Magnetic Properties and the Magnetic Phase Transitions in $R_5Rh_4Ge_{10}$ (R = Tb–Tm) Compounds

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The magnetic data for $R_5Rh_4Ge_{10}$ (R = Tb, Dy, Ho, Er, and Tm) compounds was investigated by means of the dc magnetization and dc and ac magnetic susceptibility. At low temperature all these compounds are antiferromagnets. For these with R = Tb, Ho and Er below T_N the additional phase transitions are observed. The obtained data are compared with the neutron diffraction results.

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1. Introduction

In last years ternary rare-earth germanides with the variable stoichiometry are subject of the intensive investigations. Our scientific interest is determining the magnetic properties of the compounds with the different stoichiometry. These investigations concern the compounds in R–Rh–Ge system where R is rare-earth elements. In the previous works the compounds with the stoichiometry 1:2:2 and 1:1:1 are investigated. These compounds have the simple crystal structure in which the rare-earth atoms occupy only one position in crystal unit cell and are antiferromagnets at low temperatures [1].

This work reports the results of investigations of the magnetic properties of $R_5Rh_4Ge_{10}$ (R = Tb–Tm) compounds. The compounds crystallize in tetragonal $Sc_5Co_4Si_{10}$-type structure (space group $P4/mbm$) in which the R atoms in crystal unit cell occupy three nonequivalent positions [2]. The temperature dependence of the magnetic susceptibility, specific heat and resistivity indicate the complex magnetic properties at low temperatures [3].

The neutron diffraction studies for $Tb_5Rh_4Ge_{10}$ and $Er_5Rh_4Ge_{10}$ confirm the change of the magnetic order with change of the temperature [4]. In contradiction in $Tm_5Rh_4Ge_{10}$ the change of the magnetic order was not detected [5].

For the purpose of explanation of the magnetic properties of the $R_5Rh_4Ge_{10}$ compounds (R = Tb–Tm) at low temperatures the new dc and ac magnetic measurements are performed.

2. Experimental

$R_5Rh_4Ge_{10}$ (R = Tb, Dy, Ho, Er, and Tm) polycrystalline samples were synthesized by arc melting stoichiometric amounts of high-purity elements (R of 3N purity, Rh of 4N purity and Ge of 5N purity) under argon atmosphere. Subsequently the samples were annealed in evacuated quartz tubes at 800 °C for one week. Phase analysis was done by X-ray powder diffraction (XRD) at room temperature using a Panalytical X'PERT diffractometer with the Cu K_α radiation.

The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform. Three types of magnetic measurements were performed: cooling at low temperatures at zero magnetic field (ZFC) and field (FC) equal to $H = 50$ Oe (to determine the phase transition temperatures), then scanning from 1.9 up to 300 K in a magnetic field of 1 kOe (to determine the values of the effective magnetic moment $\mu_{\rm eff}$ and the paramagnetic Curie temperatures $\theta_{\rm p}$) and finally measuring the magnetization curves up to 90 kOe at 1.9 K (to determine the values of the magnetic moment in the ordered state). For the purpose of precise determining the temperature of the phase transition the ac magnetic susceptibilities ($\chi_{\rm ac} = \chi' + {\rm i}\chi''$ where χ' is the real and χ'' imaginary component) were measured versus frequency between 10 Hz and 10 kHz and on magnetic field amplitude $H_{\rm ac}$ equal to 5 Oe in the temperature range 2–17 K.

3. Results

The analysis of the X-ray data indicates that all compounds have the tetragonal crystal structure ($P4/mbm$). The determined values of the lattice parameters are in good agreement with the previous data [3].

The results of the dc magnetic measurements are shown in Figs. 1–8. Figure 1 shows the temperature dependence of the reciprocal magnetic susceptibility of the $Tb_5Rh_4Ge_{10}$ and $Dy_5Rh_4Ge_{10}$. For both compounds the Curie–Weiss law is obeyed by the negative values of the paramagnetic Curie temperature and the effective magnetic moment near to the free R^{3+} ions value (see Table). The upper inset shows the temperature dependence of the magnetic susceptibilities $\chi_{\rm dc}$ at low temperatures. For $Tb_5Rh_4Ge_{10}$ three anomalies at 3.0, 5.5 and 11.5 K and below 7 K the difference between ZFC and FC is observed.

