

Superconductivity, Magnetism, and Atomic Rattling Phenomena in $R_3Rh_4Ge_{13}$ ($R = Y, Yb, Lu$)

A.M. STRYDOM*

Highly Correlated Matter Research Group, Physics Department, University of Johannesburg,
PO Box 524, Auckland Park 2006, South Africa

We give a first report of the physical properties of the pair of cubic intermetallic compounds $R_3Rh_4Ge_{13}$, with R being either Yb or Lu. The crystal structure can be described in terms of 3 atomic cages, and we reveal how certain thermal physical properties are inherent to this particular atomic layout. Close to room temperature, $Yb_3Rh_4Ge_{13}$ displays strong paramagnetism originating from Yb^{3+} ions, but upon cooling though 100 K the magnetic susceptibility and electrical resistivity behave according to a thermally driven valence instability, and we classify $Yb_3Rh_4Ge_{13}$ therefore as an intermediate valent f -electron system. $Lu_3Rh_4Ge_{13}$ behaves in a diamagnetic manner throughout our accessible temperature range, – first with a weakly temperature-dependent magnetic susceptibility below room temperature, and finally with a precipitous drop in the electrical resistivity to zero at 2.5 K when superconductivity sets in.

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1. Introduction

The availability of diverse materials classes in the study of correlated matter and cooperative phenomena have contributed vastly towards our understanding of exotic behaviour in metals, semiconductors, and superconductors. For example, one may consider the influential role that crystal symmetry of the lattice environment plays in the magnetic behaviour of an ion, in particular modes of thermal vibration and thermal conductivity, in anisotropy of the Kondo semiconducting state, or on the nature of superconductivity that may occur in a material's ground state.

A particularly profitable materials class in the study of correlated matter has been the ternary intermetallic family of compounds denoted by the nominal stoichiometry ratio $R_3T_4X_{13}$. R is either a rare-earth element, an early d -block element such as Sc or Y, or one of the two alkali-earth metals Ca or Sr. T stands for a Group VIII d -electron element, and X is In, Ge, or Sn. The $R_3T_4X_{13}$ series is identified by the cubic crystal structure of space group $Pm-3n$ which is adopted by the majority of R , T , and X combinations. The announcement of the formation of $R_3T_4X_{13}$ phases is generally accredited to Reimeika *et al.* [1], but the literature refers to the archetypal $R_3T_4X_{13}$ phase as either the $Pr_3Rh_4Sn_{13}$ structure type following the crystallographic analysis furnished by Vandenberg [2], or the $Yb_3Rh_4Sn_{13}$ type due to the work of Hodeau *et al.* [3]. This structure type offers a single site for occupation by each of the R and T atoms, and two distinct sites are available to the X atom.

Having initially attracted attention due to superconductivity [1], this has remained a topic of debate among

$R_3T_4X_{13}$ compounds [4, 5], with superconducting temperatures as high as $T_{sc} = 8$ K in $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$ [1]. $Ce_3Ir_4Sn_{13}$ [6] and $Ce_3Rh_4Sn_{13}$ [7] are classified as heavy-fermion systems. By comparison to the stannides, compounds having $X = Ge$ have received comparatively less attention but in $Y_3Ir_4Ge_{13}$, for instance [8], a peculiar aspect of the crystal structure in this materials class was illustrated, namely the formation of atomic cages and its effect on thermal transport and other properties, related to lattice vibration modes. We finally mention also the extraordinary behaviour found in $Yb_3Ir_4Ge_{13}$, – a compound in which exploratory studies have demonstrated the formation of a charge ordered sublattice [9].

In this work we focus on the three Rh-based germanides $Y_3Rh_4Ge_{13}$, $Yb_3Rh_4Ge_{13}$, and $Lu_3Rh_4Ge_{13}$. The formation of all three compounds was announced by Venturini *et al.* [10]. To our knowledge, the extent of physical properties reported to date on these three compounds is the superconducting critical temperature $T_{sc} = 2.3$ K reported by Segre *et al.* [11], although a later study [12] failed to detect superconductivity above 1.3 K in either $Y_3Rh_4Ge_{13}$ or $Lu_3Rh_4Ge_{13}$.

