Strongly Correlated Superconductivity in $Rh_{17}S_{15}$

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(Received 4 October 2007; published 16 January 2008)

In this Letter, we report resistivity, susceptibility, heat capacity, and upper critical field studies on a polycrystalline $Rh_{17}S_{15}$ sample which exhibits superconductivity below 5.4 K. Detailed studies suggest that the superconductivity in this compound arises from strongly correlated charge carriers presumably due to the high density of states of Rh d bands at the Fermi level. Moreover, the Hall coefficient shows a sign change and increases at low temperature before the sample becomes a superconductor below 5.4 K.

DOI: 10.1103/PhysRevLett.100.026404 PACS numbers: 71.20.Be, 74.25.Bt, 74.25.Ha, 74.70.Tx

One of the remarkable phenomena [1,2] which has 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 fermions 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 seen only in a handful of compounds [3,4]. Even in those cases, none of them exhibits superconductivity. In this Letter we demonstrate the existence of a $4d$-electron compound namely $Rh_{17}S_{15}$ that shows superconductivity arising from strong correlated charge carriers presumably due to the high density of states of d bands at the Fermi level. $Rh_{17}S_{15}$ is a naturally occurring gray colored mineral known as Miasite reported to be available in Miass River in Southern Urals, Russia. The first observation of superconductivity in a laboratory synthesized polycrystalline sample of $Rh_{17}S_{15}$ was reported by Matthias and his coworkers more than 50 years ago [5]. They were interested in studying superconductivity of transition metal chalcogenides and the observation of superconductivity in sulfides was a novelty at that time. However, until today, there has been no detailed study of many physical properties of this specimen. In this Letter, we present a comprehensive study of magnetic, thermal, and transport properties of a well-characterized polycrystalline $Rh_{17}S_{15}$ which establishes that the superconductivity arises presumably due to the presence of strongly correlated (with moderate γ value) $4d$ electrons. The title compound was prepared by reacting Rh powder (99.9% pure) with sulfur powder (99.999% pure) in an evacuated quartz tube at 950 °C. The reacted mixture was cooled at the rate of 30 °C per hour. The resulting compound was a homogenous alloy (appears to be melt textured). Powder x-ray diffraction [see Fig. 1(b)] confirmed the cubic structure with a lattice constant of 0.99093(2) nm. The Rietveld fit yielded Bragg factor (R_B) of 19% with a chisquare value of 0.9. The structure of $Rh_{17}S_{15}$ is described mainly on the basis of its belonging to cubic space group $Pm3m$ with a lattice constant of

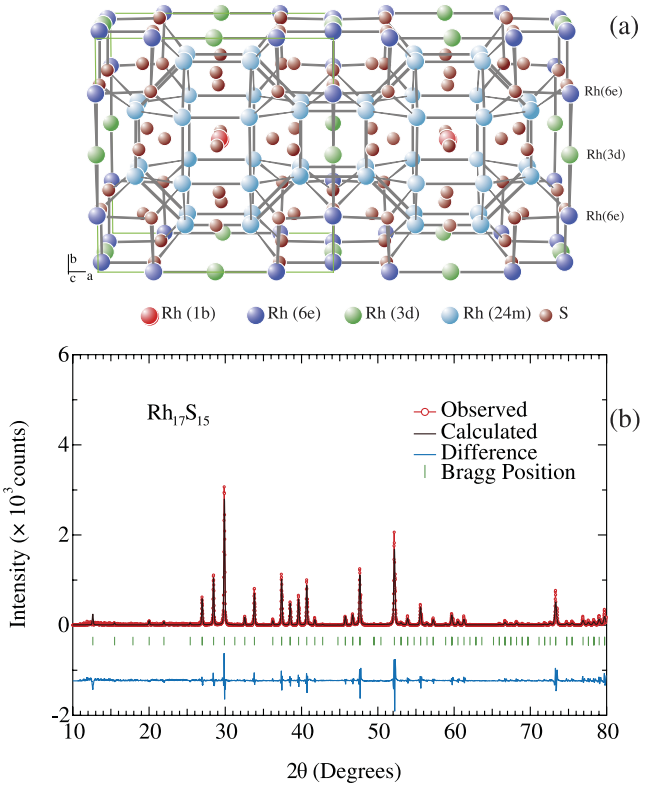

FIG. 1 (color). The crystal structure of $Rh_{17}S_{15}$ which consists of 2 f.u. with 64 atoms in the unit cell. The unit cell has 4 types of Rh atoms with position symmetry $24m$, $6e$, $3d$, and $1b$ and 3 types of sulfur atoms with position symmetry $12j$, $12i$, and $6f$. The Rh(d) has two shorter Rh(e) neighbors at 0.258 nm which together with 4 S(j) atoms completes an octahedron about Rh(d). In the pure Rh metal which has the cubic close-packed structure the nearest neighbor Rh-Rh distance is 0.269 nm suggesting strong Rh bonds in $Rh_{17}S_{15}$. The main panel shows the x-ray powder diffraction graphs of the generated [with $a =$ 0.99093(2) nm] and the observed data.

