fields of up to 120 kOe. The plot of real part \( \chi' \) of AC susceptibility with applied field is depicted in inset of Figure 2. The temperature is fixed at 3 K, i.e., well below the superconducting transition temperature.

**RESULTS AND DISCUSSION**

The synthesized \( \text{Nb}_2\text{Pd}_5 \) sample is gray in color. The room temperature fitted and observed XRD pattern for the synthesized \( \text{Nb}_2\text{Pd}_5 \) along with its unit cell is shown in Figure 1. \( \text{Nb}_2\text{Pd}_5 \) crystallizes in Centro-symmetric structure within space group \( C2/m \) (#12). There are two formula units in each unit cell comprising two sites each for Nb (Nb1, Nb2) and Pd (Pd1, Pd2) along with five S sites (S1, S2, S3, S4, S5). The schematic sketch of the unit cell is shown in inset of Fig. 1. Details of Wyckoff positions, site symmetry, and fractional occupancies being obtained from Rietveld fitting of the experimental XRD data are given in Table I. The lattice parameters are \( a = 12.134(2)\AA, b = 3.277(1)\AA, c = 15.023(3)\AA, \) with \( \alpha = 90^\circ, \beta = 103.23^\circ \) and \( \gamma = 90^\circ \). Structural detail results are in general agreement with another recently discovered similar superconducting compound \( \text{Tas}_5\text{PdS}_5 \).\textsuperscript{22}

In a very recent electronic structure determination theoretical article,\textsuperscript{23} slightly different configuration is used, i.e., high conductivity direction is labeled along \( c \)-axis instead of usual \( b \)-axis.\textsuperscript{1,22} In fact due to anisotropic nature of the conductivity in different Pd-S chains/sheets, the superconducting upper critical field is highly directional dependent in these compounds.\textsuperscript{1,22,23} In a more recent communication,\textsuperscript{24} the \( \text{Nb}_2\text{Pd}_5\text{S}_{5-y} \) fiber exhibited slightly modified superconducting parameters including higher \( T_c \) of 7.14 K. The role of off stoichiometry and directional alignment could lead to changed superconducting characteristics. Here, we stick to stoichiometric \( \text{Nb}_2\text{Pd}_5 \) bulk polycrystalline compound to minimize the complications.

**TABLE I.** Rietveld refined Wyckoff positions and fractional occupancies of the atoms in \( \text{Nb}_2\text{Pd}_5 \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>site</th>
<th>Fractional occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb1</td>
<td>0.0759(5)</td>
<td>0.5000</td>
<td>0.179(4)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>Nb2</td>
<td>0.1528(8)</td>
<td>0.0000</td>
<td>0.3783(2)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>Pd1</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>2a</td>
<td>1/2</td>
</tr>
<tr>
<td>Pd2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>2c</td>
<td>1/2</td>
</tr>
<tr>
<td>S1</td>
<td>0.3503(6)</td>
<td>0.0000</td>
<td>0.4890(1)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>S2</td>
<td>0.2537(4)</td>
<td>0.5000</td>
<td>0.2950(6)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>S3</td>
<td>0.1753(6)</td>
<td>0.0000</td>
<td>0.0977(8)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>S4</td>
<td>0.4230(3)</td>
<td>0.5000</td>
<td>0.1321(4)</td>
<td>4i</td>
<td>1</td>
</tr>
<tr>
<td>S5</td>
<td>0.4904(7)</td>
<td>0.0000</td>
<td>0.3234(6)</td>
<td>4i</td>
<td>1</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)  
**FIG. 1.** Rietveld refined Room temperature XRD patterns of \( \text{Nb}_2\text{Pd}_5 \), the unit cell of the compound is shown in inset.