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TABLE

Magnetic data for $R_5Rh_4Ge_{10}$ (R = Tb, Dy, Ho, Er and Tm) compounds; the Néel temperature (T_N), the transition temperature (T_t), paramagnetic Curie temperature (θ_p), experimental (exp.) and theoretical (theor.) values of the effective magnetic moment (μ_{eff}) and in the ordered state (μ) at $T = 1.9$ K and $H = 90$ kOe and the magnetic critical field (H_{cr}). Methods: static (dc) and dynamic (ac) susceptibilities.

R	M	T_N [K]	T_t [K]	θ_p [K]	μ_{eff} [μ_B]		μ [μ_B]		H_{cr} [kOe]	Ref.
					exp.	theor.	exp.	theor.		
Tb	dc	11.5	5.5, 3.0	−20.0	10.3	9.72	5.2	9.0	22	this work
	ac	11.5								this work
	dc	11.5	5.5, 3.0	−24.5	10.42					[3]
Dy	dc	6.9		−9.7	10.6	10.65	6.4	10.0	30	this work
	ac	6.9								this work
	dc	6.0		−11.6	10.45		5.6*			[3]
Ho	dc	6.6	4.2, 4.7	−3.3	10.4	10.61	7.3	10.0	10	this work
	ac	6.6								this work
	dc	6.0	5.0	2.5	10.07					[3]
Er	dc		4.2	5.6	9.8	9.58	6.5	9.0	11	this work
	ac		4.5							this work
	dc	5.0		8.4	9.29					[3]
Tm	dc	6.0		−3.4	7.54	7.56	4.1	7.0	10	this work
	dc	6.9		−3.5	8.15					[3]

* at $H = 5$ kOe

Temperature dependence of the χ' and χ'' component of the ac magnetic susceptibility is shown in Fig. 2. $\chi'(T)$ dependence gives the similar anomalies as in $\chi_{dc}(T)$ while in $\chi''(T)$ only anomaly 3.0 K is observed.

The magnetic field dependence of the magnetization measured at different temperatures: 1.9, 4.5, 8, and 15 K is shown in lower inset in Fig. 1. Only at 1.9 K the metamagnetic transition with the critical field H_{cr} determined from relation dM/dH vs. H equal to 22 kOe is observed. The magnetization did not saturate at $H = 90$ kOe and $T = 1.9$ K. Determined value of the Tb magnetic moment is equal to 5.2 μ_B and is smaller than the free Tb^{3+} ion value (9.0 μ_B).

For $Dy_5Rh_4Ge_{10}$ temperature dependence of the dc (see upper inset in Fig. 1) and χ' component of ac susceptibility (Fig. 3) gives the anomaly at 6.9 K. The reciprocal magnetic susceptibility obeys the Curie–Weiss law with $\mu_{eff} = 10.6$ μ_B and $\theta_p = -9.7$ K.

The magnetization curve at $T = 1.9$ K indicates the metamagnetic phase transition with the critical field H_{cr} equal to 30 kOe (see lower inset in Fig. 1). The Dy magnetic moment at $T = 1.9$ K and $H = 90$ kOe is equal to 6.3 μ_B and is much smaller than the free Dy^{3+} ion value (10 μ_B).

Temperature dependence of the reciprocal magnetic susceptibilities of $Ho_5Rh_4Ge_{10}$ and $Er_5Rh_4Ge_{10}$ compounds obey the Curie–Weiss law with a paramagnetic Curie temperature of −3.3 K for R = Ho and 5.6 K for R = Er and an effective magnetic moment $\mu_{eff} =$ 10.4(1) μ_B (Ho) and 9.8(1) μ_B (Er), respectively (Fig. 4). The values of the effective magnetic moment are close to the free R^{3+} ion values.

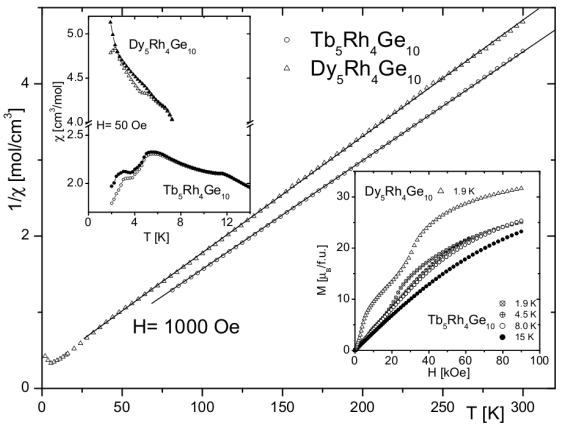

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibilities of $Tb_5Rh_4Ge_{10}$ and $Dy_5Rh_4Ge_{10}$ compounds. Insets show: the upper one — the low temperature part of the magnetic susceptibilities and the lower one — magnetization curves vs. magnetic field for $Tb_5Rh_4Ge_{10}$ at 1.9, 4.5, 8, and 15 K and $Dy_5Rh_4Ge_{10}$ at 1.9 K.

