Multiple magnetic transitions in single-crystal $Gd_5Rh_4Ge_{10}$

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Compounds belonging to the $R_5Ir_4Si_{10}$ family exhibit a variety of ground states depending on the nature of the rare-earth element R. In this work, we report resistivity, magnetization, and heat-capacity studies on a single crystal of $Gd_5Rh_4Ge_{10}$. Unusual multiple magnetic transitions are observed in $Gd_5Rh_4Ge_{10}$ (where there is no crystal-field contribution). It appears that one of the four-fold transitions which occurs at the highest temperature is a second-order (continuous) phase transition while the other three probably involving moment reorientations and noncollinear amplitude modulations. In general, the basic cause of the magnetic orderings is due to anisotropic indirect exchange interaction (Ruderman-Kittel-Kasuya-Yasida type) coupled with multiple site occupancy of the Gd atoms.

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I. INTRODUCTION

Ternary rare-earth transition-metal silicides and germanides which form in a rich variety of crystal structures display unusual physical properties.[1,2] Some of them contain traditional 3d magnetic elements such as Co, Fe, and Ni while retaining their superconducting properties. Here, the 3d elements apparently have no magnetic moment on them. However, they participate in building up a high density of states at the Fermi level, which is responsible for the superconductivity. In particular, compounds belonging to one of the structures, namely, $Er_5Ir_4Si_{10}$ and $Lu_5Ir_4Si_{10}$ ($Sc_5Co_4Si_{10}$ type $P4/mbm$) show coexistence of magnetism or superconductivity with charge-density wave (CDW) ordering at higher temperatures.[3–9] It must be stated here that none of the individual compounds exhibits coexistence of magnetism and superconductivity. However, coexistence of superconductivity and antiferromagnetism has been established in psuedoternary alloys such as $Sc_{5-x}Dy_xIr_4Si_{10}$[10,11] and $Y_{5-x}Dy_xOs_4Ge_{10}$.[12–14] One of the interesting structural features in this series is the absence of direct transition-transition-metal contacts. The transition-metal atoms are connected to each other either through a rare earth or Si/Ge atom. In this work, we present the observation of multiple magnetic ordering of Gd moments in a single crystal of $Gd_5Rh_4Ge_{10}$ which adopts the same $Sc_5Co_4Si_{10}$-type structure. This structure can be viewed as a network built by stacking of two basic building blocks, namely, trigonal prism $GeGd_6$ and distorted antiprism $RhGe_4Gd_4$. This is in marked contrast to the cluster-type compounds such as RMo_6S_8[15] and RRh_4B_4[16] which have been studied in great detail. Another structural feature is that the rate-earth (R) atoms occupy three different sites with distinct local environments. $Gd_5Rh_4Ge_{10}$ forms in the $Sc_5Co_4Si_{10}$ structure[17] and it is a well-defined local moment only ($J=S=7/2$) compound. Earlier studies[18] on polycrystalline samples indicated multiple magnetic transitions in $Gd_5Rh_4Ge_{10}$. Single or double magnetic transitions were observed in many Gd based compounds where Gd ions occupy single or multiple sites.[19] Since Gd is a $\vec{S}$-state ion with no crystal-field effect, the observed quadruple (fourfold) transitions are unique and deserve further investigations. With this in view, we report our resistivity (2–300 K), magnetization (2–300 K), and heat capacity (0.5–20 K) measurements on a single crystal of $Gd_5Rh_4Ge_{10}$. The paper is organized as follows. In Sec. II, we describe the sample preparation and details of the measurements. The data and analysis are given in Sec. III, Sec. IV deals with the discussion, and Sec. V concludes our studies in $Gd_5Rh_4Ge_{10}$ system.

