PHYSICAL REVIEW B, VOLUME 64, 224420

Superconductivity in $La_3Rh_2Ge_2$ and dense Kondo behavior in $Ce_3Rh_2Ge_2$

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(Received 10 March 2001; published 21 November 2001)

Magnetic and electrical transport measurements were carried out on two isostructural compounds $La_3Rh_2Ge_2$ and $Ce_3Rh_2Ge_2$. The La-based phase is a weak Pauli paramagnet and shows typical metallic conductivity down to $T_C=3.5$ K where it becomes superconducting. The Ce-based compound exhibits localized magnetism due to the presence of trivalent Ce ions and undergoes an antiferromagnetic phase transition at $T_N=7.5$ K. Subsequently, at $T_t=5$ K, some spin rearrangement takes place resulting in the development of a tiny ferromagnetic component. The electrical resistivity of $Ce_3Rh_2Ge_2$ shows a temperature behavior characteristic of Kondo systems.

DOI: 10.1103/PhysRevB.64.224420 PACS number(s): 75.30.Mb, 74.70.Dd, 72.15.Qm, 75.20.Hr

I. INTRODUCTION

Observation of heavy fermion properties in several cerium-based compounds stimulates continuous interest in experimental investigations on various intermetallic systems. Since the seminal discovery of heavy fermion superconductivity in $CeCu_2Si_2$ by Steglich and coworkers[1] many ternaries with the general formula CeT_2X_2 (T stands for a d-electron transition metal and X is a p-electron metalloid) have been studied thoroughly.[2] Among them were the pressure-induced superconductor $CeRh_2Si_2$ (Ref. 3) and the isostructural but not superconducting compound $CeRh_2Ge_2$.[4] Much effort has also been put on the study of equiatomic phases $CeTX$ (Ref. 5) and interesting results were obtained, e.g., for CeRhGe, which was classified as a magnetically ordered Kondo lattice with enhanced electronic specific heat.[6] More recently, moderate heavy fermion behavior was also observed in antiferromagnetic $Ce_2Rh_3Ge_5$,[7] in contrast to the weak Kondo effect established for another Rh-containing cerium germanide $CeRhGe_3$.[8]

In the ternary system Ce-Rh-Ge, besides the phases mentioned above, there exists also an orthorhombic compound $Ce_3Rh_2Ge_2$,[9] which, to the best of our knowledge, has not been studied up to date with respect to its physical behavior. In the present paper we report on the magnetic and electrical transport properties of this phase as well as its La-based isostructural counterpart $La_3Rh_2Ge_2$.

II. EXPERIMENT

Starting materials for preparation of $La_3Rh_2Ge_2$ and $Ce_3Rh_2Ge_2$ were ingots of the rare-earth metals (Ames Laboratory, 99.9%), rhodium powder (Chempur, 99.9%), and germanium lumps (Chempur, 6 N). Rhodium powder, cold-pressed into small pellets, rare-earth metals, and germanium pieces, taken in the stoichiometric atomic ratio, were arc-melted under a titanium-gettered argon atmosphere. To enhance homogeneity, the samples were turned over and remelted two times. Total sample mass was approximately 800 mg, and the weight losses after melting were less than 0.4 mass %. The samples were subsequently wrapped with molybdenum foil, sealed in evacuated silica tubes and annealed at 800 °C for two weeks.

The crystallographic characterization was performed by means of an x-ray powder-diffraction technique, employing a Huber Guinier G670 image plate camera with $CuK\alpha_1$ radiation and using silicon as an internal standard ($a=543.102$ pm). The x-ray patterns obtained were compared with the ones simulated by the program LAZY PULVERIX (Ref. 10) for the atomic parameters as given in Ref. 9. In each diffractogram only the reflections corresponding to the respective orthorhombic unit cell (space group $Pbcm$) were observed, and the refined lattice parameters were as follows: $a=576.00(6)$ pm, $b=818.90(7)$ pm, and $c=1359.6(1)$ pm for $La_3Rh_2Ge_2$ and $a=567.91(9)$ pm, $b=807.3(1)$ pm and $c=1342.1(2)$ pm for $Ce_3Rh_2Ge_2$, in good agreement with the literature data.[9] Quality of the samples was additionally checked by metallographic analysis. Microstructure photographs of both samples (Fig. 1) show the main phases $La_3Rh_2Ge_2$ and $Ce_3Rh_2Ge_2$. The minority phase was observed in the La-based sample on grain boundaries and in the interior of the grains in the amount of less than 0.3 vol %. No minor phases were observed for the Ce-based sample. Energy dispersive x-ray analysis of the main phases confirmed the ideal composition: $La_{41.8(2)}Rh_{27.2(2)}Ge_{31.0(2)}$ and $Ce_{43.0(3)}Rh_{26.7(2)}Ge_{30.3(2)}$. Uncertainties (in parentheses) were obtained from 10 measured points for each sample.