0.99093(2) nm. The structure [6] contains 2 f.u. with 64 atoms in the unit cell. There are four kinds of rhodium and three different kinds of sulfur atoms in the structure (see Fig. 1). One of the important features of this structure is that the Rh(3d) has two Rh(6e) neighbors at 0.258 nm which is shorter than the nearest neighbor Rh-Rh distance (0.269 nm) in a cubic Rh metal. This would result in narrow 4d band states in this compound.

The temperature dependence of the resistivity [($\rho(T)$] shown in Fig. 2 displays the superconducting transition at 5.4 K [inset (b) of Fig. 2] and more importantly ρ is fitted with the equation $\rho(T) = \rho_0 + AT^n$ in the temperature range from 6 to 30 K. We obtained $\rho_0 = 26.7\ \mu\Omega\,\mathrm{cm}$, $A = 0.01\ \mu\Omega/\mathrm{cm\,K^2}$, and $n = 2$. The value of ρ_0 is large because of the polycrystalline nature of the sample but the quality of the fit is quite good as reflected by inset (a) of Fig. 2. The T_2 dependence of $\rho(T)$ is different from the behavior seen in conventional transition metal alloys. The value of A is an order of magnitude smaller than the value observed in usual heavy fermion compounds. However, in view of the large residual resistivity (27 $\mu\Omega\,\mathrm{cm}$) of the present sample, a reduced value of A is understandable. It must be also stated here that A is also small in some of the Yb based heavy fermion compounds [7]. A moderate enhancement in A could be ascribed 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. Figure 3 displays the temperature dependence of the heat capacity of $Rh_{17}S_{15}$. The low temperature data show a large heat-capacity jump ($\Delta C/T = 0.24\ \mathrm{J/mol\,K^2}$) 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 to $C = \gamma T + \beta T^3$) is turned out to be 104.8 mJ/formula unit $\mathrm{K^2}$ implying that we are indeed dealing with a moderately enhanced density of states system. Although one deals with a system of large number of atoms (32 as per the one formula unit and the unit cell has 2 f.u.), only 3 Rh atoms [Rh(3d) has 12 Rh(6e) neighbors at a distance 2.58 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 $\mathrm{K^2}$) of $Rh_{17}S_{15}$ is justifiable. Substituting the values of T_C and the screened Coulomb parameter $\mu^* = 0.13$ in the McMillan [8] formula, the electron-phonon coupling constant is found to be only 0.58 which does not favor electron-phonon coupling as the main cause of the strongly coupled nature of the superconductivity in $Rh_{17}S_{15}$.

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 (shown in the inset of the Fig. 4) changes signs from negative to positive at low temperatures. 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 $2.9 \times 10^{26}/\mathrm{m^3}$ for electrons at 10 K and $25 \times 10^{26}/\mathrm{m^3}$ for holes at 120 K and they are nearly

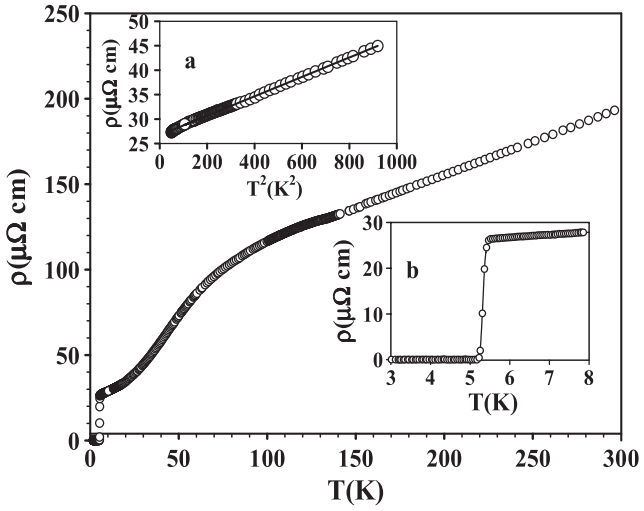

FIG. 2. The temperature dependence of the resistivity $\rho(T)$ of $Rh_{17}S_{15}$. The insets (a) and (b) show the low temperature $\rho(T)$ behavior (solid line is a fit to the T^2 dependence) and the observation of superconductivity, respectively.