II. EXPERIMENTAL DETAILS

A single crystal of $Gd_5Rh_4Ge_{10}$ was made with high-purity ($\geqslant$99.99%) elements in a triarc furnace using Czochralski technique. The high quality and composition of the crystal are ascertained using EPMA (Electron Probe Micro Analyzer, JEOL 8600 series, Japan) and the lattice constants are measured using single-crystal x-ray diffraction. The sample was cut along the a and c axes using a spark cutter after its orientation was checked by Laue x-ray diffraction. The structure of $Gd_5Rh_4Ge_{10}$ is shown in Fig. 1. The interesting structural feature of this compound is the absence of direct transition-transition-metal contacts. The transition-metal atoms are connected to each other either through a Gd

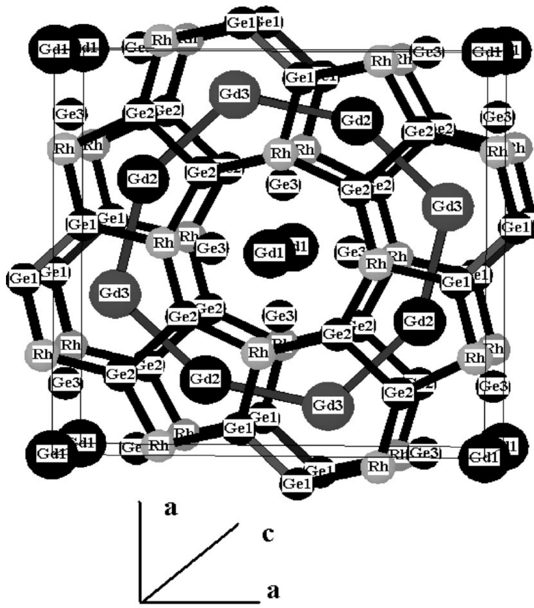

FIG. 1. Structure of tetragonal $Gd_5Rh_4Ge_{10}$ ($P4/mbm$). The unit cell is shown by the dark lines drawn on the structure. There are 38 atoms in the unit cell and no direct Rh-Rh bonds. Gd has three sites with different symmetries; Gd(1) site has the highest (fourfold) symmetry.

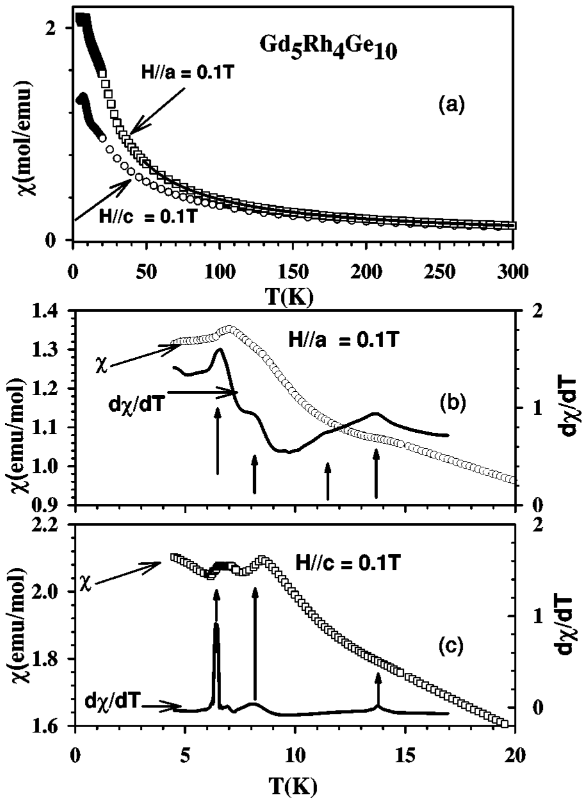

FIG. 2. Temperature dependence of the dc susceptibility χ of the single crystal of $Gd_5Rh_4Ge_{10}$ in an applied field of 0.1 T along a and c axes are shown in panel (a). The solid line is a fit to the Curie-Weiss relation (see text for details). The lower panels (b) and (c) show the low-temperature behavior of χ as well their derivatives ($d\chi/dT$) along the a and c axes, respectively. Panel (b) displays four transitions shown by the arrow marks in $d\chi/dT$), while in panel (c) only three magnetic transitions could be observed along the c axis.

or Ge atom. One can observe that Gd has three inequivalent sites. The Rh and Ge atoms form planar nets of pentagons and hexagons which are stacked parallel to the basal plane and connected along c axis via Rh-Ge-Rh zigzag chains. The pentagon and hexagon layers are separated by layers of Gd. The distances between Gd and Ge as well that of Ge and Ge are short indicating strong covalent interaction. The values of the lattice constants a and c are found to be 12.9646(3) Å and 4.2966 (3) Å which are close to the values reported in a previous study.[17,18] The temperature dependence of susceptibility χ was measured using a commercial Squid magnetometer (Quantum Design, USA) in a field of 1 kOe in the temperature range from 2 to 300 K. dc magnetizations were also obtained using the same setup. The ac susceptibility was measured using a home built susceptometer from 1.5 to 20 K. The resistivity was measured using a four-probe dc technique with contacts made using silver paint on a bar shaped sample of 4 mm length and 0.5 mm thickness. The heat capacity between 0.5 to 20 K was measured using an automated semiadiabatic heat-pulse method.

