Superconductivity in Lu$_3$Os$_4$Ge$_{13}$

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Abstract. We report the normal and superconducting state properties of high quality single crystal of Lu$_3$Os$_4$Ge$_{13}$ grown by Czochralski method. Lu$_3$Os$_4$Ge$_{13}$ crystallises in the cubic crystal structure (space group Pm3n). Lu$_3$Os$_4$Ge$_{13}$ is a type-II superconductor ($T_c=3.1$ K) as determined by the electrical transport, magnetisation and heat capacity measurements. The thermopower measurement shows a large phonon drag effect at low temperatures. The electronic band structure calculations show a multi-valley type band structure and a complex Fermi surface in Lu$_3$Os$_4$Ge$_{13}$, making it a possible candidate to observe a magnetic field induced triplet superconductivity at ultra-low temperatures.

1. Introduction

Understanding the nature and origin of superconductivity in semiconductors and semi-metals is a challenging problem and it is hampered by the fact that only a handful of well characterised compounds have been studied till date [1, 2, 3, 4, 5]. The occurrence of superconductivity in these low carrier density compounds is surprising since low carrier density is an unfavourable element for superconductivity within the conventional framework of Bardeen-Cooper-Schrieffer (BCS) [6] or Migdal-Eliashberg [7, 8] theories. Here, one may have to look beyond the conventional framework of BCS or Migdal-Eliashberg theories in order to understand the unconventional superconductivity in these compounds. There is another reason to study superconductivity in new low carrier density compounds as earlier theoretical investigations [9, 10] demonstrated the presence of a new triplet superconducting phase in a donor-doped multi-valley semiconductor or multi-valley semi-metal, at very high magnetic fields and untra-low temperatures. This phase is a mirror image of the spin-up, spin-down Cooper-pair condensation, where the spins are replaced by the indices of the valleys. Because the magnetic field does not couple to the indices, this transition is strongly enhanced in the presence of a magnetic field. There has been some attempts to observe this effect in a semi-metal like Bismuth [11], but no compound has been investigated till date. It is worthwhile to look such exotic superconducting state in semi-metals such as, Lu$_3$Os$_4$Ge$_{13}$. In this report, we present single crystal growth and a detailed study of physical properties of Lu$_3$Os$_4$Ge$_{13}$, supported by electronic band structure calculations.

2. Experimental Details

Lu$_3$Os$_4$Ge$_{13}$ single crystal has been grown using the Czochralski crystal pulling method in a tetra-arc furnace under inert Argon atmosphere. A stoichiometric mixture (10 g) of high purity elements (Lu: 99.99%, Os: 99.99%, Ge: 99.99%) was melted several times in a tetra-arc furnace under argon atomosphere to make a homogeneous poly-crystal of Lu$_3$Os$_4$Ge$_{13}$. The single
crystal was pulled at the rate of 10 mm/h for about 6 hrs using a tungsten rod as seed to get 5-6 cm long cylindrical crystal with 3-4 mm diameter. The grown crystal was examined by various experimental techniques such as room temperature powder X-ray diffraction (PXRD), electron probe micro-analyzer (EPMA) and energy dispersive x-ray analysis (EDX) and no trace of impurity phases was observed. The single crystal was oriented along the principal crystallographic direction [100] using Laue back reflection method in Huber Laue diffractometer. The crystal was cut to the desired shape and dimensions using a spark erosion cutting machine. The electrical resistivity was measured using standard four-probe technique in a home made setup using a 50μm gold wire. The contacts were made using indium solder. A commercial SQUID magnetometer was used for the magnetic susceptibility measurements and heat capacity measurement was done using Physical Property Measurement System (PPMS). The thermopower was measured from 7.2-275 K in a home made setup.

3. Results and Discussion

Lu₃Os₄Ge₁₃ crystal structure has cubic symmetry with space group “Pm3n” (space group # 223) with two formula units per unit cell resulting in 40 atoms per unit cell. The crystal structure of Lu₃Os₄Ge₁₃ is shown in Fig. 1. The Rietveld analysis of the room temperature powder x-ray diffraction (χ² = 2.8) is shown in Fig. 2. The value of lattice constant obtained from the refinement is a = 8.946 (± 0.001 Å).