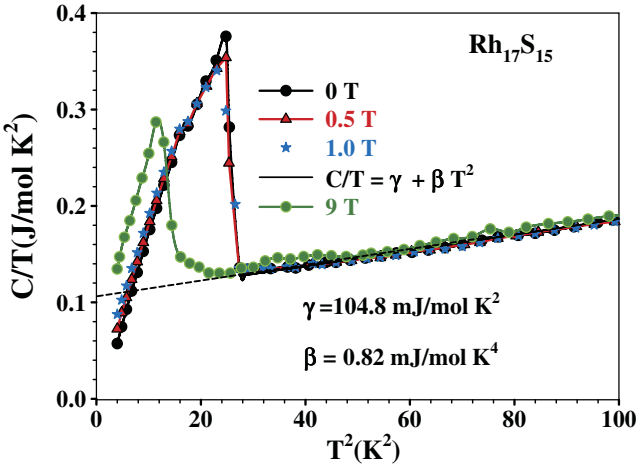

FIG. 3 (color). The temperature dependence of the heat capacity of $Rh_{17}S_{15}$ from 2 to 10 K in a field of 0, 0.5, 1, and 9 T. The jump in the heat capacity ($\Delta C/T$) is 0.24 J/mol $\mathrm{K^2}$. The Sommerfeld coefficient (γ) is estimated to be 104.8 mJ/mol $\mathrm{K^2}$ and $\Delta C/\gamma T_C \approx 2$ suggesting the existence of strong coupling superconductivity in this sample.

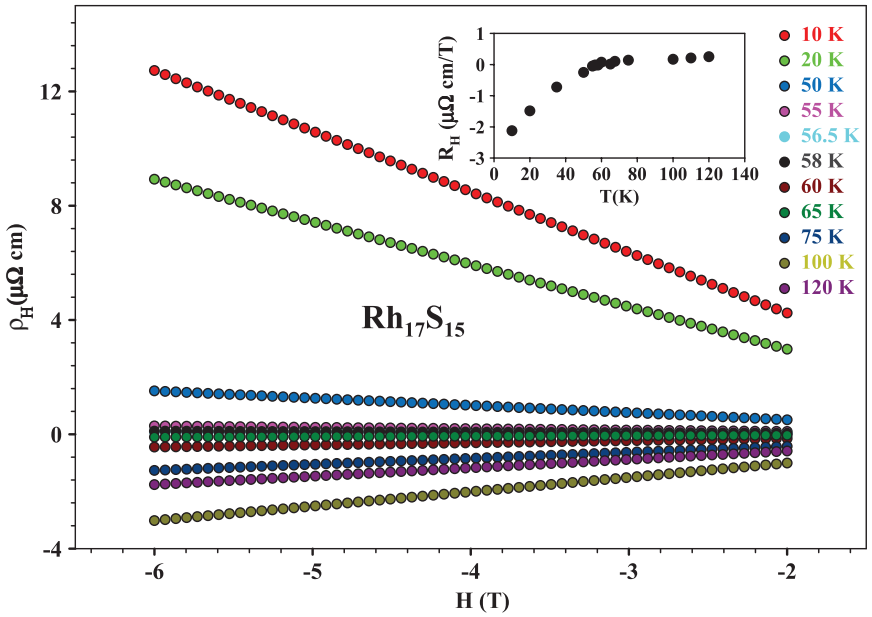

FIG. 4 (color). The Hall resistivity as a function of magnetic field at several temperatures. The temperature dependence of the Hall constant R_H is shown in the inset. One can clearly see the slope change as a function of temperature and the linearity of Hall resistance shows field independency of R_H. The sign reversal of R_H shows the presence of hole end electron conduction in $Rh_{17}S_{15}$.

2–3 orders of magnitude less than that of conventional metals. Since carrier concentrations of electrons and holes are unequal, one cannot regard $Rh_{17}S_{15}$ as a compensated metal. A temperature driven sign change of Hall coefficient has also been seen [9] in oxides such as $CaRuO_3$ and $SrRuO_3$, which is attributed to the unusual structure of the Fermi surface from the band structure calculations. In this scenario, there are broad regions of the Fermi surface where the bands disperse across the Fermi level with nearly zero curvature. However, the physical mechanism for the sign change of R_H is still poorly understood in many compounds. It is interesting to note that the carrier concentration decreases rapidly at low temperatures and the sample undergoes superconducting transition below 5.4 K.

