Superconductivity in partially filled skutterudite $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$

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Abstract. We have investigated the partially filled Skutterudite $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ for its superconducting properties. Resistivity measurements of $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ down to 2K and in the presence of fields up to 2T are reported. The superconducting transition, $T_c$, of ~7.66K observed from zero fields of Resistivity and Heat Capacity measurements. The interesting observation is that the superconductivity survives even at a 50% filling of Pr in the parent compound and its $T_c$ is equal to that of fully doped $\text{PrPt}_4\text{Ge}_{12}$. We have estimated relevant parameters of interest like the electron phonon coupling constant, critical field, energy gap ratio, coherence length etc.

1. Introduction

Skutterudites form a class of very interesting materials with exotic thermoelectric properties that also show different ground states such as semiconducting, superconducting, magnetic and heavy fermion etc. $\text{LaPt}_4\text{Ge}_{12}$, $\text{PrPt}_4\text{Ge}_{12}$ show the superconducting transitions are respectively 8.27K, 7.91K. It is customary that vibrations of La atoms can be described by a low-energy Einstein term while the polyanionic host $[\text{Pt}_4\text{Ge}_{12}]$ is treated by the Debye approximation while analyzing the specific heat measurements. From the obtained Heat Capacity jump and energy gap ratio values, $\text{PrPt}_4\text{Ge}_{12}$ shows strong coupling character than $\text{LaPt}_4\text{Ge}_{12}$. These systems don’t follow a standard BCS formalism [1]. $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$ are superconducting below 5.35K and 5.10 K [2]. The normal state of these systems doesn’t follow the simple metallic behavior whereas they follow Woodard-Cody (WC) equation. The characteristic temperatures are 123K and 121 K respectively for $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$. From DFT calculations, guest atoms strongly stabilize the compound and the calculated DOS around $E_F$ is composed of hybridized of both Ge 4$p$-like and Pt 5$d$-like states in both the systems. Hence the superconducting state is formed from the cage of Pt-Ge structure [2]. A clear $T^3$ dependence of electronic heat capacity, Gap function has point nodes as evidenced from $\mu$SR data and superfluid density data in $\text{PrPt}_4\text{Ge}_{12}$ [3].

The critical current density and flux pinning forces of $\text{PrPt}_4\text{Ge}_{12}$ are explained in double exponential model shows the existence of a two gap superconductor [4]. Distinct positive curvatures in $H_{c1}$ (T) & $H_{c2}$ (T), linear temperature dependence of $J_C$ (T, H=0) are the evidence for two superconducting gaps in $\text{PrPt}_4\text{Ge}_{12}$. The nearly linear temperature dependence of the superfluid density at low temperature is the indication for presence of line nodes in the larger gap. The existence of two gaps with a line node in the $\text{PrPt}_4\text{Ge}_{12}$ is clear from the above results [5].

In this manuscript we present the results on 50% Pr filled $\text{Pt}_4\text{Ge}_{12}$ sample that shows the survival of superconductivity even up to a void filling of 50% and the possible presence of point nodes in its...
energy gap from the evidence of $T^3$ dependence of electronic heat capacity. We have discussed in detail with different parameters.

2. Experimental Details
Polycrystalline sample $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ is prepared by Argon arc melting using stoichiometric amounts elemental constitutes on water cooled copper hearth. The sample was remelted several times to promote the homogeneity. The sample in quartz tube is evacuated and annealed at 800°C for 12 days [1]. The sample was characterized phase by X-ray diffraction. Resistivity using four probe method, Heat Capacity using relaxation method were carried out using Quantum Design PPMS down to 2K and in the presence of magnetic fields up to 2T.

3. Results and Discussion
The XRD pattern of $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ is as shown in ‘figure 1’. Since there is a trend to have threshold value for filling, 50% level of Pr doping segregates impurity phases and are denoted by * symbol. The obtained lattice parameters are 8.615Å. It is in agreement with the reported value [1]. In spite of the impurities; we could observe a strong signal for superconductivity in Resistivity and Heat Capacity. The Superconducting transition of $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ ~7.66K in zero fields from Resistivity and Heat Capacity measurements (‘figure 2, 4’) and this transition is almost equal of parent compound transition $\text{PrPt}_4\text{Ge}_{12}$. The Superconducting transition is considered to arise from Pt-Ge cage structure [2]. This zero field transition shifts towards the low temperature by the applying magnetic fields as shown in inset of ‘figure 2’.