![Figure 1. Crystal structure of Lu₃Os₄Ge₁₃. Lutetium atoms are inside the cage shown in violet colour at 6d position, osmium atoms are shown in green colour at 8e position and germanium atoms are shown in dark red colour at 2a and 24k Wyckoff positions.](image1)

![Figure 2. XRD data and Rietveld analysis of Lu₃Os₄Ge₁₃. Profile reliability factor Rₓ = 17.5%, weighted profile R-factor Rₓₓ = 17.2%, Bragg R-factor = 8.46% and RF-factor = 7.44% were obtained from the best fit.](image2)
expression\cite{12}, \( \mu_0 H_{c2}(0) = -0.693 T_c \frac{dH_{c2}}{dT} \bigg|_{T=T_c} \) in the dirty limit for type-II superconductors. The slope \( \frac{dH_{c2}}{dT} \bigg|_{T=T_c} \) is used to calculate \( \mu_0 H_{c2} = 5.72 \) T for Lu\(_3\)Os\(_4\)Ge\(_{13}\) using the dirty limit of the WHH formula. The value of \( \mu_0 H_{c2} \) is smaller than the weak coupling Pauli paramagnetic limit \( \mu_0 H_{Pauli} = 1.82 T_c = 5.80 \) T. The upper critical field value \( \mu_0 H_{c2}(0) \) can be used to estimate the Ginzburg-Landau coherence length \( \xi(0)_{GL} = \Phi_0/2\pi H_{c2}(0) = 78 \) Å, where \( \Phi_0 = \hbar c/2e \) is the magnetic flux quantum.

Figure 3. Temperature dependence of the electrical resistivity (\( \rho(T) \)) for the current applied along the [100] direction. Resistivity data shows the semi-metallic nature of Lu\(_3\)Os\(_4\)Ge\(_{13}\).

Figure 4. The field dependence of electrical resistance of Lu\(_3\)Os\(_4\)Ge\(_{13}\) for current and magnetic field parallel to [100] direction. The superconducting transition gets broadened at higher magnetic fields.

Figure 5. \( \mu_0 H_{c2} \) as a function of temperature for Lu\(_3\)Os\(_4\)Ge\(_{13}\). The bold red curve shows the dirty limit WHH formula fit to the data. The best fit is obtained for \( \alpha = 0, \lambda = 0 \).

Figure 6. Specific heat capacity \( C_p \) vs temperature of Lu\(_3\)Os\(_4\)Ge\(_{13}\) from 1.8-300 K. The inset shows the low temperature data and the sharp jump in heat capacity confirms occurrence of bulk superconductivity at 3.1 K.

The heat capacity \( C_p \) of Lu\(_3\)Os\(_4\)Ge\(_{13}\) as a function of temperature \( (1.8 \leq T \leq 300K) \) measured at H= 0 is shown in Fig. 6. The inset in Fig. 6 shows a sharp jump in \( C_p \) at 3.1 K which confirms the bulk superconductivity in the compound.

The superconducting transition is fully suppressed under a 7 T magnetic field and the low
temperature normal state specific heat can be well fitted with the equation \( \frac{C_p}{T} = \gamma + \beta T^2 \) as shown in Fig. 7, where \( \gamma T \) represents the electronic contribution and \( \beta T^3 \) describes the lattice-phonon contribution to the specific heat in the normal state. By fitting the data using the above equation, we find the electronic specific heat coefficient \( \gamma = 25.4 \frac{mJ}{mol K^2} \) and the phonon/lattice contribution coefficient \( \beta = 2.30 \frac{mJ}{mol K^3} \). The coefficient \( \beta \) gives the Debye temperature \( \Theta_D = 257 \) K, according to the formula \( \Theta_D = (12\pi^4 RN/5\beta)^{\frac{1}{3}} \), where \( R \) is the molar gas constant and \( N(=20) \) is the number of atoms per formula unit (f.u.). The sharp jump in \( C_{el}(T) \) at \( T_c \), namely \( \Delta C_{el}(T) = 90 \) mJ/mol K, which gives \( \Delta C_{el}/\gamma T_c = 1.15 \). The ratio \( \Delta C_{el}/\gamma T_c \) can be used to measure the strength of the electron-phonon coupling. This value \( \Delta C_{el}/\gamma T_c = 1.15 \) is smaller than the weak-coupling limit value of 1.43 for a conventional BCS superconductor, which does not agree with the values for moderately coupled superconductors. Therefore, the above analysis suggests that \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \) is a BCS type anisotropic-gapped superconductor.

