Resistivity and magnetic-susceptibility studies in the $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Ho, Er, Yb, Lu, and Y) system

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In this paper we report the susceptibility and resistivity studies of cubic $R_3Ru_4Ge_{13}$ (R=Nd–Y) from 1.5 to 300 K. We find that the compounds (R=Nd–Yb) show paramagnetic behavior above 1.5 K whereas $Lu_3Ru_4Ge_{13}$ and $Y_3Ru_4Ge_{13}$ exhibit diamagnetism and Pauli paramagnetism above 4.2 K, respectively. They also undergo a superconducting transition at 2.3 K and 1.8 K, respectively. The resistivity of all the samples except that of $Yb_3Ru_4Ge_{13}$ increases with the decrease of temperature from 300 K down to 1.5 K. The most interesting aspect is the positive temperature coefficient of resistivity of the Yb sample in the same temperature range. The results are compared with the RBiPt system where one has observed similar results.

I. INTRODUCTION

A large number of studies have been made on the subject of magnetism and superconductivity in ternary rare earth intermetallics such as RMo_6S_8 and RRh_4B_4.[1] In these compounds, superconductivity arises due to Mo or Rh clusters whereas the magnetism arises due to the rare-earth atom. A series of intermetallic compounds with no metalloids was reported by Remeika *et al.*[2] These compounds ($R_3Rh_4Sn_{13}$) crystallize in cubic structure $Pm3n$. Among these compounds, those of La, Yb, and Th are superconducting whereas for Gd and Eu compounds a magnetic transition was observed.[3] Efforts were made to look for similar systems with germanides which can display superconductivity and magnetism. Segre and Braun[4] were successful in reporting superconductivity and magnetic order in $R_3Ru_4Ge_{13}$ which crystallize in the same $Pm3n$ structure. However, no detailed measurements of the temperature dependence of the susceptibility or resistivity were reported except for the lattice constants and the transition temperatures of these compounds. In this paper we have studied the temperature dependence of the susceptibility and resistivity of all the compounds from 1.5 to 300 K. Although the susceptibility data exhibit normal Curie-Weiss behavior (for magnetic rare-earth atoms) their resistivity behavior is quite anomalous. Similar behavior has been recently reported in the RBiPt (Ref. 5) series.

II. EXPERIMENTAL DETAILS

All the samples of the $R_3Ru_4Ge_{13}$ system were made by melting the individual constituents taken in stoichiometric proportions in an arc furnace under a high purity argon atmosphere. The purity of the rare-earth elements is 99.9% whereas the purity of Ru and Ge is 99.99%. The samples were annealed at 900 °C for 2 weeks in a sealed quartz tube with a He atmosphere. All the samples were found to have a cubic structure of the type $Pm3n$ ($Yb_3Rh_4Sn_{13}$ structure) and the lattice constant a agrees with the previously published values.[4] The variation of lattice constant a with R (R=Ce–Lu) in $R_3Ru_4Ge_{13}$ is shown in Fig. 1. The temperature dependence of the susceptibility (χ) was measured using a Faraday balance in a field of 4 kOe from 80 to 300 K and a home built ac susceptometer[8] was used in the temperature range from 1.5 to 100 K. The resistivity was measured using a four probe dc technique and the contacts were made using ultrasonic soldering iron (with nonsuperconducting solder) on a cylindrical sample of 2 mm diameter and 10 mm length. The temperature was measured using a calibrated Si diode (Lake Shore Inc.) sensor. The sample voltage was measured with a Keithley nanovoltmeter with a current of 25 mA using a 20 ppm stable HP current source. All the data are collected using an IBM compatible PC/AT via IEEE-488 interface.