Temperature dependence of the DC magnetic susceptibility at low temperatures (see inset in Fig. 4) give for:
— $Ho_5Rh_4Ge_{10}$ a broad maximum at 4.2 K (ZFC) and 4.7 K (FC) and additional small anomaly at 5.4 K;
— $Er_5Rh_4Ge_{10}$ one maximum at 4.3 K for ZFC curve and at 4.1 K for FC curve.

For $Ho_5Rh_4Ge_{10}$ both the χ' and the χ'' dependence give a sharp maximum at 5 K and broad at 6.6 K (Fig. 7). In case of $Er_5Rh_4Ge_{10}$ only small intensity is observed in

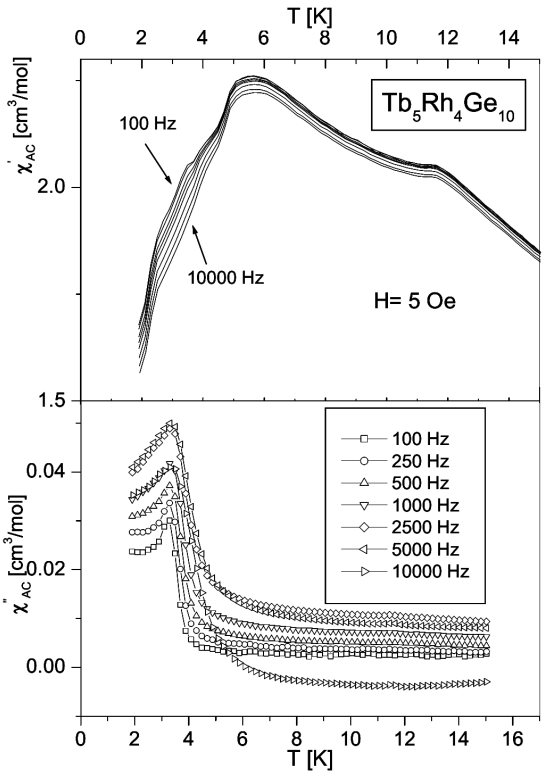

Fig. 2. Temperature dependence of the χ' and χ'' component of the ac magnetic susceptibility for $Tb_5Rh_4Ge_{10}$ versus frequency varied between 10 Hz and 10 kHz.

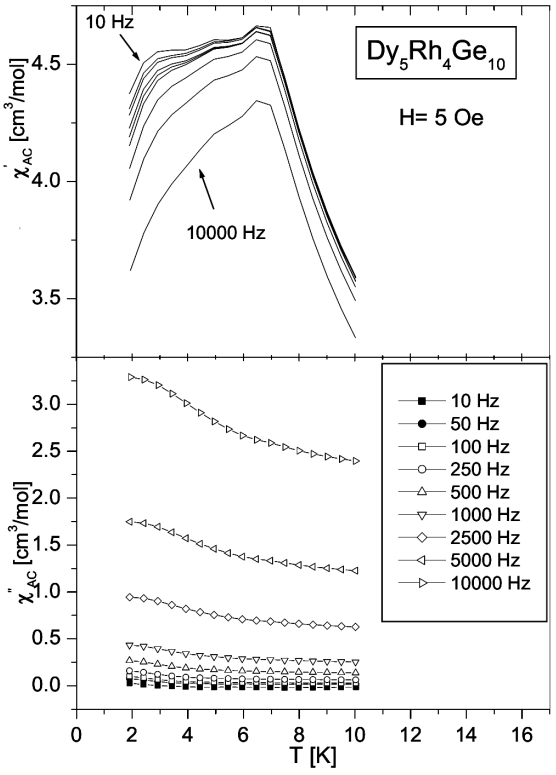

Fig. 3. Temperature dependence of the χ' and χ'' component of the ac magnetic susceptibility of $Dy_5Rh_4Ge_{10}$ versus frequency varied between 10 Hz and 10 kHz.

