Superconductivity in Rh$_{17}$S$_{15}$ and Pd$_{17}$Se$_{15}$: A comparative study

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Abstract. The presence of strongly correlated superconductivity in Rh$_{17}$S$_{15}$ has been recently established. In this work we estimate normal and superconducting parameters of a single crystal of Rh$_{17}$S$_{15}$ and compare them with those of a polycrystalline sample of Pd$_{17}$Se$_{15}$ which is reported here for the first time to be a superconductor below 2.2 K. The presence of superconductivity in two iso-structural (space group Pm3m) compounds provides an opportunity to understand the strongly correlated superconductivity in Rh$_{17}$S$_{15}$. We see that large unit volume of Pd$_{17}$Se$_{15}$ and the large separation of Pd-Pd atoms in its structure as compared those in a pure Pd metal lead to the absence of strong correlations in this compound. Finally Pd$_{17}$Se$_{15}$ can be characterized as an intermediate type-II superconductor as opposed to the strongly correlated superconductivity in Rh$_{17}$S$_{15}$.

1. Introduction
Recently there has been intense activity in the study of transition metal sulphides and selenides due to a variety of their properties such as, strongly correlated superconductivity, spin and charge density waves. In our effort to understand the physical properties of noble metal chalcogenides, we have studied cubic Rh$_{17}$S$_{15}$ [1, 2] which is considered as an excellent catalyst by chemists [3, 4]. Rh$_{17}$S$_{15}$ (known as Miasite), a mineral mainly found near the Mias river in Russia, and Pd$_{17}$Se$_{15}$ (known as Palladseite), a mineral mainly found in Brazil, are iso-structural cubic compounds (space group Pm3m) whose crystal structure is shown in the Fig. 1. They have a large unit cell with 64 atoms in each (two formula units) and Rh (or Pd) occur in four inequivalent crystallographic sites.

Figure 1. The crystal structure of Rh$_{17}$S$_{15}$ which consists of two formula units with 64 atoms in the unit cell.
Some of us had reported the observation of strongly correlated superconductivity \( (T_c = 5.4 \text{ K}) \) in \( \text{Rh}_{17}\text{Se}_{15} \) \cite{1, 2} via magnetization, resistivity, heat capacity and Hall coefficient measurements. The compound was remarkable for its unusually high upper critical field \( (H_c^2(T)) \) values (around 13 T at 3 K) well above the Pauli paramagnetic limiting field (9.9 T) \cite{5, 6}. The observation of \( T^2 \) dependence of resistivity, enhanced susceptibility, moderate Sommerfeld coefficient \( (\gamma) \), large value of the upper critical field and large heat capacity jump \( (\Delta C / \gamma T_C = 2.5) \) suggest that \( \text{Rh}_{17}\text{Se}_{15} \) is a strongly correlated system. Or estimates of 2 for Wilson’s coefficient \( (\pi^2 k_B^2 \chi(0)/3\mu_B^2 \gamma) \) and \( 5 \times 10^{-5} \) for the Kadawaki-Woods ratio \( (A/\gamma^2) \) further substantiate our claim that \( \text{Rh}_{17}\text{Se}_{15} \) is a strongly correlated system. One way to achieve a moderate density of low-energy fermionic excitations (as seen by the appreciable value of \( \gamma \)) is from the large density of states of the narrow 4d band of Rh at the Fermi level \cite{5, 6, 7}. This is supported by the structure \cite{8} where some of the Rh atoms (Rh atoms at the 3d and 6e positions) are only 0.258 nm apart (the nearest Rh-Rh distance in Rh element is 0.269 nm). In this work, we will establish that \( \text{Pd}_{17}\text{Se}_{15} \) is a conventional superconductor below 2.2 K. The existence of \( \text{Pd}_{17}\text{Se}_{15} \) and its superconductivity provide us a way to understand the strongly correlated superconductivity in \( \text{Rh}_{17}\text{Se}_{15} \).

2. The Samples
Both compounds were prepared by heating stoichiometric compositions of the two elements at the rate of 8 C/hr to a temperature of 1150 C in an alumina crucible. The alumina crucible was sealed in an evacuated quartz tube. The reacted mixture is annealed at 1080 C for two days and then cooled down firstly at 8 C/hr till 600 C and further at 30 C/hr. In this method we obtained a single crystal of \( \text{Rh}_{17}\text{Se}_{15} \) with a residual resistivity ratio (RRR) of 10 and a polycrystalline sample of \( \text{Pd}_{17}\text{Se}_{15} \) with an RRR of 7. The samples were characterized using powder XRD and Laue spectrometers. The single crystal of \( \text{Rh}_{17}\text{Se}_{15} \) showed clear Laue spots indentifying the space group Pm3m. The lattice constants were 9.912 Å for \( \text{Rh}_{17}\text{Se}_{15} \) and 10.607 Å for \( \text{Pd}_{17}\text{Se}_{15} \).