Magnetic studies were carried out in the temperature range 1.7–400 K and in applied magnetic fields up to 5 T, using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer. The electrical resistivity was measured over the temperature interval 1.5–300 K, employing a conventional four-point dc technique.

III. RESULTS AND DISCUSSION

Magnetic measurements have shown that $La_3Rh_2Ge_2$ is a weakly temperature-dependent paramagnet with the mag-

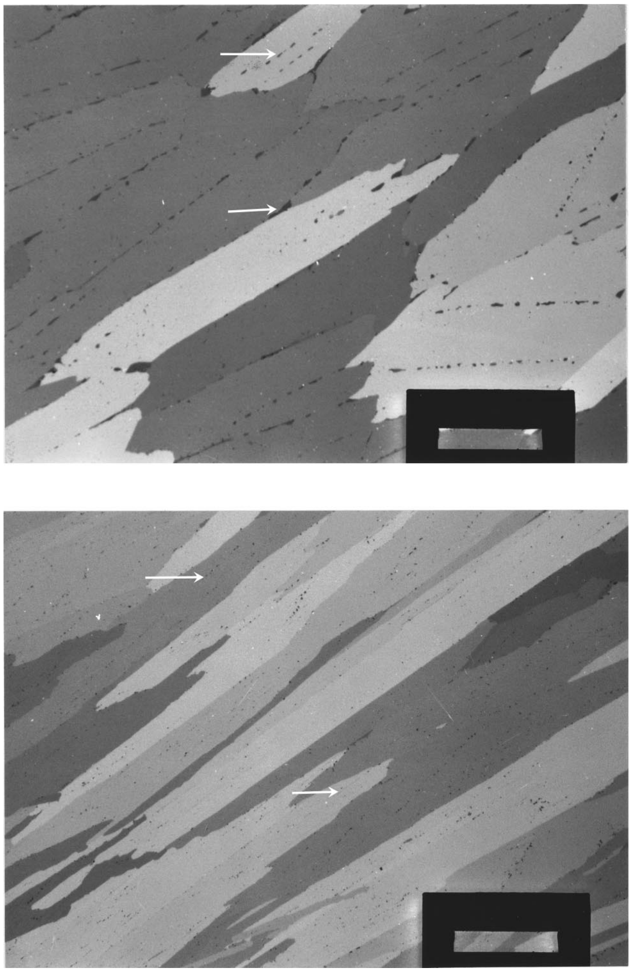

FIG. 1. Microphotographs of the $La_3Rh_2Ge_2$ (upper part) and $Ce_3Rh_2Ge_2$ (lower part) samples in polarized light. The scale slab accords to 100μm. The differences in color of particular grains result from their different orientation with respect to incoming light. For $La_3Rh_2Ge_2$ the arrows show the minority phase on the grain boundaries and in the interior of the grains. For $Ce_3Rh_2Ge_2$ the arrows mark the microcracks.

netic susceptiblity at room temperature of about 4×10^{-7} emu g^{-1} (1×10^{-3} emu mole^{-1} per La atom). Yet, as displayed in Fig. 2, below $T_C=3.5$ K a rather strong diamagnetism occurs in weak magnetic fields, characteristic of a superconducting state. With increasing magnetic field, the absolute value of the magnetization at 1.72 K initially increases, goes through a maximum of approximately 2.5 emu g^{-1} at $H=300$ Oe, and then systematically decreases, being however still not fully suppressed in a field of 5 kOe. No reentrant behavior is observed in $\sigma(T)$ at any field applied. Interestingly, the critical temperature does not change appreciably with increasing field, which implies rather large $(\mathrm{d}H_{c2}/\mathrm{d}T)_{|T_C}$, where H_{c2} is the upper critical field. Characteristic superconductivity features are evident also from the field dependence of the magnetization in $La_3Rh_2Ge_2$ (see Fig. 3). Apparently, the hysteresis loop $\sigma(H)$ taken at $T=1.72$ K is typical for a type-II superconductor. The maximum diamagnetic volume susceptibility observed at this temperature is about -0.662×10^{-3}, which