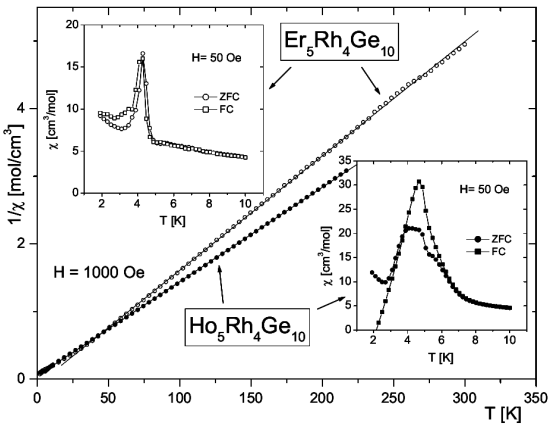

Fig. 4. Temperature dependence of the reciprocal dc magnetic susceptibility at 1 kOe for $R_5Rh_4Ge_{10}$ for R = Ho and Er. The solid lines present the fit of Curie–Weiss law. Insets: dependence of the magnetic susceptibilities at low temperatures at $H = 50$ Oe. The data concerning ZFC (lower curve) and FC (upper curve) are shown.

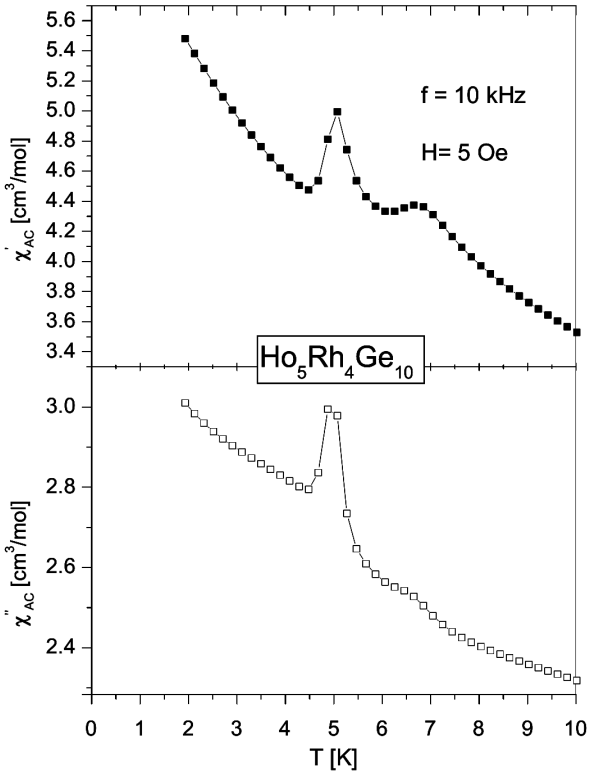

Fig. 5. Temperature dependence of the real χ' and imaginary χ'' part of the AC magnetic susceptibility of $Ho_5Rh_4Ge_{10}$ measurements at $H_{ac} = 5$ Oe and $f = 10$ kHz.

$\chi'(T)$ while in $\chi''(T)$ a strong maximum at $T = 4.5$ K is observed. The temperature of maximum is independent of the frequency.

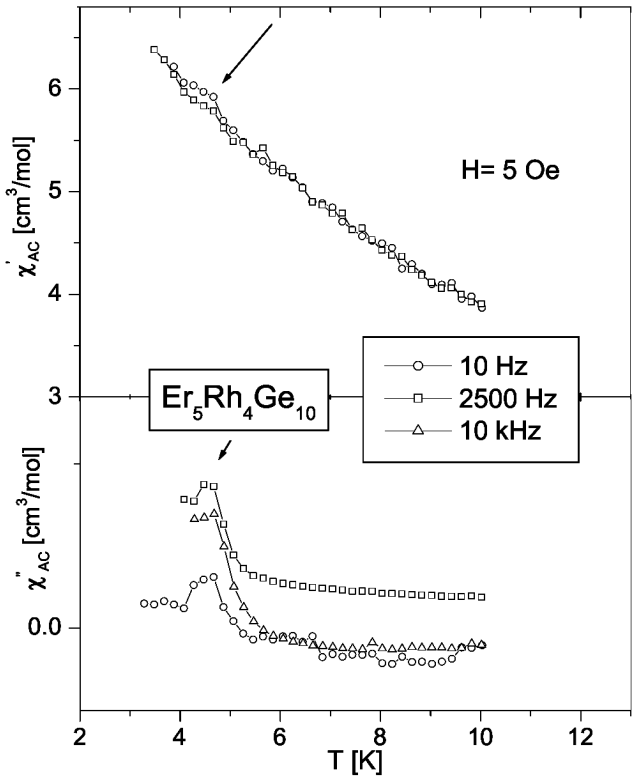

Fig. 6. χ' and χ'' for $Er_5Rh_4Ge_{10}$ measured at some frequency.