III. RESULTS AND DISCUSSION

A. Magnetization studies

Temperature dependences of the dc magnetic susceptibility χ data for a single crystal of $Gd_5Rh_4Ge_{10}$ in a field of 1 kOe from 4.2 K to 300 K along a and c axes are shown in panel (a) of Fig. 2. Note that the anisotropy in χ builds up below 80 K due to magnetic fluctuation effects and ultimately χ_c is 1.6 times χ_a at 4.2 K. The lower panels (b) and (c) display the low-temperature χ data along both axes with their respective temperature derivatives. From this plot we can clearly distinguish quadruple magnetic transitions at 6.5 K, 8.3 K, 11.5 K, and 13.8 K along the a axis. However, only three such transitions (6.5, 8.3, and 13.8 K) are discernable along c axis. The high-temperature data ($100\ \mathrm{K} < T < 300$ K) could be fitted to the Curie-Weiss expression from which we estimated $\mu_{eff} = 8.0\mu_B$ and $\theta_p = -20$ K. Although the effective moment agrees with the theoretical value of $7.9\mu_B$ for Gd^{3+} ion, θ_p value is larger than that of the first antiferromagnetic transition temperature (14 K) but it is comparable to the value of 26 K obtained from the susceptibilty data of a polycrystalline sample.[18] This difference could be attributed to the magnetic frustration effects (due to geometry), which is admissible in the 5-4-10 structure.

We have also performed isothermal magnetization studies of the same $Gd_5Rh_4Ge_{10}$ crystal at various temperatures from 5 to 25 K (data not shown). The nonlinear behavior in M vs. H along the c axis at 5 K agrees with the notion of antiferromagnetic ordering of Gd spins. However, it is not possible to find the change in the four-fold transitions due to the magnetic field using the magnetization data. The multiple magnetic transitions observed from the $d\chi/d$T data at 0.1 T are no longer distinctly seen in the χ data for fields greater than 0.4 T. Moreover, the absolute value of χ decreases with

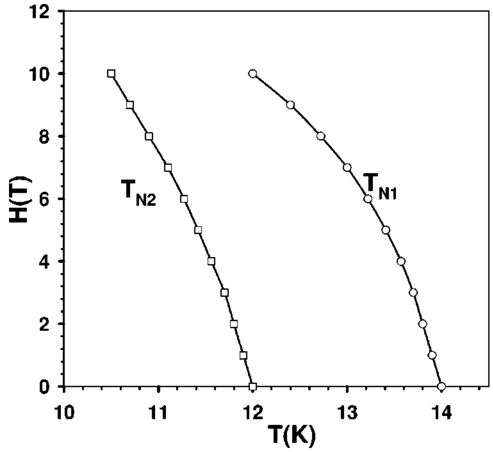

FIG. 3. The field dependence of the upper two transitions obtained from heat-capacity studies. This dependence is in broad agreement with the data obtained from magnetization studies (see text for details).

application of field. We would like to reiterate here that the sample is of high quality as ascertained by EPMA and Laue studies. Therefore, we rule out extrinsic effects such as impurities as the cause for the above-mentioned behavior. However, one could determine the effect of magnetic field on at least two magnetic transitions by heat-capacity studies in magnetic field (see below). The two lower transitions are quickly suppressed by the field above 2 T while the transition temperatures of the top two magnetic transitions decrease with the increase of field. This is shown in Fig. 3. These results are in agreement with those obtained from the susceptibility studies under different magnetic fields. The shift of the first (second-order) transition appears to be more than the second one. Microscopic investigations such as electron paramagnetic resonance (EPR) or magnetic dichroism are needed to understand this behavior.