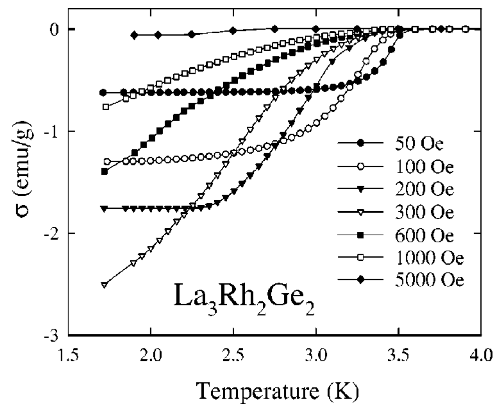

FIG. 2. Low-temperature variations of the magnetization in $La_3Rh_2Ge_2$, measured in different magnetic fields upon cooling the sample in zero field.

corresponds to approximately 83% of the theoretical bulk value of $-1/4\pi$.

Further evidence for the existence of bulk superconductivity in this compound comes from the electrical resistivity data. As shown in Fig. 4, $\rho(T)$ of $La_3Rh_2Ge_2$ exhibits a rapid drop to zero resistance at $T_C=3.5$ K, i.e., just at the onset of diamagnetism. Above T_C the resistivity of $La_3Rh_2Ge_2$ is about 40 $\mu\Omega$ cm and it increases with rising temperature in a strongly nonlinear manner up to approximately 260 $\mu\Omega$ cm at room temperature. A pronounced concave curvature in $\rho(T)$, accompanied by large absolute resistivity values, are characteristic of spin fluctuations in itinerant systems.[11] Hence, it seems that $La_3Rh_2Ge_2$ is a spin fluctuator due to the specific behavior of 4d electrons of rhodium and possibly 5d electrons of lanthanum. In this context it is worth noting that the $\rho(T)$ variation of this compound cannot be described by a simple Bloch-Grüneisen expression, nor will it be explained if a Mott term, which describes interband scattering processes,[12] is added.

The inverse magnetic susceptibility of $Ce_3Rh_2Ge_2$ follows above 120 a modified Curie-Weiss law with the effective magnetic moment μ_{eff} of $2.52\mu_B$, the paramagnetic Curie temperature θ_p of -90 K, and the temperature-

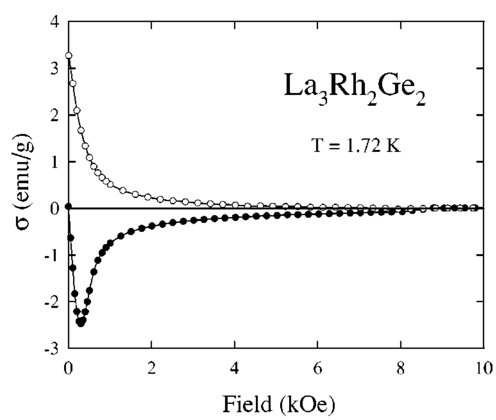

FIG. 3. Field dependence of the magnetization in $La_3Rh_2Ge_2$, taken at $T=1.72$ K with increasing (full circles) and decreasing (open circles) magnetic field.

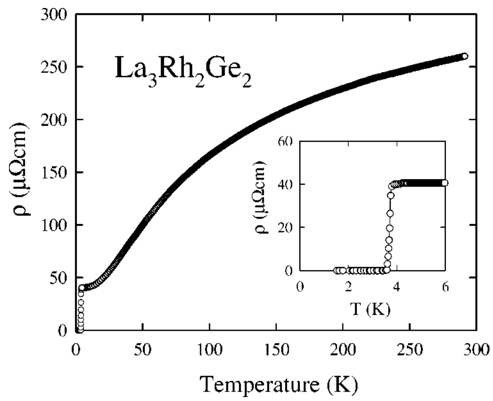

FIG. 4. Temperature dependence of the electrical resistivity of $La_3Rh_2Ge_2$. The inset presents $\rho(T)$ in the vicinity of the superconducting phase transition.