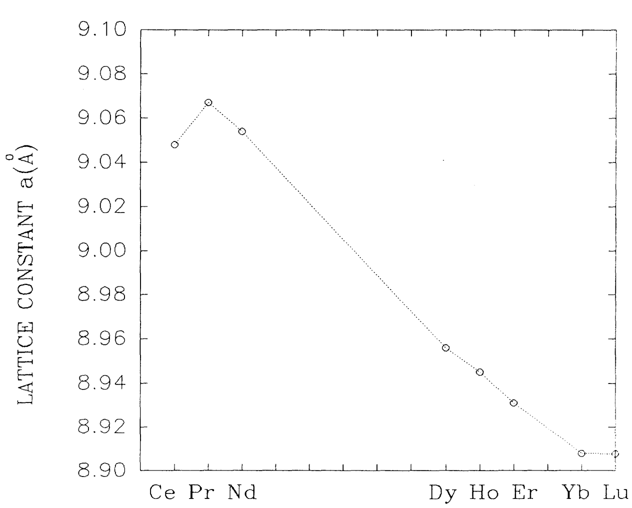

FIG. 1. Variation of lattice constant a with R in $R_3Ru_4Ge_{13}$. The dashed line is a guide to the eye.

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III. RESULTS AND DISCUSSION

A. Susceptibility studies

The temperature dependences of the inverse susceptibility ($1/\chi$) for $R_3Ru_4Ge_{13}$ (R= Ho, Dy, and Er) in the temperature range 5 to 300 K are shown in Fig. 2. Similar data for Nd and Yb samples are shown in Fig. 3. The temperature dependence of χ fits well to the Curie-Weiss relation $\chi = C/(T - \theta_p)$ in the temperature range 150–300 K (which is shown as a solid line in the respective figures) except for the Yb sample. For the Yb sample, we have used a modified expression, $\chi = \chi_0 + C/(T - \theta_p)$. The values of the lattice constants C, χ_0, θ_p, μ_{eff}, and μ_{free} are given in Table I. From this table one can see that the values of μ_{eff} are close to that expected from Hund's rules for the trivalent rare-earth ions except for the Yb sample. Our data agree with the qualitative data (since their upper limit of measurement is only 18 K) of Segre and Braun.[4] The positive values of θ_p suggest that we have ferromagnetic coupling between the rare-earth ions for Nd, Dy, and Er samples whereas the negative θ_p values for Ho and Yb samples suggest the coupling is antiferromagnetic in nature. The effective moment of Yb sample is much smaller than the free ion moment. Moreover from Fig. 1, one can observe an anomaly in the lattice constant for the Yb sample since its measured value is almost the same as that of the Lu sample. This value is different from the expected value based on the lanthanide contraction. This could imply that the Yb sample is probably mixed valent in this series. Preliminary results[10] show that $Ce_3Ru_4Ge_{13}$ is a mixed valent compound. We have also carried out ac susceptibility measurements on these samples down to 1.5 K which do not show any magnetic ordering. This is consistent with the previously published data of Segre and Braun.[4]

The temperature dependences of χ of the Lu and Y samples are shown in Figs. 4 and 5 respectively. The Lu sample is weakly diamagnetic at room temperature with

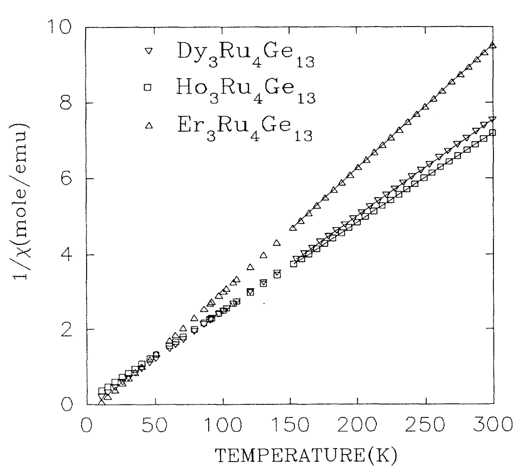

FIG. 2. Variation of inverse susceptibility ($1/\chi$) of $R_3Ru_4Ge_{13}$ (R=Dy, Er, and Ho) from 5 to 300 K. The solid line indicates the fit to Curie-Weiss law from 150 to 300 K.