![Figure 2](image2.png)  
**FIG. 2.** AC susceptibility \( \chi(T) \) behavior of the \( \text{Nb}_2\text{Pd}_5 \) sample at frequency 333 Hz and 10 Oe AC drive amplitude of 10 Oe, the inset shows the real part of the same in applied dc fields of up to 120 kOe.
of 6 K. It is clear from inset of Fig. 2 that the studied Nb$_2$PdS$_5$ is bulk superconducting (diamagnetic) at 3 K in up to 100 kOe applied field. The upper critical field ($H_c^2$) is above 100 kOe just 3 K below the superconducting transition temperature ($T_c$). This is first indication that Nb$_2$PdS$_5$ is quite robust superconductor against magnetic field. More will be discussed after magneto-transport results in the following paragraphs.

DC magnetic susceptibility of Nb$_2$PdS$_5$ sample is shown in Figure 3. The magnetization is done in both FC (Field cooled) and ZFC (Zero-field-cooled) protocol under applied magnetic field of 10 Oe. The compound shows superconducting onset, in terms of FC and ZFC bifurcation from 5.7 K. This is clear from the zoomed inset of Figure 3. There is evidence for substantial flux trapping too. The bifurcation of FC and ZFC below $T_c$ marks the irreversible region. The shielding fraction as evidenced from ZFC diamagnetic susceptibility is quite appreciable (~58%). An interesting fact we found repeatedly in case of Nb$_2$PdS$_5$ superconductor is the appearance of paramagnetic meissner effect (PME) in FC magnetization. PME generally appears in heavily pinned superconductors and could be a good prior indication of high $H_c^2$.

Figure 4 depicts the resistivity versus temperature ($\rho$-$T$) measurement with and without applied magnetic field. The resistance of the sample decreases with temperature and confirms superconductivity with onset $T_c$~ 6.3 K and $T_c$ ($\rho=0$) at 5.9 K. The normal state conduction is of metallic type. From the fitting of resistivity $\rho = \rho_0 + AT^2$ for low temperatures ($T < T_c < 50$ K), we obtained residual resistivity $\rho_0 = 1.27$ m$\Omega$-cm and $A = 1.126 \times 10^{-4}$ m$\Omega$-cm/K$^2$ values. The quadratic variation in resistivity with temperature is shown as red solid curve in Fig. 4, which is a clear indication of Fermi-liquid nature of Nb$_2$PdS$_5$. To study the impact of applied magnetic field on superconductivity of Nb$_2$PdS$_5$ compound, the magneto-transport measurements are carried out in superconducting region, and the results are shown in inset-I of Fig. 4. With applied field of 110 kOe, the $T_c$ ($\rho=0$) decreases from 5.9 K (zero-field) to 2.4 K (110 kOe). As sketched in inset-II of Fig. 4, we have estimated upper critical field $H_c^2(T)$ by using the conservative procedure of $90\%$, $50\%$, and $10\%$ dropping of resistivity from normal state into the superconducting transition line. While the applicability of WHH (Werthamer-Helfand-Hohenberg) approximation can be debated in this new superconductor, a simplistic single band extrapolation leads to $H_c^2(0) = 0.69 T_c dH_c^2/dT_{tr}$ value of 240 kOe, 185 kOe, and 170 kOe with of $90\%$, $50\%$, and $10\%$ criterion, respectively. These values match with the experimentally ascertained bulk diamagnetic response of Nb$_2$PdS$_5$ superconductor at 3 K in 100 kOe field (inset Fig. 2). The estimated values of upper critical field are close to the earlier reported values. Interestingly, the $H_c^2(0)$ value for Nb$_2$PdS$_5$ superconductor is more than the one as being expected within Pauli Paramagnetic limit of $H_c^2(0) = 1.84T_c$ of around 110 kOe.

The relative decrement of superconductivity with applied field i.e., $dT_c/dH$ is around 0.3 K/10 kOe from absolute $T_c$ ($\rho=0$) criteria. When this is compared with the best of HTSc cuprates (3 K/10 kOe), Fe pnictides (1 K/10 kOe), and Chevrel phase (0.4 K/10 kOe) compounds, one finds that Nb$_2$PdS$_5$ is the most robust superconductor against magnetic field till date.