Finally, the temperature dependence of the upper critical field $[H_{C2}(T)]$ illustrated in Fig. 5 clearly deviates from the behavior seen in conventional superconductors in several aspects. To begin with, the temperature dependence of H_{C2} near T_C is different from what one observes in conventional superconductors. Such a concave-upwards curvature curve of H_{C2} vs T is observed in several unconventional superconductors. Second, the large value of the upper critical field ($H_{C2}(T) > 12$ T at 2.5 K which is larger than the Pauli paramagnetic limiting field of 9.99 T) and the fact that $H_{C2}(T)$ 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 $Rh_{17}S_{15}$. Moreover, the solid line shown in the Fig. 5 is a good fit to the formula, $H_{C2}(T) = H_{C2}(0)\,[1 - (T/Tc)^{3/2}]^{3/2}$ where T_C is the transition temperature at zero field. The estimated value of $H_{C2}(0)$ is 23.5 T and the value of T_C is 5.4 K. This temperature dependence of the upper critical field is a characteristic feature of charged bosons in the narrow-band system [10,11]. For charged bosons, a large value of $H_{C2}(0)$ is expected and one expects a λ-type anomaly in the heat capacity at T_C which is not seen here (Fig. 3 shows nearly a mean-field–like superconducting transition).

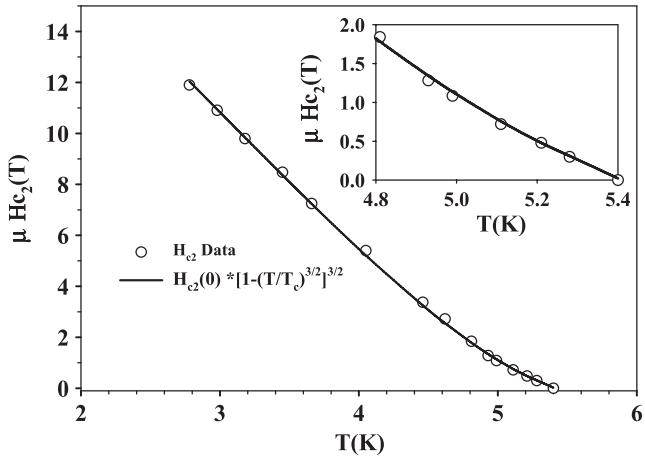

FIG. 5. The temperature dependence of the upper critical field $H_{C2}(T)$ of $Rh_{17}S_{15}$. The inset shows the variation of $H_{C2}(T)$ near T_C which is different from the expected behavior for conventional superconductors. The upper critical field at 2.5 K is more than 12 T and its temperature dependence does not show any tendency towards saturation implying unconventional nature of the superconductivity in this system. The solid line is a fit to the theory (see text).

However, such a fit has been used to explain the temperature dependence of the upper critical field of oxides ($Ba_{1-x}K_xBiO_3$) as well of intermetallic superconductors such as borocarbides [10,11]. The experimental results suggest that the narrow $4d$ band electrons play an important role in the superconducting pairing mechanism in $Rh_{17}S_{15}$.

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 sublattice 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 [12]. Although 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 [13–15]. 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. However, the observation of T^2 dependence of $\rho(T)$, enhanced susceptibility, moderate γ, large value of the upper critical field, 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. Clearly one requires theoretical input to understand the superconductivity in the low carrier system $Rh_{17}S_{15}$.

From the experimental point of view, one needs investigation on high quality single crystals of this compound. The presence of cage structure allows us to tune the properties of this sulfide and in this regard, it is interesting to compare $Rh_{17}S_{15}$ with a related structure of Co_9S_8 [16] which has a larger unit cell. It is a distinct possibility that more complex bonding and packing of atoms in the $Rh_{17}S_{15}$ structure leads to the shortening of the bonds of the single Rh atom in the unit cell having octahedral coordination thereby achieving the reduction in the unit cell volume compared to that of Co_9S_8 [16]. Detailed substitution studies in which Rh is replaced by Co in $Rh_{17}S_{15}$ as well as Co replaced by Rh in Co_9S_8 will lead to better understanding of structure as well as effects on the superconductive properties of $Rh_{17}S_{15}$. In addition, the insertion of alkali or alkaline earth metals is possible in large vacancies in the c positions (surrounded by 8 Rh and 2 S atoms) of $Rh_{17}S_{15}$ [17]. Such studies are in progress.

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