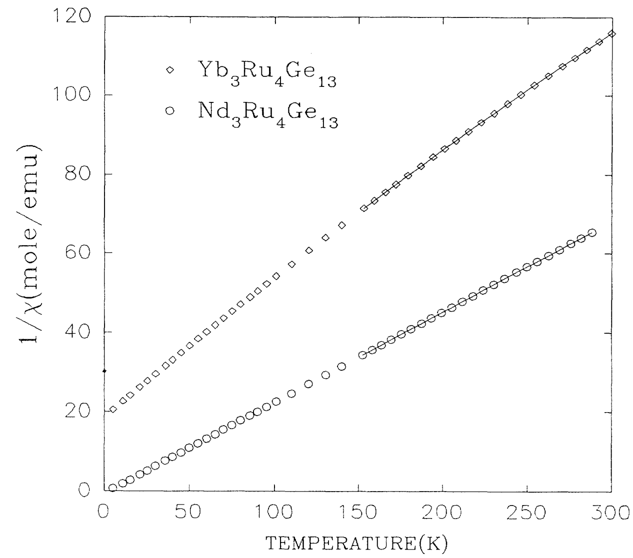

FIG. 3. Variation of inverse susceptibility ($1/\chi$) of $Nd_3Ru_4Ge_{13}$ and $Yb_3Ru_4Ge_{13}$ from 5 to 300 K. The solid line indicates the fit to Curie-Weiss law from 150 to 300 K.

TABLE I. Magnetic properties of $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Er, Ho, and Yb).

R	θ_p	χ_0	C	μ_{eff}	μ_{free}	Ref. 4[a]
Nd	2.7 K		4.4 emu/mol K	$3.4\mu_B$	$3.62\mu_B$	$3.8\mu_B$
Dy	2.3 K		39.5 emu/mol K	$10.3\mu_B$	$10.6\mu_B$	$10.6\mu_B$
Er	8.3 K		30.6 emu/mol K	$9.04\mu_B$	$9.6\mu_B$	$10.0\mu_B$
Ho	-6.0 K		42.5 emu/mol K	$10.6\mu_B$	$10.6\mu_B$	$10.6\mu_B$
Yb	-49.2 K	0.0013[b]	2.6 emu/mol K	$2.6\mu_B$	$4.5\mu_B$	$2.6\mu_B$

[a]The values of μ_{eff} are reported in Ref. 4 obtained by fitting χ data from 4 K to 18 K.
[b]Value of χ_0 for $Yb_3Ru_4Ge_{13}$ in emu/mol.

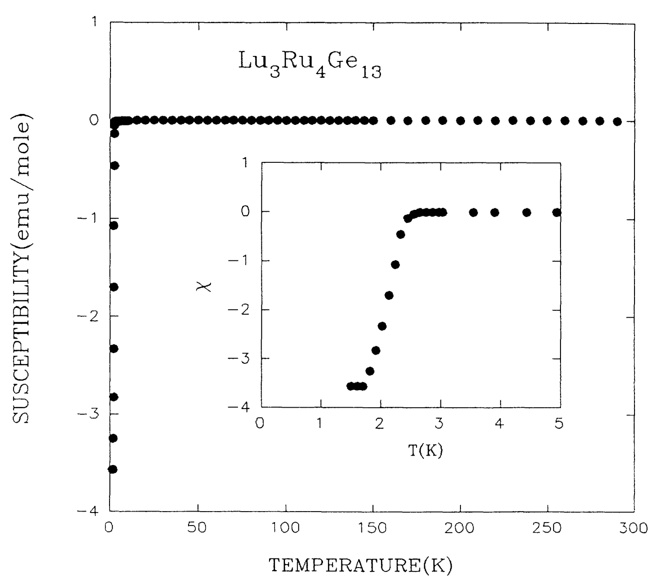

FIG. 4. Temperature dependence of the susceptibility of $Lu_3Ru_4Ge_{13}$ from 1.5 to 300 K. The inset shows the superconducting transition.

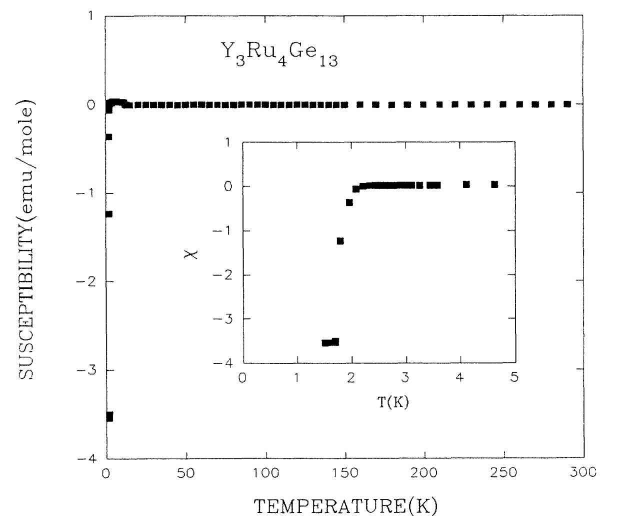

FIG. 5. Temperature dependence of the susceptibility of $Y_3Ru_4Ge_{13}$ from 1.5 to 300 K. The inset shows the superconducting transition.