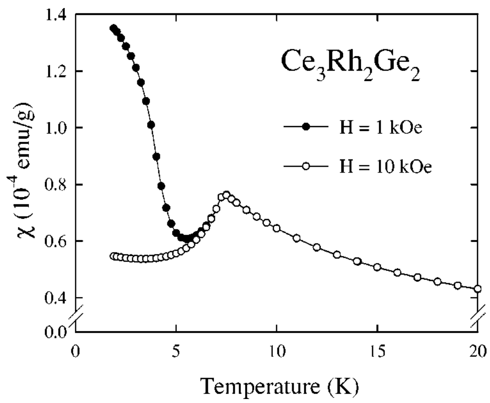

FIG. 6. Low-temperature dependence of the mass magnetic susceptibility of $Ce_3Rh_2Ge_2$, measured in a field of 1 kOe (full circles) and 10 kOe (open circles) upon cooling the sample in zero field.

independent term $\chi_0 = 2.2\times 10^{-4}$ emu mole^{-1} (Ce atom)$^{-1}$ (see Fig. 5). The large negative θ_p may hint at strong antiferromagnetic exchange interaction or rather at a possible Kondo effect, especially since the magnetic ordering temperature is an order of magnitude smaller than θ_p (see below). A slightly convex curvature of $\chi^{-1}(T)$, yielding a non-negligible χ_0 term, may indicate unusually large crystal-field splitting of the $^2F_{5/2}$ ground multiplet of the Ce^{3+} ion or/and it may result from some Pauli contribution of the conduction electrons that presumably have a predominant rhodium $4d$ character. The latter interpretation seems more likely if one notes that the experimental value of μ_{eff} is nearly equal to the Russell-Saunders value for a free Ce^{3+} ion ($g\sqrt{J(J+1)} = 2.54$), and a clear deviation of $\chi(T)$ from the modified Curie-Weiss law, due to gradual thermal depopulation of crystal-field energy levels, occurs only below 120 K.

As inferred from a characteristic maximum in $\chi(T)$ (see Fig. 6), $Ce_3Rh_2Ge_2$ orders antiferromagnetically at $T_N = 7.5$ K. Just below this temperature the susceptibility is independent of magnetic-field strength and the magnetization isotherm taken at $T=7$ K shows an almost straight-line behavior up to 50 kOe with no hysteresis and no remanence (see Fig. 7). Moreover, a careful inspection of this isotherm reveals a slight change in slope around 30 kOe, characteristic of metamagnetic transition, thus corroborating an antiferromagnetic nature of the ordering. However, below $T_t = 5$ K the susceptibility measured in weak fields ($H = 1$ kOe in Fig. 6) exhibits a pronounced ferromagneticlike rise, and in the $\sigma(H)$ dependencies (exemplified by the $T = 1.9$ K isotherm in Fig. 7) there is observed a small but measurable remanent magnetization σ_R. These features indicate that at temperatures lower than T_t a tiny ferromagnetic component develops in the magnetic structure of $Ce_3Rh_2Ge_2$. From the value of σ_R this ferromagnetic component is estimated to be as low as $10^{-3}\mu_B$ (Ce atom)$^{-1}$. Such a small spontaneous magnetization may result either from a small canting of the antiferromagnetically ordered cerium magnetic moments or a little imbalance between the two magnetic sublattices, associated with the two inequivalent positions of cerium atoms in the crystallographic unit cell of $Ce_3Rh_2Ge_2$.[9] In both cases the magnetic ordering remains antiferromagneticlike, as indicated by the field-dependent magnetization $\sigma(H)$ that shows a straight-line behavior in low fields and a clear metamagnetic transition at about 30 kOe.

At room temperature the electrical resistivity of $Ce_3Rh_2Ge_2$ is rather large, possibly because the presence in

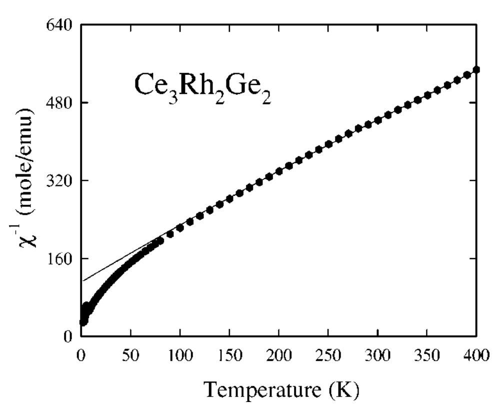

FIG. 5. Temperature dependence of the inverse molar magnetic susceptibility of $Ce_3Rh_2Ge_2$. The solid line is a modified Curie-Weiss fit with the parameters given in the text.