2. Experimental

Polycrystalline samples of the three title compounds were prepared by a stoichiometric composition of starting elements of 99.99 wt.% purity or better. The Y- and Lu-based samples were arc-melted in a static atmosphere of purified argon gas. $Yb_3Rh_4Ge_{13}$ was synthesized by a solid-state reaction that profited from the relatively low melting temperature (824 °C) of Yb metal, following a finely controlled temperature profile and repeated mechanical homogenization. Powder x-ray diffraction surveys were conducted to ensure phase purity. Magnetic properties were studied in a squid-based magnetometer

*e-mail: amstrydom@uj.ac.za

from Quantum Design Inc. (San Diego), and physical properties were collected using various measurement options on a PPMS station also from Quantum Design.

3. Results and discussion

Figure 1 shows an X-ray diffractogram obtained on a powdered sample of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$, together with a least-squares profile refinement. The material was deemed phase-pure, as were the $\text{Y}_3\text{Rh}_4\text{Ge}_{13}$ and $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ compounds. For $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ we determined a cubic lattice parameter of $8.926(1)$ Å, which is within less than 0.2% of the value in the literature [10].

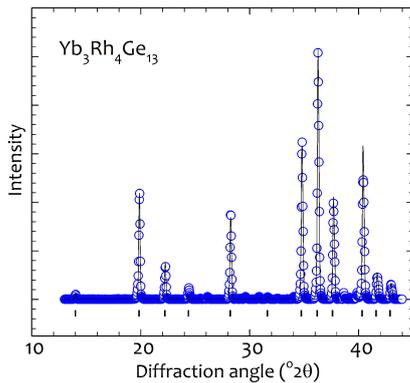


Fig. 1. Powder X-ray diffractogram of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$, representing the compounds synthesized in this work. The solid line represents a Rietveld refinement according to the expected Bragg diffraction peak positions (vertical markers).

Figure 2 plots the inverse Yb-molar magnetic susceptibility of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. Above ~ 300 K there is Curie-Weiss behaviour evident, $1/\chi \propto T$, in accordance with an effective magnetic moment of $4.53(1)\mu_B$. This is close to the $\mu_{eff} = 4.54\mu_B$ value for ytterbium in its magnetic Yb^{3+} state. In the 50–300 K range χ deviates from its high-temperature free-ion behaviour. There are two likely origins for this behaviour. One is crystal-electric field action on the Yb^{3+} ion. A thermally driven hybridization into the $4f^{13+\delta}$ intermediate-valent state between $4f$ electrons and conduction electrons may however also be responsible for the decrease in $\chi(T)$ below 300 K, and we believe this to be the more plausible mechanism in the case of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. We note furthermore that $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ achieves at $T = 2$ K and $B = 7$ T a magnetization (not shown) of only $M = 0.06\mu_B/\text{Yb}$, which also points towards a severely reduced magnetic moment of Yb. This issue is addressed further below. Shown in the inset of Fig. 1 is a low-temperature view of $\chi(T)$. A cusp is reached at ~ 3 K before $\chi(T)$ diminishes below a well-defined inflection point at $T_N = 2.3$ K. We tentatively ascribe this to antiferromagnetic ordering of the Yb-sublattice. Further work is in progress to clarify the ground state of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ in this regard. $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$

has a small and nearly temperature-independent diamagnetic susceptibility (not shown) over most of the temperature range below 300 K.

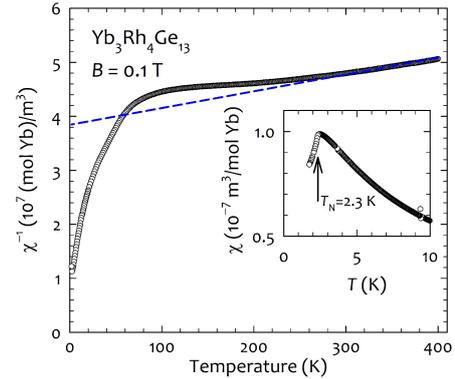


Fig. 2. Inverse magnetic susceptibility of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ (main panel) with a Curie-Weiss fit (blue line) of the high-temperature data. In the inset the low-temperature data are shown with a peak feature at $T_N = 2.3$ K.

In Fig. 3 we illustrate the electrical resistivity of the three title compounds on a common temperature axis. Very different temperature dependencies are evident, and metallic behaviour with a positive temperature coefficient of the electrical resistivity $\rho(T)$ is found only in the case of the magnetic compound $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. However, the resistivity of this compound resembles the behaviour of conduction electrons that become so strongly hybridized with $4f$ electrons that the Yb ions are reduced to an intermediate valent state. We illustrate the effect of these dynamics by means of a comparison with the blue line in Fig. 3, which represents the typical progression for electron-phonon scattering for an ordinary metal.