B. Resistivity studies

The temperature dependence of the resistivity ρ of the same single crystal of $Gd_5Rh_4Ge_{10}$ along *a* and *c* axes are shown in panel (a) of Fig. 4. The anisotropy in the resistivity is about 3 at 300 K but increases to 5 at 2 K suggesting considerable contribution to the magnetic scattering along the *a* axis. Panels (b) and (c) show the low-temperature ρ data along *a* and *c* axes on an expanded scale. The temperature dependence of the low-temperature resistivity along both axes are quite complex indicating the complicated nature of the underlying magnetic ordering of Gd moments. The ρ data along the *c* axis show a cusp in resistivity at 14 K representing antiferromagnetic ordering (T_{N1}) of Gd^{3+} ions. However, one could not observe such a clear cusp in ρ along the *a* axis. But a steplike structure is seen along the *a* axis below the second magnetic transition T_{N2}. We have also observed a change of slope in ρ data along the a-axis at 14 K, 11 K, 8.2 K, and 6.7 K, respectively, representing (shown by the arrows) all the transitions which have been seen in χ data at 0.1 T. In the paramagnetic region (15 K$<T<$40 K), the

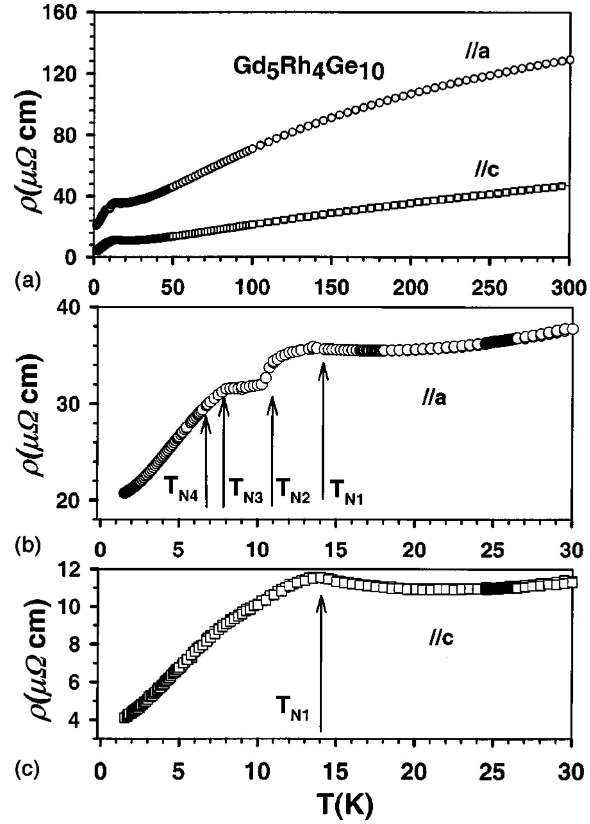

FIG. 4. Temperature dependence of resistivity ρ of single-crystal $Gd_5Rh_4Ge_{10}$ from 2 to 300 K along the *a* and *c* axes are shown in panel (a). Panels (b) and (c) display low-temperature behavior of ρ along *a* and *c* axes from 2 to 40 K. The cusp at 14 K in ρ [which is prominent in panel (c)] implies antiferromagnetic transition. Note the step change around 12 K in panel (b) and this probably indicates one of the first-order transitions seen at 11.5 K. The other two transitions can be seen only in the $d\rho/dT$ data (not shown here for brevity).

temperature dependence of ρ could be fitted to the $T^{3/2}$ dependence, which suggests the dominance of short-range magnetic order above T_N.

C. Heat-capacity studies

The temperature dependence of the magnetic contribution to the heat capacity C_m from 0.5 to 20 K of same $Gd_5Rh_4Ge_{10}$ is shown in part (a) of Fig. 5. The lattice contribution to the heat capacity of $Gd_5Rh_4Ge_{10}$ is estimated from the heat-capacity data of $Lu_5Rh_4Ge_{10}$ with appropriate correction for the molar mass of Gd compound (see Ref. 19 for further details). The magnetic contribution to the heat capacity is obtained by subtracting this lattice heat capacity from the observed heat-capacity data of $Gd_5Rh_4Ge_{10}$. The estimated value of the entropy *S* is also shown. The large jump in C_m at 14.0 K ($\Delta C_m \sim 40$ J/mol K) shows the bulk nature of magnetic ordering which has been seen in susceptibility and resistivity data as well. We also observed bulk transitions at 12, 8.5, and 7 K in C_m data which are in accordance with χ and ρ data. The λ shape of the transition at 14 K suggests a usual second-order magnetic transition while