![Figure 1. XRD pattern of $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$. Due to excess voids, impurities segregates and they are shown as asterisk (*).](image1)

![Figure 2. Resistivity as a function of temperature of $\text{Pr}_{0.5}\text{Pt}_4\text{Ge}_{12}$ and red line shows WD-Cody fit. Inset shows in the presence various magnetic fields.](image2)

The normal state $T>T_c$ of this compound doesn’t follow a simple metallic behaviour. This may be attributed to the electron-phonon interaction strength which is responsible for the formation of cooper pairs. The overall resistivity follows the Woodward and Cody formalism [6] as shown in inset of ‘figure 2’ and is given by:

$$\rho=\rho_0+\rho_1T+\rho_2\exp[-T_0/T]$$

The obtained characteristic temperature ($T_0$) of the present system is 139.89K and almost matches the reported values of $\text{BaPt}_4\text{Ge}_{12}$ and $\text{SrPt}_4\text{Ge}_{12}$ [2]. The residual resistivity ratio of the present system is $\rho_{300}/\rho_0=22.6$ which is less than the $\text{PrPt}_4\text{Ge}_{12}$, $\text{LaPt}_4\text{Ge}_{12}$ and more than the $\text{BaPt}_4\text{Ge}_{12}$, $\text{SrPt}_4\text{Ge}_{12}$. 
We have plotted the critical field with respective temperature as shown in ‘figure 3’ and fitted with the BCS equation and linear equation. There is a clear deviation from the BCS fit and the data fits well with a linear fit. The obtained critical field from such a linear fit is $H_{c2}(0) = 2.13T$. The estimated coherence length of the present compound is $\xi \approx 12.43$nm using the equation $\xi^2 = \frac{\phi_0}{2\pi H_{c2}(T)}$ [7]. This value is similar to the $\xi$ value of BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$.

The plot of $C/T$ vs $T^2$ of the present system is as shown in ‘figure 4’ and its inset. The normal state Heat Capacity of $C/T$ ($C = \gamma T + \beta T^3$, $\gamma$ is the Sommerfeld coefficient and $\beta$ is proportional to the Debye temperature $\theta_D$) was fitted by linear equation as shown in inset of ‘figure 4’. The obtained $\gamma$ value is 3.1mJ/mol-K$^2$ and $\theta_D$ is 198K for the present system and the Debye temperature matches with the reported values of MPt$_4$Ge$_{12}$ (M=Pr, La, Sr, Pr). Debye temperatures of LaPt$_4$Ge$_{12}$, PrPt$_4$Ge$_{12}$, BaPt$_4$Ge$_{12}$ and SrPt$_4$Ge$_{12}$ are respectively 209 K, 198 K, 247K and 220K.
The C(T) vs T is as shown in inset of ‘figure 5’. We have subtracted the phonon part from total Heat Capacity to get the electronic Heat Capacity ($C_e$) and plotted as $C_e/T$ vs T as shown in ‘figure 5’. The Superconducting state of $C_e/T$ (T) doesn’t follow the BCS equation. A good fit is obtained by adding a $T^2$ term in BCS equation, viz $C_e/T = (A/T)\exp(-\Delta/k_B T) + BT^2$. The Normal state simply becomes a $\gamma$ which is almost constant and is shown as linear fit that is quite flat. The line which we have taken at the transition is according to entropy conservation. Here the clear $T^3$ dependence of $C_e(T)$ is the evidence for point nodes in energy gap of present system. The energy gap ratio is 1.13 which is lower than the BCS value and the corresponding energy gap is 0.37meV only. These values indicate that the present system is in the weak coupling limit which is in contrast to the parent compound that requires further investigation.

4. Conclusions
The superconducting transition of Pr$_{0.5}$Pt$_4$Ge$_{12}$ is 7.66K. Superconductivity survives even at 50% Pr filling and shows transition temperature is almost the same as that of its parent counterpart. This supports the fact that Pt-Ge cages are superconducting. The estimated characteristic temperature of Woodard-Cody equation is 140 K, coherence length is 12.4nm and the Debye temperature is 198K. These values are in line with the values reported for the Pr fully filled system. However, the parameters in the superconducting state predicts a weak coupling limit which is in contrast to the fully Pr filled system. This may be due to the fact of pronounced point nodes as revealed by heat capacity data.

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References
[1] Gumeniuk R., Schnelle W., Rosner H., Nicklas M., Leithe Jasper A. and Grin Yu 2008 Phy Rev Lett 100 017002
[2] Bauer E., Grytsiv A., Qiu Chen X, Melnychenko Koblyuk N., Hilscher G., Kaldarar H., Michor H 2007 Phy Rev Lett 99 217001
[3] Maisuradze A., Nicklas M., Gumeniuk R., Baines C., Schnelle W., Rosner H., Leithe Jasper A., Grin Yu. and Khasanov R 2009 Phy Rev Lett 103 147002
[4] Sharath Chandra L S, Chattopadhyay M K and Roy S B 2012 Supercond. Sci. Technol. 25 105009
[5] Sharath Chandra L.S., Chattopadhyay M. K. and Roy S.B. 2012 Phil. Mag. 92 3866
[6] Woodard D.W. and Cody G.D. 1964 Phys. Rev. 136 166.
[7] Ohashi Y., Masubuchi Y., Venkateshwarlu D., Ganesan V., Yakhmi J. V., Yoshida T., Kikkawa S 2014 J Solid State Chem. 210 238.