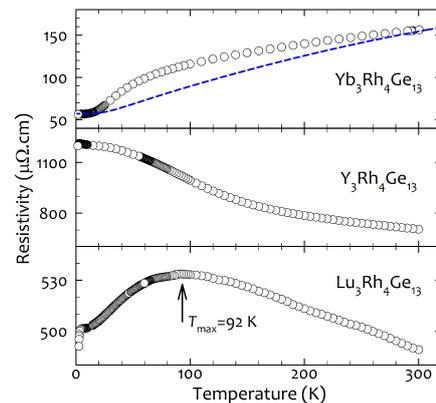


Fig. 3. Temperature dependence of electrical resistivity of the three $R_3\text{Rh}_4\text{Ge}_{13}$ compounds studied in this work.

The electrical resistivity of the two nonmagnetic compounds $\text{Y}_3\text{Rh}_4\text{Ge}_{13}$ and $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ is illustrated in Fig. 3. For both the resistivity is found to increase

with decreasing temperature below 300 K, culminating in residual $T \rightarrow 0$ resistivity values that are 10–20 times as high as that of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. These two nonmagnetic compounds may therefore be classified as semiconducting. There is a broad maximum in $\rho(T)$ of $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ at $T_{max} = 92$ K, but the origin of this anomaly is not known at present. The semiconducting behaviour found in $\text{Y}_3\text{Rh}_4\text{Ge}_{13}$ and $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ continues the trend that was earlier established in the Ru-based compounds $\text{Y}_3\text{Ru}_4\text{Ge}_{13}$ and $\text{Lu}_3\text{Ru}_4\text{Ge}_{13}$ [13]. However the prevalence of semiconduction among the ruthenates is not exclusive to nonmagnetic compounds, since $R_3\text{Ru}_4\text{Ge}_{13}$ compounds with $R = \text{Nd}, \text{Dy}, \text{Ho}, \text{and Er}$ [13] behave in a similar manner in spite of the involvement of local-moment rare earth ions. In $\text{Yb}_3\text{Ru}_4\text{Ge}_{13}$ an effective high-temperature moment of only about a half of that of the free-ion moment was found [13], and its electrical resistivity is also rather metallic-like with a temperature dependence similar to that of the present intermediate-valent compound $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ becomes superconducting below $T_{SC} = 2.5$ K. The findings of an earlier report [11] are thus confirmed, and we illustrate the electrical resistivity of $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ in Fig. 4 on a semi-log plot, together with exploratory data collected of $\rho(T)$ in an applied field of 1.5 T.

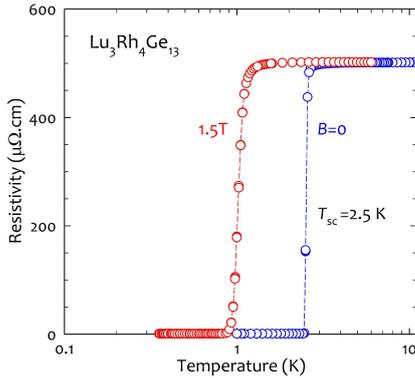


Fig. 4. Electrical resistivity of $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ at low temperature on a semi-log plot, in zero and $B = 1.5$ T applied fields.

The thermoelectric power $S(T)$ is of particular value in sensing changes that occur in the location of the narrow $4f$ electron bands of correlated materials, and in principle a temperature-driven hybridization is expected to have shifts in the $4f$ -electron spectral weight at the Fermi energy mimicked by $S(T)$. In Fig. 5 we illustrate the thermoelectric power of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$. As a first approach, two regions of $S(T)$ linear in T are identified, across 60–160 K, and again between 10–20 K, which are separated by a change in the sign of S at 65 K. For normal metals with light charge carriers, with a spherical Fermi surface and with an isotropic relaxation time, the drift thermopower, evaluated from the linearized Boltzmann equation in the degenerate limit ($k_B T \ll E_F$), may be written [14] as $S(T) = (\pi^2 k_B^2 T / 3e) [\partial \ln N(E) / dE]_{EF} =$

$S_0 T [\partial \ln N(E) / dE]_{EF}$, which is linear in T to a first approximation. At low temperatures furthermore, where the scattering relaxation time is limited by defect scattering, the free-electron approximation again yields $S(T) = S_0 T / E_F$. However the first of the above expressions is considered to be sound even in the case of a multiband Fermi liquid, as well as when strong electronic correlations are present [15]. The negative $S(T)$ of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ at low temperatures is characteristic of correlated electron ytterbium compounds, and this distinct behaviour, as opposed to the generally positive $S(T)$ of Ce compounds, is also understood from the theoretical point of view [15].