3. Results and Discussion

3.1. Superconducting and Normal state properties of \( \text{Rh}_{17}\text{Se}_{15} \)

Fig. 2 shows a plot of the heat capacity \( (C_p) \) versus temperature \( (T) \) for the single crystal of \( \text{Rh}_{17}\text{Se}_{15} \) in the absence of applied magnetic field from 2 to 15 K.

A fit to the equation

\[
C_p = \gamma T + \beta T^3 + \delta T^5
\]

is also shown in the same figure where \( \gamma \) is due to the electronic contribution, \( \beta \) is due to the lattice contribution and \( \delta \) is the contribution due to anharmonicity. The estimated values of \( \gamma, \beta \) and \( \delta \) are 110 mJ/mol-K\(^2\), 0.63 mJ/mol-K\(^4\) and 1.5 \( \mu \text{J/mol-K}^6 \) respectively. The significant value of \( \delta \) suggests a complex phonon structure that could arise from the involved crystal structure of this compound. From the \( \beta \) value, one can estimate the Debye temperature \( \theta_D \) to be 456 K. Using the value of \( \theta_D \) and \( T_c \) (\( T_c = 5.27 \text{ K} \) as obtained by an equal entropy estimate at the superconducting transition), we can estimate the electron-phonon coupling parameter, \( \lambda \), from McMillan’s formula \cite{10} to be 0.58 which puts \( \text{Rh}_{17}\text{Se}_{15} \) as an intermediate electron-phonon coupling superconductor. However, the large heat capacity jump of \( \Delta C = 2.18 \text{ J/mol K} \) gives a \( \Delta C / \gamma T_c = 2.5 \) which suggests that the observed superconductivity is in the strong coupling regime. This contradiction suggests that the system is an unconventional superconductor. We can also estimate the density of states at the Fermi level \( N^*(0) \) using the relation, \( N^*(0) = 0.4248 \gamma \text{ states/eV-formula unit} \) where \( \gamma \) is expressed in mJ/mol-K\(^2\). We get a value of 46 states/eV-formula unit for \( N^*(0) \).

Fig. 3 shows the temperature dependence of the upper critical field measurement from 70 mK to 5.4 K as estimated from dc and ac magnetization, heat capacity and resistance measurements.
Figure 2. A plot of the heat capacity ($C_p$) vs temperature ($T$) from 2 to 15 K of a single crystal of Rh$_{17}$S$_{15}$. The solid line is a fit to the expression which is described in the text.

Figure 3. The temperature dependence of the upper critical field ($H_{c2}$) of Rh$_{17}$S$_{15}$ down to 70 mK. The inset shows the temperature dependence of $H_{c2}$ near the superconducting transition.

The very low temperature data (below 2 K) have been included from a recent study [6]. From this one can estimate the value of the upper critical field at $H_{c2}$ at 0 K to be 20 T which is in agreement with the recent single crystal study of Settai al [5]. The slope ($dH_{c2}/dT$) near the superconducting transition is estimated to be 3.6 T/K which is smaller than the value quoted by Settai al [5]. Using this, one can estimate a value of 13.3 T for $H_{c2}(0)$ from the WHH theory expression[11],

$$H_{c2}(0) = 0.693 \, T_c \, (dH_{c2}/dT)_T$$

This value (13.3 T) is much smaller than the observed value of 20 T. Moreover, the Pauli paramagnetic limiting field ($H_p(0) = 1.84 \times T_c$) is only 9.9 T which means that the system is not Pauli limited implying unconventional superconductivity in Rh$_{17}$S$_{15}$. We have also estimated the penetration depth $\lambda_0$ as 7000 Å from the $\mu$SR measurements performed at the PSI, Switzerland recently [12]. From the estimation of the upper critical field $H_{c2}(0)$, one can calculate the coherence length ($\xi_0$) which is given by, $\xi_0^2 = \phi_0/2\pi H_{c2}(0)$. This gives a value of 40 Å for $\xi_0$. Using $\lambda_0$ and $\xi_0$, this we can calculate the lower critical field $H_{c1}$ using the relation,$$

H_{c1}(0) = \frac{\phi_0}{4\pi \lambda_0^2} \ln(\kappa_0)

(3)

$$

where $\kappa_0 = \lambda_0/\xi_0$. The value of the lower critical field is 1.7 mT which makes Rh$_{17}$S$_{15}$ as an extreme($\kappa=175$) type-II superconductor.