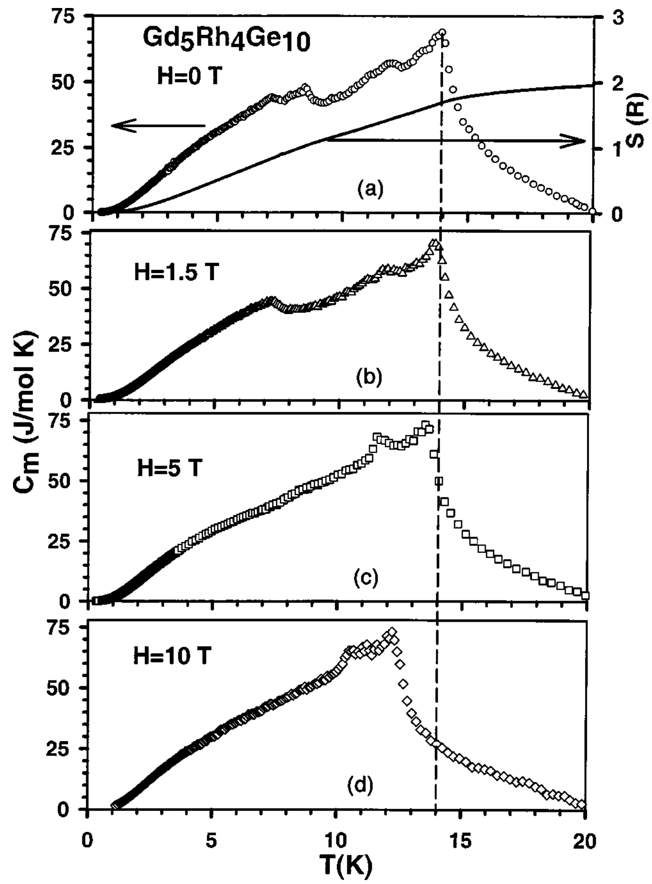

FIG. 5. Plot of C_m vs T of the single-crystal $Gd_5Rh_4Ge_{10}$ from 0.5 to 20 K. Four magnetic transitions due to ordering of Gd^{3+} spins can be seen at 14 K, 12 K, 8.5 K, and 7.0 K as displayed in panel (a). The calculated values of entropy S_m are also given in the same panel. Panels (b), (c), and (d) show the temperature-dependence of C_m at 1.5 T, 5 T, and 10 T. One can observe the suppression of the lower two transitions for fields greater then 1.5 T while the upper two transitions decrease gradually with the increase of field.

the other transitions are more subtle and probably due to spin reorientation or change of amplitude modulations below the second-order antiferromagnetic ordering. The estimated entropy per Gd ion displayed in the top panel is 1.97R which is almost equal to the total entropy for Gd^{3+} ion [$R\ln(2J+1)$]. However, it is evident that the full entropy is not released at 14.0 K, which implies the existence of short-range correlations above T_{N1}.

IV. DISCUSSION

Usually one observes at most only two magnetic transitions in Gd based intermetallic compounds.[19] Hence, the observation of four transitions in $Gd_5Rh_4Ge_{10}$ is a unique feature and to the best of our knowledge has not been reported in any Gd based intermetallic compounds. See Table I for the fourfold transition temperatures obtained from various measurements. These results are compared with the polycrystalline data obtained from an earlier study.[18] The small difference in the transition temperature could be due to the difference in composition of these two compounds. Note that the lattice constants of the present crystal are also slightly different from those of the polycrystalline compound. It is also interesting to note that ρ_a/ρ_c is about 3 which is similar to the value reported in $Lu_5Ir_4Si_{10}$[8] and $Er_5Ir_4Si_{10}$,[9] which are classified as CDW sytems. Similar behavior is also observed in the susceptibility data as well. This implies that the observed anisotropy in resistivity and susceptibility is inherent in the $Sc_5Co_4Si_{10}$ type ($P4/mbm$) structure. It is worthwhile to recall here that there is no CDW transition in $R_5Rh_4Ge_{10}$ compounds.[18]

TABLE I. Magnetic transition temperatures obtained from various measurements for single crystal and polycrystalline $Gd_5Rh_4Ge_{10}$. The values for the polycrystal are given in brackets from Ref. 18).