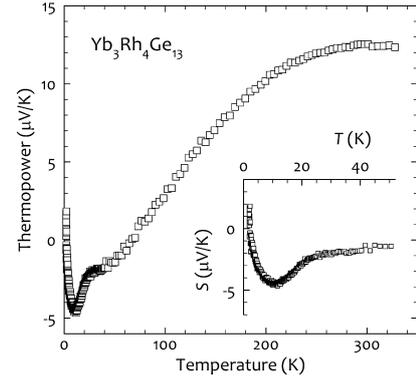


Fig. 5. Overall thermoelectric power $S(T)$ of $\text{Yb}_3\text{Rh}_4\text{Ge}_{13}$ (main panel) and low-temperature limiting behaviour (inset).

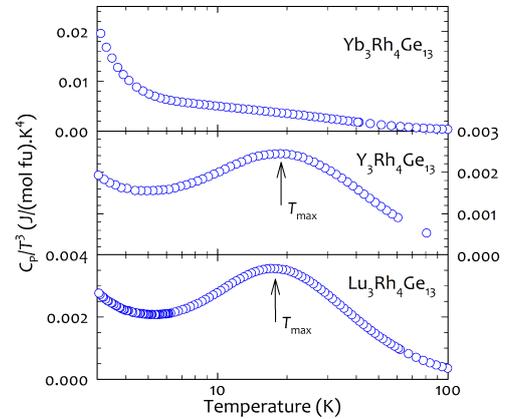


Fig. 6. Specific heat in the form $C_P(T)/T^3$ of the three title compounds on a log T axis. Maxima achieved in the cases of $\text{Y}_3\text{Rh}_4\text{Ge}_{13}$ and $\text{Lu}_3\text{Rh}_4\text{Ge}_{13}$ are related to the excitation of optical lattice vibration modes as discussed in the text.

Finally, we turn to the specific heat of the presented three compounds. In materials having filler atoms confined to over-sized atomic cages, the anharmonic motion of the filler atoms may produce optical phonon modes superimposed upon acoustic vibration modes, that originate from the thermal phonons being excited by the re-

remainder of the lattice. For the number of optical modes N_E we have, for the Einstein model of heat capacity, $C_E(T) = (3N_ER)y^2 e^y / (e^y - 1)^{-2}$, with $y = \theta_E/T$. It can be shown [8] that casting the specific heat as $C_P(T)/T^3$ results in a maximum at $T_{max} \approx \theta_E/5$, in case when optical phonon modes are present to any significant measure. Figure 6 compares the specific heats of $Y_3Rh_4Ge_{13}$, $Yb_3Rh_4Ge_{13}$, and $Lu_3Rh_4Ge_{13}$ in this manner. The specific heat of $Yb_3Rh_4Ge_{13}$ is clearly without the signature maximum in $C_P(T)/T^3$, whereas in both the nonmagnetic compounds maxima are found, at 18.7 K (Y) and at 17 K (Lu). The R atom as well as one of the two Ge atoms in the $R_3Rh_4Ge_{13}$ unit cell can be considered as filler atoms, and although we refrain at this stage of our investigation from a quantitative assignment of the modes involved, we note nevertheless that as the compound with the smaller molecular mass, $Y_3Rh_4Ge_{13}$ would in fact be expected to yield on average the higher frequency spectrum (higher θ_E) of optical phonons compared to $Lu_3Rh_4Ge_{13}$.

4. Conclusions

The three cubic compounds $Y_3Ru_4Ge_{13}$, $Yb_3Rh_4Ge_{13}$, and $Lu_3Rh_4Ge_{13}$ exhibit contrasting electronic properties. The two nonmagnetic compounds (Y and Lu) are semiconducting, and yet $Lu_3Rh_4Ge_{13}$ becomes superconducting below 2.5 K which classifies this as a rare low-charge carrier density superconductor containing only metallic elements. The two nonmagnetic compounds furthermore display the presence of optical modes in their phonon excitation spectra and this we ascribe inherently to details of the cage-like crystal structure found in the class of material. $Yb_3Rh_4Ge_{13}$ on the other hand is a strong paramagnet with $4f$ -conduction electron hybridization, that turns it into an intermediate valent state. Interestingly, the electronic ground state of $Yb_3Rh_4Ge_{13}$ compound is played out by magnetic ordering among Yb^{3+} ions, – probably of antiferromagnetic nature.

Further characterization of the low-temperature properties of these compounds is in progress, and will be the subject of future reports.

Acknowledgments

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