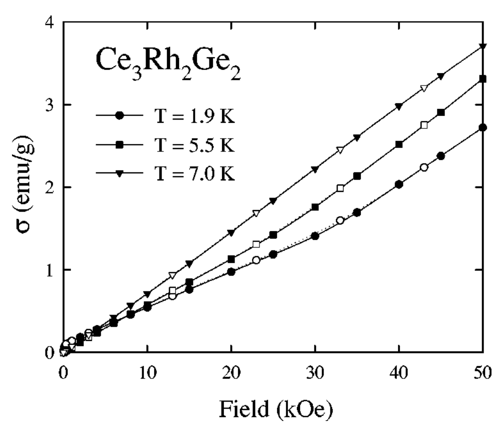

FIG. 7. Field variation of the magnetization in $Ce_3Rh_2Ge_2$, taken at $T = 1.9$ K (circles), 5.5 K (squares), and 7.0 K (triangles) with increasing (full symbols) and decreasing (open symbols) magnetic field.

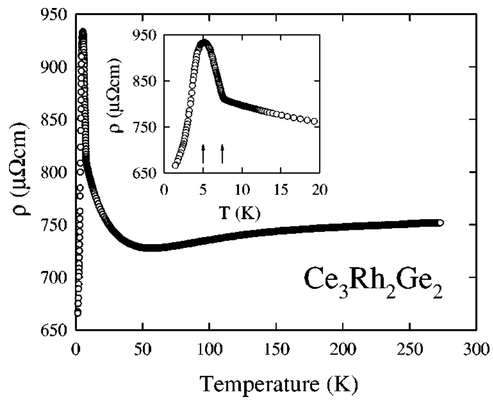

FIG. 8. Temperature dependence of the electrical resistivity of $Ce_3Rh_2Ge_2$. The inset presents $\rho(T)$ in the vicinity of the magnetic phase transitions (marked by the arrows).

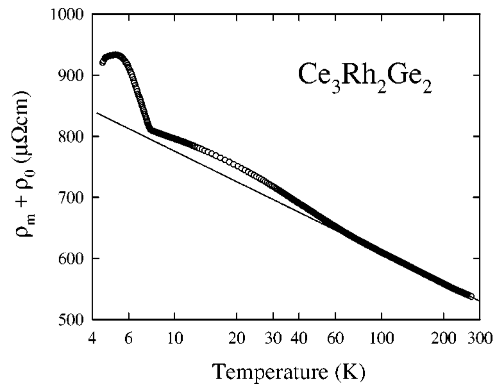

FIG. 9. Temperature variation of the magnetic contribution to the total electrical resistivity of $Ce_3Rh_2Ge_2$ (enlarged by the residual resistivity). Note a semilogarithmic scale. The solid line marks a logarithmic behavior of $\rho_m(T)$.

the specimen measured some microcracks, typical for very brittle materials (see Fig. 8, compare also Fig. 1). With decreasing temperature the resistivity initially slightly decreases, goes through a broad minimum centered at about 50 K, and then starts to rise rapidly towards lower temperatures. At the antiferromagnetic phase transition, $\rho(T)$ shows a pronounced kink (see the inset in Fig. 8), and accordingly the temperature derivative of the resistivity exhibits a deep minimum. The ordering temperature deduced from the resistivity data is 7.5 K, in good agreement with T_N derived in the magnetic-susceptibility studies. In turn, the spin reorientation at $T_t = 5$ K coincides with a peak in $\rho(T)$ and it is clearly seen as a sharp maximum in $d\rho/dT$.

On entering the antiferromagnetc state the resistivity rises first very sharply and subsequently $\rho(T)$ forms a maximum at about 5 K. According to Elliott and Wedgwood's theory[13] such a maximum in $\rho(T)$ of antiferromagnetically ordered compounds results from the presence of new gaps at the limits of the Brillouin zone in a reduced zone scheme. Because in such a case the magnetic scattering potential must have different periodicity than the crystal, it can be presumed that the magnetic unit cell of $Ce_3Rh_2Ge_2$ is larger than the crystallographic one.