Figure 5 shows the heat capacity ($C_p$) versus temperature (T) plots at different applied fields of 0, 10, 50, and 140 kOe in superconducting region i.e., 2–8 K for studied Nb$_2$PdS$_5$ superconductor. In normal state i.e., at 200 K, the value of $C_p$ is around 180 J/mol K, see inset of Figure 5. The superconducting transition temperature ($T_c$) is seen clearly as a hump in $C_p$ at around 6 K. As evident from Fig. 5, the $C_p$ peak temperature shifts to lower temperatures with application of external field and is namely at 5.5 K, 5.2 K, and 4.2 K at 0, 10 kOe, and 50 kOe, respectively. The $C_p$ hump and associated peak temperature is not seen down to 2 K at 140 kOe magnetic field. This shows the compound is not superconducting down to 2 K in applied field of 140 kOe.

Figure 6 shows the low temperature normal-state 140 Koe $C_p(T)$ data from 2–10 K, which is fitted to the Sommerfeld–Debye expression as $C_p(T) = \gamma T + \beta T^3 + \delta T^5$. The values of Sommerfeld constant ($\gamma$) and $\beta$ are obtained...
from the fitting of the experimental data are as 
\[ \gamma = 32 \text{ mJ/mol-K}^2, \quad \beta = 1.79 \text{ mJ/mol-K}^4 \text{ and } \delta = -3.48 \times 10^{-2} \text{ mJ/mol-K}^6. \]

The heat capacity jump \((\Delta C_p = C_p - C_n)\) is estimated by subtracting superconducting heat capacity \((C_p)\) to the normal state fitted \(C_p\) and the same is shown in the inset of Fig. 6. The normalized value of jump \((\Delta C_p / T_c)\) is \(\sim 0.75\), which is less than in comparison to the Bardeen–Cooper–Schrieffer (BCS) value of 1.43. As seen from inset of Fig. 6, the \(C_p\) peak exhibits multiple gap superconductivity signatures with three different \(T_c\), with slight upturn near 2 K. The relatively higher value of \(\gamma = 35 \text{ mJ/mol-K}^2\) is an indication that the Nb2PdS5 is a strongly coupled superconductor.23 Worth mentioning is the fact that \(\beta \) and \(\gamma \) values change slightly, when instead of extended low \(T\) fitting of experimental \(C_p\) to normal state, the 140 kOe low \(T\) experimental data are taken as normal state. Yet, the fact remains that the normalized value of \(C_p\) jump is smaller than BCS value and the same clearly demonstrates the multi gap superconductivity. The Debye temperature is calculated by using \(\Theta_D = (234zR/\beta)^{1/3} \) here, \(z\) being number of atoms per formula unit and \(R\) is the gas constant. Taking the fitted value of \(\beta (1.79 \text{ mJ/mol-K}^4)\), the calculated value of \(\Theta_D\) is 263 K.

