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Superconductivity in highly correlated $Rh_{17}S_{15}$

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ABSTRACT

We establish the highly correlated nature of the superconductivity in $Rh_{17}S_{15}$ via transport, magnetization and heat capacity measurements. In particular, we discuss the presence of strong correlation using resistivity, susceptibility, heat capacity and upper critical field studies on a well-characterized polycrystalline $Rh_{17}S_{15}$ sample which exhibits superconductivity below 5.4 K.

1. Introduction

Heavy fermion compounds [1] have attracted the interest of condensed matter physicists for more than a quarter of a century is the observation of compounds where the charge carriers have large effective masses due to strong electron correlations. These compounds are known as heavy fermion which contain either 4f (Ce or Yb) or 5f (U, Np or Pu) elements as one of their constituents which provide the necessary magnetic correlations. They display a variety of ground states ranging from antiferromagnetism, ferromagnetism, superconductivity or even a combination of any of the above. Unlike the f-electron systems, the occurrence of heavy fermion state in d-electron systems is a rare event [2] with none of them exhibiting superconductivity. In this work [3] we show the existence of a 4d-electron compound $Rh_{17}S_{15}$ that shows superconductivity arising from strong correlated charge carriers presumably due to the high density of states of d-bands at the Fermi level. The title compound was prepared by reacting Rh powder (99.9% pure) with Sulphur powder (99.999% pure) in an evacuated quartz tube at 950 °C. The reacted mixture was cooled at the rate of 30 °C/hour. The resulting compound was a homogenous alloy (appears to be melt textured). Powder X-ray diffraction confirmed the cubic structure with a lattice constant of 0.99093(2) nm. The temperature dependence of the resistivity ($\rho(T)$) shown in Fig. 1 displays the superconducting transition at 5.4 K (inset (b) of Fig. 1): ρ is fitted to $\rho = \rho_0 + AT^2$ (shown in the inset (a)) in the temperature range from 6 to 30 K. The T^2 dependence of low temperature resistivity is different from the behavior seen in conventional metals. The value of the coefficient A ($\sim 10^{-8}$ μΩ cm K^2) is an order of magnitude smaller than the value observed in usual heavy fermion compounds. A moderate enhancement in A could be due to strong electron–electron interactions. The magnetic susceptibility [$\chi(T)$] at 290 K has a small positive value (7.4×10^{-3} emu/mol) and it increases with the decrease of temperature (figure not shown here for brevity). Such an increase could be ascribed to the temperature dependence of Pauli spin susceptibility due to the narrow 4d band at the Fermi level. We observe the enhancement of $\chi(T)$ at low temperatures indicating the presence of strong electron correlations.

The low temperature data (Fig. 2) show a large heat capacity jump ($\Delta C/T = 0.24$ J/mol K^2) at the superconducting transition establishing the strongly correlated nature of the superconductivity. Further, the value of $\Delta C/\gamma T_C = 2$ suggests that strongly coupled electrons are involved in the superconductivity of this compound. The value of γ (obtained by fitting the high temperature data) is 104.8 mJ/fu K^2 implying that we are indeed dealing with moderately enhanced density of states system. Although one deals with

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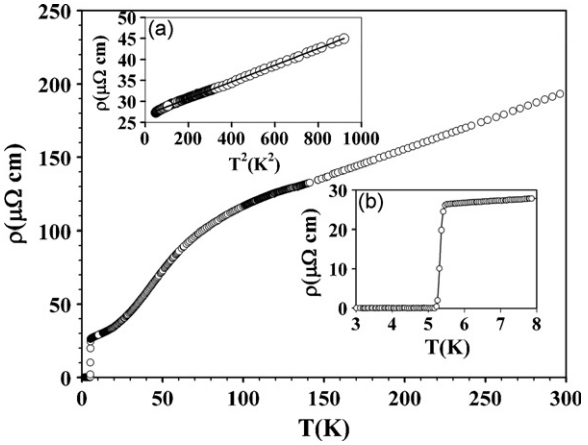

Fig. 1. The temperature dependence of the resistivity $\rho(T)$ of $Rh_{17}S_{15}$. The insets (a) and (b) show the low temperature $\rho(T)$ behavior (solid line is a fit to the T^2 dependence) and the observation of superconductivity, respectively.

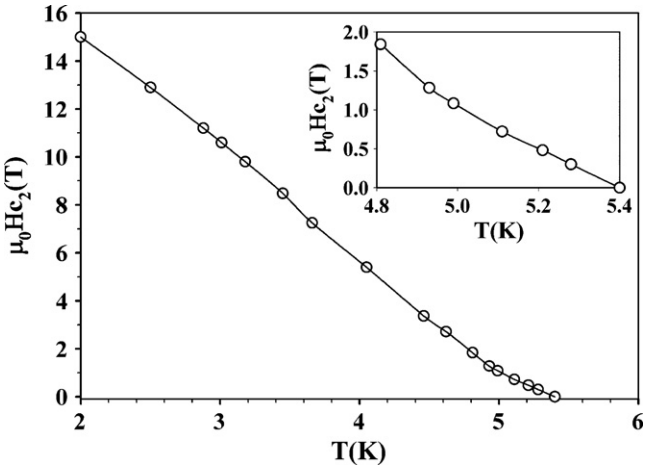

Fig. 3. The temperature dependence of the upper critical field $Hc_2(T)$ of $Rh_{17}S_{15}$. The inset shows the variation of $Hc_2(T)$ near T_C which is different from the expected behavior for conventional superconductors.

system of large number of atoms (32 as per the one formula unit and the unit cell has two formula units), only 15 Rh atoms (Rh(3d) has 12 Rh(6e) neighbors at a distance 0.258 nm which lead to a narrow 4d Rh band at the Fermi level) are responsible for the large value of γ. Hence, our claim of moderately high γ ($104.8 \times 2/15 = 14$ mJ/Rh atom K^2) of $Rh_{17}S_{15}$ is justifiable. Substituting the values of T_C and the screened Coulomb parameter $\mu^* = 0.13$ in the McMillan formula, the electron–phonon coupling constant is found to be only 0.58 which does not favor the electron–phonon coupling as the main cause of strongly coupled nature of the superconductivity in $Rh_{17}S_{15}$.