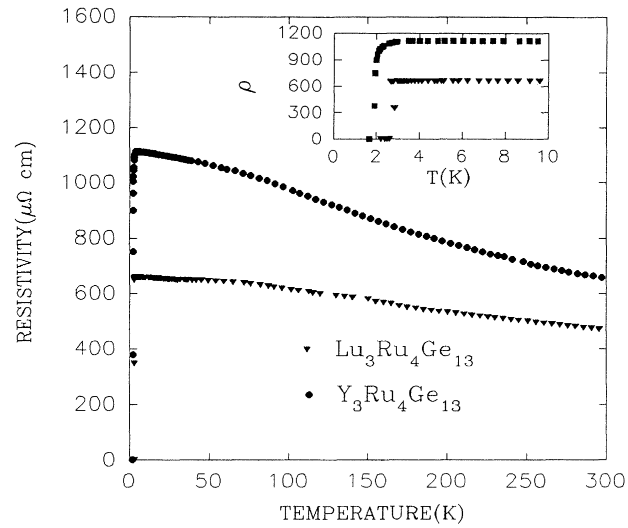

FIG. 7. Temperature dependence of the resistivity $\rho(T)$ of $R_3Ru_4Ge_{13}$ (R=Lu and Y) from 1.5 to 300 K. The inset shows the superconducting transition of these two samples.

very little temperature dependence down to 3 K. The Y sample is Pauli parmagnetic and also exhibits very little temperature dependence down to 2 K. The insets show the diamagnetism at 2.3 K for the Lu sample and 1.8 K for the Y sample. These studies indicate that apart from the Yb sample, the temperature dependences of χ of this series are quite normal and they are expected from that of typical rare-earth intermetallics. However, the temperature dependence of the resistivity of $Yb_3Ru_4Ge_{13}$ is quite anomalous as we shall see in the next section.

B. Resistivity studies

The temperature dependence of resistivity (ρ) for $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Ho, and Er) samples are shown in Fig. 6. The temperature dependences of ρ for the Y and Lu samples are shown in Fig. 7. The inset shows the superconducting transitions of these two samples. The temperature dependence of ρ for the Yb sample is shown in Fig. 8. The inset shows the low temperature behavior of ρ. As we can see, all the samples except for Yb show *unusual semiconducting behavior* from 1.5 to 300 K. In fact, the plots of lnρ vs $1/T$ are linear (from 100 to 300 K) which are shown in Figs. 9 and 10 for these compounds. The $d\rho/dT$ decreases monotonically as the rare-earth series is traversed. Such a dependence (shown in Fig. 11) suggests that the resistivity values of these compounds are dominated by the unit cell volume. Here, the value of $d\rho/dT$ is computed at 297 K. The resistivity of the Yb sample is smaller than that of other members of this se-

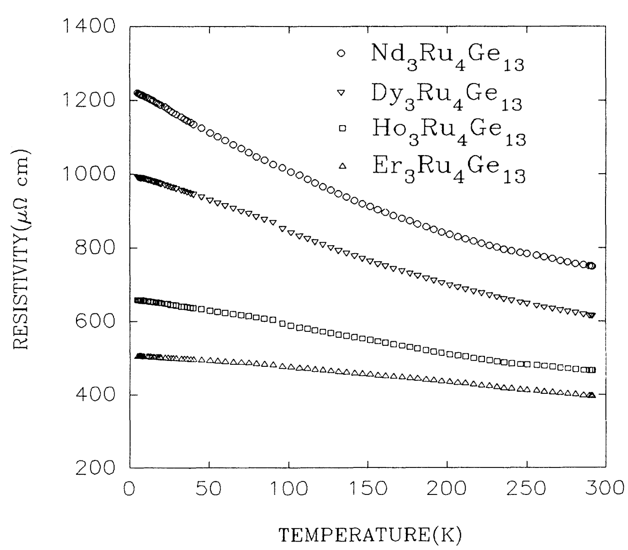

FIG. 6. Temperature dependence of the resistivity $\rho(T)$ of $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Er, and Ho) from 1.5 to 300 K.