In order to understand the carries contribution to transport properties in un-doped Nb2PdS5, Hall resistivity \((\rho_{xy})\) and Hall coefficient \((R_H)\) measurements were carried out in normal state at different temperatures. Figure 7 depicts the Hall resistivity \((\rho_{xy})\) results for studied Nb2PdS5 superconductor at various temperatures of 250 K, 200 K, 100 K, 50 K, and 10 K up to applied magnetic field of 80 kOe. The magnetic field is applied perpendicular to the current flow direction and the voltage is recorded by five probe resistivity measurement method to minimize the magneto resistance contribution. It is clear from Fig. 7 that holes dominate the transport below temperatures 100 K, whereas electrons at and above 100 K. Clearly, this indicates that the Nb2PdS5 exhibits a change in type of dominating charge carriers at around 100 K. To assert this behavior further, the Hall coefficient \((R_H)\) of Nb2PdS5 sample is measured under three different applied magnetic fields 5 kOe, 30 kOe, and 50 kOe in the temperature range of 2 to 300 K, which is shown in Fig. 8. It can be observed from Fig. 8 that the \(R_H\) changes its sign from negative (electron type) to positive (hole type) around 190 K.
for all the three fields just after meeting together. $R_H$ is known to be sensitive to curvature of Fermi surface and renormalized Fermi velocity which may lead to change in the sign of Hall coefficient with temperature.\textsuperscript{28} Alternatively, this behavior can be understood by compensated two band model as proposed by Rullier-Albenque et al. to explain transport behavior of LiFeAs.\textsuperscript{29} This compensated two band transport property in normal state corroboration multiband superconductivity as claimed by heat capacity study for Nb$_2$PdS$_5$ compound. Spectroscopic investigations need to further furnish this claim. It is also observed that in normal state, the maximum of $R_H$ (i.e., carrier concentration, $n$, is minimum) is at $T_{RIH}(\text{max}) \approx 80$ K even for three different magnetic fields though value of $R_H$ differs. It is interesting to note that this temperature [$T_{RIH}(\text{max})$] is very close to temperature at which Hall resistivity ($\rho_{xy}$) changes its sign from negative to positive and not at which $R_H$ changes its sign. Hall coefficient ($R_H$) sharply peaked to maximum at superconducting transition as shown in the inset of Fig. 8. For the applied field of 5 kOe, $R_H = 7.01 \text{ cm}^2$/C which is equivalent to hole concentration $n = 1/e R_H = 8.92 \times 10^{12}$/cm$^2$. Similar type of carrier sign change is seen in another related superconductor 2H-NbS$_2$.\textsuperscript{28,30} Interestingly, 2H-NbS$_2$ is a known superconductor with $T_c$ above 6 K.\textsuperscript{28,30,31} This prompted us to check if the reported superconductivity of Nb$_2$PdS$_5$ could arise possibly due to minor 2H-NbS$_2$ phase. To exclude the possibility of 2H-NbS$_2$ impurity phase driven superconductivity in Nb$_2$PdS$_5$, we synthesized the NbS$_2$ compound by same heat treatment of quartz vacuum encapsulation and heating of up to 850 °C. Thus obtained NbS$_2$ is crystallized in R3$m$ space group with $a$ and $c$ parameters of 3.335 Å and 17.86 Å (Ref. 32) and is not superconducting down to 2 K, plots not shown. This clearly excluded the possibility of appearance of NbS$_2$ impurity driven superconductivity in Nb$_2$PdS$_5$. To further the investigation of transport properties of Nb$_2$PdS$_5$ resistivity as a function of temperature, $\rho(T)$, is measured under various hydrostatic pressures up to 1.98 GPa, which is shown in Fig. 9. There is no appreciable change on $T_c$ as can be seen from the inset of Fig. 9. The normal state resistivity is though slightly increased for lower pressures of up to 0.97 GPa, the same exhibits decreasing trend for 1.68 and 1.97 GPa pressures. On the other hand, we found nearly no change in $T_c$.

\section*{CONCLUSIONS}

In conclusion, we have synthesized the new layered sulfide Nb$_2$PdS$_5$ superconductor and established its bulk superconductivity by magnetization, transport, and heat capacity measurements below 6 K, with high upper critical field outside Pauli paramagnetic limit. The $C_p$ measurements exhibited multiple gap superconductivity signatures with three different $T_c$. The Sommerfeld constant ($\gamma$) and Debye temperature ($\Theta_D$) as determined from low temperature fitting of $C_P(T)$ are 35 mJ/mole-K$^2$ and 253 K, respectively. Hall studies in conjugation to heat capacity measurements affirm the possibility of multiband superconductivity in Nb$_2$PdS$_5$.

\section*{ACKNOWLEDGMENTS}

Authors would like to thank their Director Professor R. C. Budhani for his keen interest in the present work. This work was supported by DAE-SRC outstanding investigator award scheme to work on search for new superconductors. H. Kishan thanks CSIR for providing Emeritus Scientist Fellowship.

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