In the paramagnetic region, the electrical resistivity of a simple magnetic compound is usually considered as a sum of contributions coming from the scattering of conduction electrons on lattice imperfections (ρ_0), phonons (ρ_{ph}), and disordered spins (ρ_0^∞). Whereas ρ_0 and ρ_0^∞ are temperature independent (the latter only at temperatures at which the crystal-field effect can be neglected), ρ_{ph} is strongly temperature dependent, as given by the Bloch-Grüneisen formula. In the case of $Ce_3Rh_2Ge_2$, apart from these three ordinary scattering mechanisms, one could expect an additional magnetic contribution to the total resistivity, which originates from spin fluctuations associated with $4d$ electrons of rhodium and possibly also a contribution brought about by Kondo-like spin-flip conduction-electron scattering on localized magnetic moments of cerium. Assuming that the phonon scattering and the spin-fluctuation scattering in $Ce_3Rh_2Ge_2$ have a similar magnitude as its La-based counterpart, the magnetic resistivity due to $4f$ electrons can be derived. The result is presented in Fig. 9 as a plot of $\rho_m + \rho_0$ versus $\ln T$ (because the resistivity of $Ce_3Rh_2Ge_2$ does not show any tendency to saturation down to the lowest temperature measured, the term ρ_0 could not be determined and it was not subtracted). As seen from this figure, the magnetic resistivity of $Ce_3Rh_2Ge_2$ exhibits a strong temperature variation with a negative logarithmic temperature coefficient, characteristic of Kondo systems. The least-squares fit of the $\rho_m + \rho_0$ data in the range 60–300 K to the Kondo formula, $\rho_m(T) = \rho_0^\infty - c_K \ln T$, yields for the Kondo coefficient c_K a quite large value of about 72 $\mu\Omega$ cm, thus hinting at an enhanced density of electronic states at the Fermi level. At lower temperatures, the $\rho_m(T)$ vs $\ln T$ variation exhibits a distinct upward curvature and this effect may be attributed to crystal-field interactions. Indeed, just in this temperature region there occurs in $Ce_3Rh_2Ge_2$ salient changes in the population of crystal-field energy levels, as evidenced in the afore-discussed magnetic susceptibility results (see Fig. 5).

IV. CONCLUSIONS

In the present work we investigated two isostructural ternary intermetallics $La_3Rh_2Ge_2$ and $Ce_3Rh_2Ge_2$. The magnetic and electrical measurements have revealed that the La-based germanide is a Pauli paramagnet, which becomes superconducting at $T_C = 3.5$ K. Although there are known in the literature a few La-Rh-based binary and ternary superconductors, such as, for example, La_7Rh_3,[14] LaRhAl,[15] LaRhSb,[16] and $La_2Rh_3Sn_5$,[17] as well as several La-based superconducting germanides, e.g., $LaGe_2$,[18] $LaPd_2Ge_2$,[19,20] $LaPt_2Ge_2$,[20] and $LaIr_2Ge_2$,[21] the critical temperature T_C found for $La_3Rh_2Ge_2$ is the highest in both series.

The other material considered, viz., $Ce_3Rh_2Ge_2$, has been found to be a magnetically ordered dense Kondo system. The long-range magnetic order sets in at $T_N = 7.5$ K and initially has a pure antiferromagnetic character but at somewhat lower temperature, namely, at $T_t = 5$ K, there occurs some spin reorientation that results in the development of a tiny ferromagnetic component. To clarify the nature of magnetic structures in $Ce_3Rh_2Ge_2$ neutron-diffraction studies are required. Moreover, because of the smallness of the uncompensated magnetic moment it would also be worth pursuing muon spectroscopy measurements.

Another interesting topic which demands further studies is the role played in both compounds by rhodium 4*d* electrons. In the electrical resistivity of $La_3Rh_2Ge_2$ and $Ce_3Rh_2Ge_2$, as well as in the magnetic susceptibility of $Ce_3Rh_2Ge_2$, we have recognized some evidence for spin fluctuations and tentatively attributed them to a rhodium constituent. It seems likely that just the 4*d* contribution gives rise to complex magnetic behavior encountered at low temperatures in $Ce_3Rh_2Ge_2$, yet this hypothesis still requires reliable verification.

ACKNOWLEDGMENTS

D.K. is indebted to the Max Planck Society for the Advancement of Science for a scholarship. The authors thank Mrs. M. Eckert for help in metallographic investigation.

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