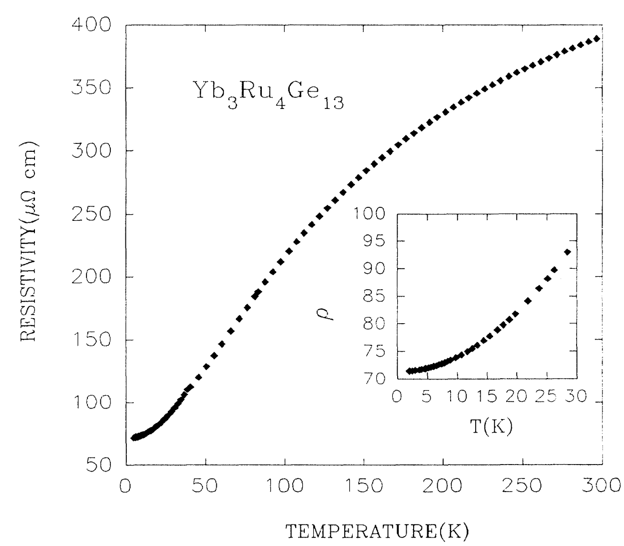

FIG. 8. Temperature dependence of the resistivity $\rho(T)$ of $Yb_3Ru_4Ge_{13}$ from 1.5 to 300 K. The inset shows the resistivity from 1.5 to 30 K.

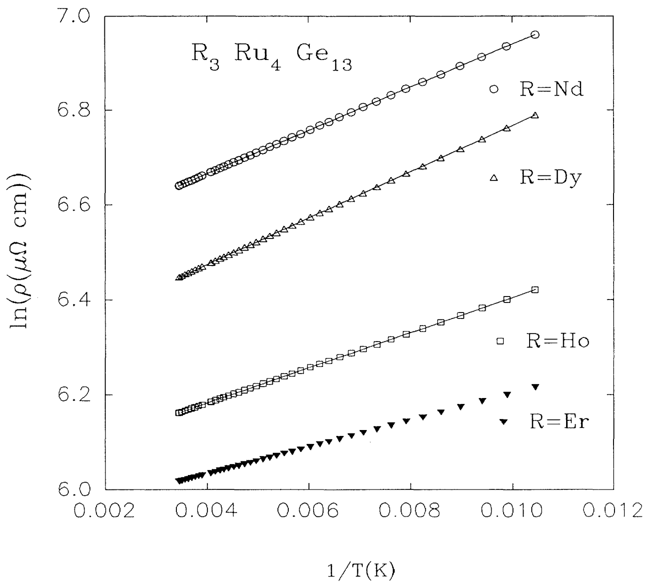

FIG. 9. Plot of ln(ρ) vs $1/T$ of $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Ho, and Er) from 150 to 300 K.

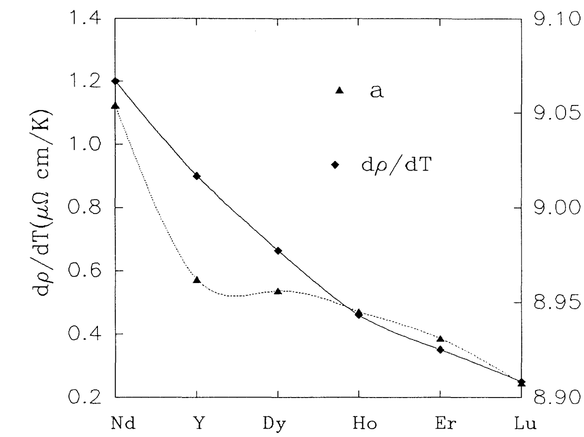

FIG. 11. Values of $d\rho/dT$ (room temperature) and lattice constant a for $R_3Ru_4Ge_{13}$ (R=Nd, Dy, Ho, Er, Lu, and Y). The lines are a guide to the eye.