3.2. Normal and superconducting state properties of Pd$_{17}$Se$_{15}$ and its comparison with those of Rh$_{17}$S$_{15}$

Fig. 4 shows the temperature dependence of the resistivity ($\rho(T)$) of a polycrystalline sample of Pd$_{17}$Se$_{15}$ from 1.6 to 300 K as compared with that of the single crystal of Rh$_{17}$S$_{15}$. The inset (a) shows the superconducting transitions in these compounds ($T_c = 2.2$ K for Pd$_{17}$Se$_{15}$). A $T^2$ fit to the low temperature data ($\rho = \rho_0 + A \, T^2$) of Pd$_{17}$Se$_{15}$ gives a value of 43.2 $\mu\Omega$ cm for the residual resistivity and a value of 0.014 $\mu\Omega$ cm/K$^2$ for the coefficient $A$. The value of $A$ for Pd$_{17}$Se$_{15}$ is comparable to that of Rh$_{17}$S$_{15}$ [1].
Figure 4. Comparison of the temperature dependence of the resistivity of the single crystal Rh$_{17}$S$_{15}$ with that of the polycrystalline Pd$_{17}$Se$_{15}$.

Figure 5. A plot of the heat capacity ($C_p$) vs temperature $T$ from 2 to 15 K of a polycrystalline Pd$_{17}$Se$_{15}$. The solid line is a fit to an expression which is described in the text.

The two curves are distinctly different in the appearance of a knee-like feature at around 60 K in Rh$_{17}$S$_{15}$ which is completely absent in Pd$_{17}$Se$_{15}$. We do not, at present, understand the reason for the knee-like feature. However, we note that there is a change of sign of majority charge carriers occurs around 60 K in Rh$_{17}$S$_{15}$ which was seen in the Hall measurements reported earlier [1]. Though the absolute value of the resistivity of both samples are comparable at 300 K, there is a distinct possibility that the strongly correlated behavior observed in Rh$_{17}$S$_{15}$ could be related to this feature.

Fig. 5 shows a plot of $C_p$ versus $T$ for the polycrystalline Pd$_{17}$Se$_{15}$ in the absence of applied magnetic field from 2 to 15 K. Our range of $C_p$ measurement, unfortunately cannot capture the transition region well. The solid line in the same figure is a fit to the equation (1) described earlier. The fit yields a $\gamma$ of 22 mJ/mol-K$^2$, $\beta$ of 4.3 mJ/mol-K$^4$ and $\delta$ of 9.2 $\mu$J/mol-K$^6$. From the value of $\beta$ we obtain a Debye temperature ($\theta_D$) of 233.3 K which indicates that Pd$_{17}$Se$_{15}$ is a much softer lattice as compared with Rh$_{17}$S$_{15}$. However, the anharmonicity term $\delta$ is much larger for Pd$_{17}$Se$_{15}$ as compared to that of Rh$_{17}$S$_{15}$. More importantly, the enhanced density of states, $N^*(0)$, as calculated from the earlier expression is around 9.35 states/eV-formula unit is smaller than that of Rh$_{17}$S$_{15}$ by a factor of 5 indicating that the correlations are much weaker in Pd$_{17}$Se$_{15}$. From the values of $\gamma$ and $\theta_D$, we have also estimated a value of 0.54 for the electron-phonon coupling constant $\lambda$ (from [10]) for Pd$_{17}$Se$_{15}$ which is very similar to the $\lambda$ value of Rh$_{17}$S$_{15}$. We believe that Pd$_{17}$Se$_{15}$ is truly a conventional and intermediate type-II superconductor where Mcmillan’s equation gives a good estimate of $\lambda$. However, Rh$_{17}$S$_{15}$ is a strongly correlated unconventional superconductor where one cannot use Mcmillan’s equation to get the correct estimate of $\lambda$. The reduction in the density of states in Pd$_{17}$Se$_{15}$ as compared to that of Rh$_{17}$S$_{15}$ is also reflected in the temperature dependence of normal state magnetic susceptibility as shown in the Fig. 6.