The low temperature dc-susceptibility data of \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \) shows a diamagnetic transition at \( 3.1 \) K as shown in Fig. 8. Significant amount of vortex pinning can be observed by comparing the zero field cooled (ZFC) and the field cooled (FC-Meissner) data below the transition temperature.

Many compounds having cage like crystal structure have been found to be good thermoelectric materials. This prompted us to measure the thermoelectric power of \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \). Figure 9 shows the thermoelectric power (S) measurement of \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \) single crystal. The measurement was done in a home made setup from 7-275 K. The magnitude of S is comparable to the iso-structural compounds like \( \text{R}_3\text{Ru}_4\text{Ge}_{13}(\text{R=Y, Lu}) [13] \). The presence of a peak like feature starting at \( \approx 50 \) K is not fully understood at the moment but it may be caused by phonon drag resulting from electron-phonon scattering contributing to the thermoelectric power. This contribution is most important in the temperature region where phonon-electron scattering is predominant. This typically happens at temperatures \( T = \Theta_D/5 \) K [14], which comes out to be \( \approx 52 \) K for \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \), thus the existence of peak in the thermopower at temperatures below \( 50 \) K supports the hypothesis of phonon drag contribution to the thermopower.

The electronic band structure calculations were performed by density functional theory (DFT) using WIEN2k code with a full-potential linearised augmented plane-wave and local orbitals (FP-LAPW + lo) basis together with Perdew-Burke-Ernzerhof (PBE) parametrization of the

### Figure 7. \( C_p/T \) vs \( T^2 \) data of \( \text{Lu}_3\text{Os}_4\text{Ge}_{13} \) at 7 T magnetic field. The heat capacity data is well described by the equation \( \frac{C_p}{T} = \gamma + \beta T^2 \).
Figure 9. Thermopower (S) vs T data for Lu₃Os₄Ge₁₃. The thermopower data shows a peculiar peak at low temperature (< 50 K), which is attributed to the contribution from the phonon drag in the compound.

Figure 10. Electronic band structure calculations of Lu₃Os₄Ge₁₃. A multi-valley type band structure is observed. Three bands cross the Fermi-surface and contribute to the semi-metallic character of the compound.

Figure 11. Analysis of DOS of Lu₃Os₄Ge₁₃. The total DOS curve has a local maximum at the edge of the Fermi energy. The partial DOS curves shows that major contribution to the total DOS is coming from Os and Ge atoms. Lu atoms have least contribution to the total DOS.

Figure 12. Calculated Fermi surface of Lu₃Os₄Ge₁₃. Three bands cross the fermi level resulting in a non-spherical complex fermi surface.

generalized gradient approximation (GCA), with no spin-orbit coupling. The plane wave cutoff parameter \( R_{MT} K_{MAX} = 7 \) was taken with 5000 k-points. Figure 10 shows the band structure of Lu₃Os₄Ge₁₃ around Fermi level. A multi valley type character [9] is observed in the band structure. Three bands are found to cross the Fermi level. Figure 11 shows the calculated density of states (DOS) for one formula unit of Lu₃Os₄Ge₁₃. Three bands cross the Fermi level leading to a complex Fermi surface as shown in Fig. 12.
4. Conclusion
We have grown a single crystal and characterized the normal and superconducting properties of semi-metallic compound Lu$_3$Os$_4$Ge$_{13}$. A bulk superconducting transition is confirmed through electrical transport, magnetization and heat capacity measurements. Heat capacity studies confirm that Lu$_3$Os$_4$Ge$_{13}$ is a moderately electron-phonon coupled, anisotropic gapped BCS superconductor. The thermoelectric power measurements show a peak like feature at low temperatures which are attributed to phonon drag contribution. The electronic band structure calculations show a multi-valley type band structure and a total of three bands cross the Fermi surface creating a complex Fermi surface making Lu$_3$Os$_4$Ge$_{13}$ a possible candidate to observe a magnetic field induced triplet superconductivity at ultra-low temperatures.

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