ries and shows a metallic behavior. The energy gap value (E_g/k_B, extracted from the high temperature plot) decreases from 50 K for the Nd sample to 28 K for the Lu sample. During their attempt to grow single crystals of the $R_3Bi_4Pt_3$ series, Canfield *et al.*[5] discovered a series RBiPt where R is the rare-earth element beyond Y. The x-ray diffraction of powdered single crystals shows that the RBiPt series forms in cubic AgAsMg structure.[6] One of the interesting features of these compounds [apart from the heavy fermion behavior of YbBiPt (Ref. 7)], is the negative dR/dT, where R is the electrical resistivity of these compounds. Except for the Yb and Lu samples of the RBiPt series, the resistivity of all compounds show similar behavior from just above their antiferromagnetic transition temperature (T_N) to room temperature. Here

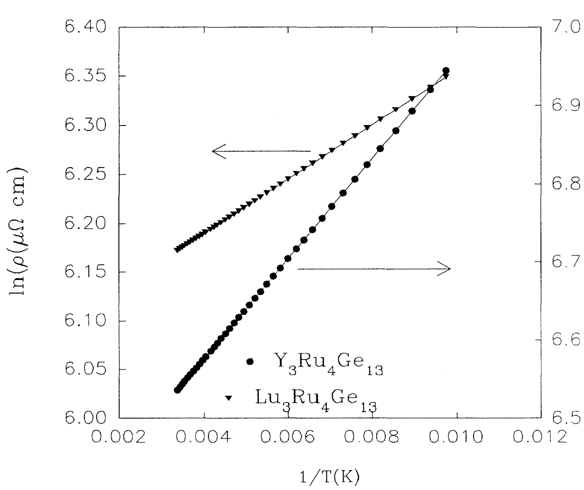

FIG. 10. Plot of ln(ρ) vs $1/T$ of $R_3Ru_4Ge_{13}$ (R=Lu and Y) from 150 to 300 K.

one also sees semiconducting behavior but these compounds order antiferromagnetically above 1.5 K. They have suggested that a RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction may be responsible for this ordering and it would have to be mediated by a possibly smaller number of conduction electrons, given the high resistance of these compounds. Further, they seemed to indicate that the resistive anomalies seen in these compounds can be attributed to the development of a superzone gap, implying the existence of an s-f interaction necessary for the RKKY mechanism. We suggest that the resistive anomalies seen in the $R_3Ru_4Ge_{13}$ series are similar to those of the RBiPt series. Failure to observe the magnetic transition in our compounds could be ascribed to the large value of the R-R distance in $R_3Ru_4Ge_{13}$ where the lattice constant a is 1.5 times that of the RBiPt series.

Another interesting aspect of our studies is that we have also found two superconducting samples $Lu_3Ru_4Ge_{13}$ (T_C=2.3 K) and $Y_3Ru_4Ge_{13}$ (T_C=1.8 K) which have negative temperature coefficient of resistivity. Their normal state susceptibility data show only a weak temperature dependence. The susceptibility of the Lu sample is diamagnetic and has a value of 3×10^{-4} emu/mol at 297 K whereas that of the Y sample is Pauli paramagnetic and has a value of 7×10^{-5} emu/mol at the same temperature. Observation of superconductivity in these semiconducting samples is rather unusual.[9] It will be extremely interesting to do the Hall effect and heat capacity measurements on these samples. The samples $Ce_3Ru_4Ge_{13}$ and $Pr_3Ru_4Ge_{13}$ also form in this structure and their data will be reported elsewhere.[11]

IV. CONCLUSION

The resistivity studies on the $R_3Ru_4Ge_{13}$ series show anomalous semiconducting behavior similar to those of the recently published RBiPt (Ref. 6) series. However, none of the members of the former series shows magnetic transition above 1.5 K unlike the members of the latter series. We suggest that this could be due to the large value of the R-R distance in $R_3Ru_4Ge_{13}$ where the lattice constant a is 1.5 times larger than that of the RBiPt series. Further Lu and Y samples of the $R_3Ru_4Ge_{13}$ series undergo a superconducting transition which is rather unusual because of their semiconducting behavior in resistivity. The temperature dependence of the resistivity of $Yb_3Ru_4Ge_{13}$ is quite interesting and needs further study.

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