T_N (K)	χ (from $d\chi/dT$)	ρ (from $d\rho/dT$)	C_p
T_1	13.8(14)	14(14)	14(14)
T_2	11.5(11)	11.0(11)	12(11)
T_3	8.3(8.5)	8.2(9)	8.5(9)
T_4	6.5(6.5)	6.7(6.5)	7.0(6.5)

Since Gd compounds have zero angular momentum due to their **S** state, their ground-state multiplet $J=7/2$ remains fully degenerate even in the presence of crystalline electric field. Only a magnetic field can remove this $(2J+1)$ degeneracy. Therefore, the temperature dependence of C_m or χ depends on the way the energy levels evolve within the internal field of the ordered state. Magnetic ordering in Gd compounds can be classified as either due to equal-moment (EM) systems or due amplitude modulated (AM) systems.[20,21] The first type includes ferromagnetic, simple antiferromagnetic or helical as well as cycloidal magnetic structures that are incommensurate with the crystal lattice. The well known λ anomaly observed in the heat-capacity data of a magnetically ordered system is strongly reduced and possibly smoothed off in AM systems. The heat-capacity data of $Gd_5Rh_4Ge_{10}$ suggests a possible AM-type transition. Moreover, the jump in the heat capacity at 14 K is only 8 J/mol Gd K which is much smaller than the expected mean-field value of 20.15 J/mol K. Normally such a mean-field value for the heat-capacity jump is expected for a ferromagnet or simple antiferromagnet[20] (EM systems). Since the observed C_p jump in $Gd_5Rh_4Ge_{10}$ is small there is a possibility that the magnetic-moment amplitude may vary periodically from one site to another, evolving from a sine-wave shape just below T_{N1} to an antiphase type at low temperatures. Such amplitude modulated moments possibly undergo multiple reorientation as we have observed here. It must be stated here that the reduced jump observed here is much smaller than the value given by the theory[20] which indicates that magnetic fluctuations (ignored in the model) play a crucial role as far as magnetism is considered in this compound. It is also of interest to note that the two lower transitions are suppressed for fields greater than 2 T while the upper two transitions decrease slowly with field. This is displayed in panels (b), (c), and (d) of Fig. 5. The value of the jump in C_m at 12 K and 14 K changes very little (if any) with field. The vertical line represents the shifting of the 14-K transition as a function of field.

Recent theory of amplitude modulations in Gd compounds by Rotter *et al.*[21] has explicitly included anisotropic exchange, which is certainly expected in our compound. This leads to noncollinear amplitude modulated antiferromagnetic order. Here the magnetic specific heat was calculated for both commensurate and incommensurate structure with different propagation vectors (within and outside the Brillouin-zone boundary). A direct comparison with $Gd_5Rh_4Ge_{10}$ is difficult. Since there are four transitions affecting the specific heat, we cannot relate the anomalies to that predicted by the theory. Also there is a problem of three different Gd sites which is not considered by the theory. We believe that indirect Ruderman-Kittel-Kasuya-Yasida interaction is responsible for the observed antiferromagnetism in this compound. The local symmetry, coordination, and Gd-Ge and Gd-Rh distances are different for these three sites, which in principle could lead to different interactions leading to the fourfold magnetic transitions. Since neutron-diffraction or magnetic x-ray scattering studies are absent in this compound, we strongly suggest such experiments as a critical test of noncollinear amplitude modulation.

V. CONCLUSION

In conclusion we have observed quadruple magnetic transitions in a single crystal of $Gd_5Rh_4Ge_{10}$ via resistivity, susceptibility, and heat-capacity studies. The λ-like anomaly in C_p at 14 K implies a typical continuous phase transition whereas the other three distinct transitions, which occur at low temperatures, could be due to successive spin reorientation effects or amplitude modulation effects. The local symmetry of the individual Gd ion could also play a crucial role here. However, at present, this is only a conjecture, which has to be verified by direct microscopic techniques such as neutron diffraction, magnetic x-ray scattering, electron paramagnetic resonance and muon spin resonance (μSR) studies. Once such studies are available it would be most interesting to draw a full comparison with theory[21] and verify strong possibility of noncollinear amplitude modulated magnetic order in $Gd_5Rh_4Ge_{10}$.

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