The concave-upwards temperature dependence of $Hc_2(T)$ (Fig. 3) is also different from what one observes in conventional superconductors. Secondly, the large value of the upper critical field ($Hc_2(T) > 12$ T at 2.5 K (which is larger than the Pauli paramagnetic limiting field of 9.99 T)) and the fact that $Hc_2(T)$ does not seem to show any tendency towards saturation at low temperatures (in the limited temperature range) possibly reflect the unconventional nature of the superconductivity in $Rh_{17}S_{15}$.

The Hall resistivity as a function of magnetic field at several temperatures is shown in Fig. 4. The linear dependence of the Hall voltage suggests that the Hall coefficient R_H is independent of the applied magnetic field. The value of R_H changes sign from negative to positive at low temperatures (Fig. 4). If one uses a simple one-band picture, the estimated carrier density [$n = 1/(R_H Q)$], where Q is the electronic charge (+e for holes and −e for electrons) is 2.9×10^{26} m^{-3} for electrons at 10 K and 25×10^{26} m^{-3} for holes at 120 K and they are nearly 2–3 orders of magnitude lesser than that of conventional metals. Temperature driven sign change of Hall coefficient has also been seen in oxides such as $CaRuO_3$ and $SrRuO_3$ which is attributed to the unusual structure of the Fermi surface.

In the case of heavy fermion compounds, the large electronic effective mass, 100 or more times larger than the bare electron mass, arises from an antiferromagnetic interaction between conduction electrons and the local magnetic moments (Kondo effect) residing on a sub-lattice of atoms in the metal. There exists an indirect intersite interaction between the local moments as well, which compete with Kondo effect, causing a variety of ground states in this system. In the case of 3d heavy fermion LiV_2O_4, its spinel structure leads to frustrated antiferromagnetic interactions leading to a spin liquid with strong correlations [2]. Though, LiV_2O_4 is a paramagnetic system it nevertheless exhibits a change from ferromagnetic correlations at high temperatures to antiferromagnetic correlations at low temperatures with a large γ. Unlike in the case of LiV_2O_4, the presence of magnetic correlations in paramagnetic $Rh_{17}S_{15}$ is not evident from our present data of bulk properties.

However, the observation of T^2 dependence of ρ, enhanced susceptibility, moderate γ, large value of the upper critical field

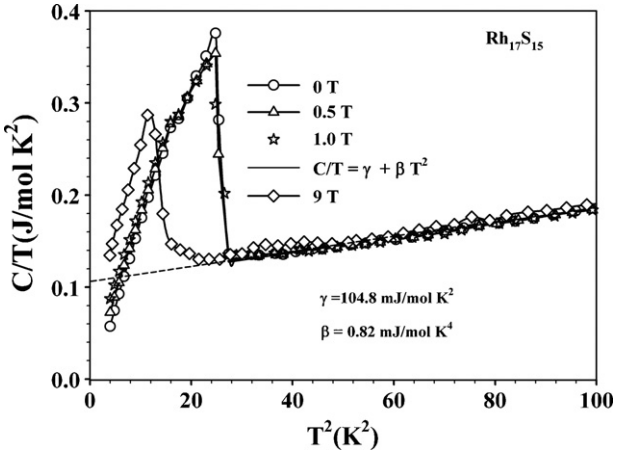

Fig. 2. The temperature dependence of the heat capacity of $Rh_{17}S_{15}$ from 2 to 10 K in a field of 0, 0.5, 1 and 9 T.

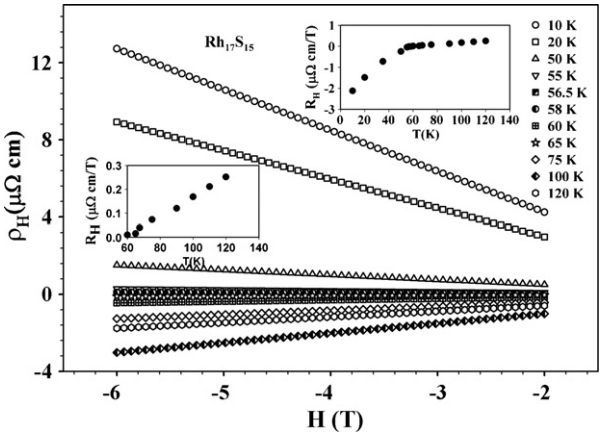

Fig. 4. The Hall resistivity as a function of magnetic field at several temperatures. The temperature dependence of the Hall constant R_H is shown in both insets.

and large heat capacity jump ($\Delta C/\gamma T_C = 2$) suggest that $Rh_{17}S_{15}$ is a strongly correlated system. This conjecture is further substantiated by the estimated value of 2 for the Wilson's coefficient ($\pi 2{k_B}^2\chi(0)/3\,{\mu_B}^2\gamma$) and 5×10^{-5} for the Kadawaki–Woods ratio (A/γ^2). The only way to achieve a moderate density of low-energy fermionic excitations as seen by the appreciable value of γ is from the large density of states of the narrow 4d-band of Rh at the Fermi level. This is supported by the structure since some of the Rh–Rh distances are smaller than those that exist in the pure Rh metal. It is important to carry out detailed band structure calculations to ascertain whether enhanced effective mass observed here arises out of band structure or additional electronic correlations.

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