Since none of Rh, Pd, S or Se carry a magnetic moment we expect to see a temperature independent susceptibility essentially sum of Pauli paramagnetism, Landau diamagnetism and core diamagnetism. However, although the values of susceptibility ($\chi(T)$) are small, the data display a distinct temperature dependence for Rh$_{17}$S$_{15}$. There is a gradual increase in susceptibility as one goes to lower temperatures until the superconducting transition. The weak
Figure 6. The temperature dependence of the susceptibility of Pd$_{17}$Se$_{15}$ and Rh$_{17}$S$_{15}$ in a field 0.1 T.

Figure 7. The temperature dependence of the upper critical field ($H_{c2}$) of Pd$_{17}$Se$_{15}$ down to 270 mK.

temperature dependence of $\chi(T)$ could arise due to a sharp density of states at the Fermi level which leads to the temperature dependence of the Pauli spin susceptibility. We believe that the mechanism is similar to the observed in V$_3$Si [13]. This conjecture is recently supported by the observation of temperature dependent Knight shift from the $^{103}$Rh-NMR experiment [7]. In fact, the value of susceptibility per Rhodium atom in Rh$_{17}$S$_{15}$ is of the same order as that of susceptibility per Vanadium atom in V$_3$Si [13]. However the $\chi(T)$ of Pd$_{17}$Se$_{15}$ is diamagnetic and shows very weak temperature dependence and its $\chi(T)$ is much smaller that of Rh$_{17}$S$_{15}$ indicating that the density states is much smaller which is confirmed by the heat capacity data.

Finally, we show the temperature dependence of the upper critical field ($H_{c2}$) of Pd$_{17}$Se$_{15}$ from 270 mK to 2.2 K in Fig. 7. The curvature of $H_{c2}$ near $T_c$ is more like a conventional superconductor as opposed the one seen in Rh$_{17}$S$_{15}$ [1]. However, both show a tendency to saturate at lower temperatures. The saturation is better seen in Rh$_{17}$S$_{15}$ because we have data upto 70 mK whereas, we have presented data only upto 270 mK in Pd$_{17}$Se$_{15}$. The $H_{c2}(0)$ is estimated to be 3.3 T by an extrapolation which is nearly 6 times smaller than that of Rh$_{17}$S$_{15}$. The BCS coherence length $\xi_0$ is 100 Å as estimated from the $H_{c2}(0)(3.3$ T$)$. The slope ($dH_{c2}/dT$) near $T_c$ is 1.5 T/K which yields a value of 2.3 T for $H_{c2}(0)$ from the WHH theory. However, the Pauli paramagnetic limiting field ($H_p(0)$) is estimated to have a value of 4 T which suggests that that orbital critical field is Pauli limited in contrast to the situation in Rh$_{17}$S$_{15}$.

4. Conclusion

Table 1 contains the values of various estimated parameters for both Rh$_{17}$S$_{15}$ and Pd$_{17}$Se$_{15}$. Earlier, [1], we have conjectured that the strong correlations in Rh$_{17}$S$_{15}$ could be due to a high density of states of Rh-4d band at the Fermi level arising due to strong Rh-Rh interactions. On the other hand Pd$_{17}$Se$_{15}$ has a large unit cell volume and Pd-Pd distances are larger than that of pure Pd metal. Hence, we see the absence of strong correlations from its small values of $\gamma$ and the normal state susceptibility ($\chi(T)$). More over, the superconducting state properties of Pd$_{17}$Se$_{15}$ can be explained by the intermediate type-II superconductivity ($\lambda=0.54$) with its upper critical field (3.3 T) Pauli limited as in conventional superconductors unlike the case of Rh$_{17}$S$_{15}$. Finally, our comparative study supports our conjecture that strong correlations seen
in Rh$_{17}$S$_{15}$ comes from the strong Rh-Rh interactions which lead a narrow 4-d band at the Fermi level. It will be interesting to investigate other superconducting noble metal chalcogenides for strong correlations due to narrow 4d and 5d bands at the Fermi level [3, 14].

Table 1. Normal and superconducting state properties of Pd$_{17}$Se$_{15}$ and Rh$_{17}$S$_{15}$.

| sample name   | $\rho_{300 K}$ | $\gamma$ | $\theta_D$ | $\chi_{300 K}$ | $T_c$ | $\xi_0$ | $\lambda$ | $H_p$ |
|---------------|----------------|----------|------------|----------------|------|---------|----------|-------|
| Rh$_{17}$S$_{15}$ | 195           | 110.0    | 424        | 1.07           | 5.4  | 40.0    | 7500     | 9.9   |
| Pd$_{17}$Se$_{15}$ | 310           | 22.0     | 234        | -0.25          | 2.2  | 100.0   | -        | 4.0   |

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