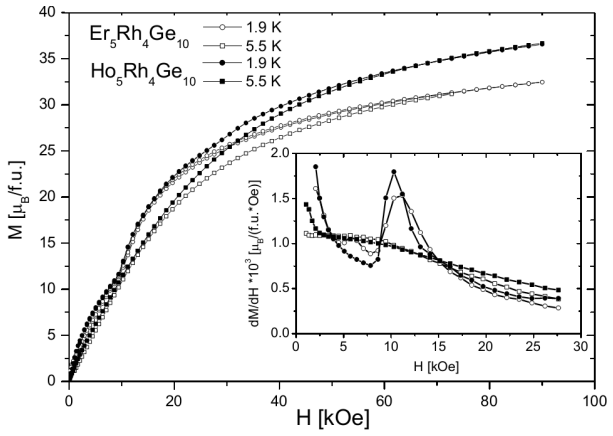

Fig. 7. Magnetization versus magnetic field up to 90 kOe at $T = 1.9$ and 5.5 K for $Ho_5Rh_4Ge_{10}$ and $Er_5Rh_4Ge_{10}$. Inset shows the field dependence of the $\frac{dM}{dH}$.

The magnetization curves in the magnetic field up to 90 kOe collected at 1.9 K exhibit a metamagnetic character with a critical field of about 10 kOe for R = Ho and 11 kOe for R = Er (see inset in Fig. 7). The metamagnetic character disappears on the magnetization curves measurement at 5.5 K. The magnetic moment at $T = 1.9$ K and $H = 90$ kOe are 7.3(1) μ_B for R = Ho and 6.5(1) μ_B for R = Er and are smaller than the free R^{3+} ion values of 10.0 and 9.0 μ_B, respectively. The small temperature hystereses are observed.

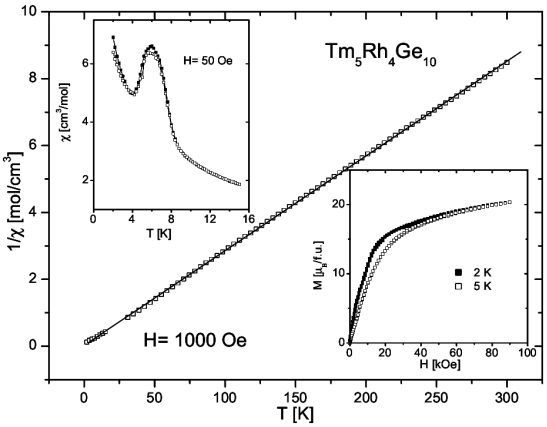

Fig. 8. Temperature dependence of the reciprocal magnetic susceptibility for $Tm_5Rh_4Ge_{10}$. Insets show: the upper ones — temperature dependence of the magnetic susceptibilities: ZFC (lower curve) and FC (upper curve) and the lower ones — magnetization curves up to 90 kOe at 2 and 5 K.

The reciprocal magnetic susceptibility of $Tm_5Rh_4Ge_{10}$ obeys the Curie–Weiss law with the μ_{eff} equal to 7.54 μ_B and paramagnetic Curie temperature equal to −3.4 K (Fig. 8). Temperature dependence of the dc susceptibility for $Tm_5Rh_4Ge_{10}$ give broad maximum at $T = 6$ K.

The magnetization curve in the magnetic field up to 90 kOe collected at 1.9 K have a metamagnetic character with the critical field H_{cr} equal to 10 kOe.

4. Discussion

Presented in the work results of the magnetic measurements of $R_5Rh_4Ge_{10}$ (R = Tb–Tm) compounds suggest that these compounds are antiferromagnets at low temperature. The magnetic data are summarized in Table. The values of the effective magnetic moments are in agreement with these for the free R^{3+} ion values. The magnetization curves are not saturated in the magnetic field equal to 90 kOe which indicates the strong magnetocrystalline anisotropy. The average magnetic moments per atoms are equal to: 5.2 μ_B for R = Tb, 6.4 μ_B for R = Dy, 7.3 μ_B (Ho), 6.5(1) μ_B (Er) and 4.1(1) μ_B (Tm) and are smaller than the free R^{3+} ion values (see Table). The understate values of the magnetic moments indicate the strong influence of the crystal electric field.

Negative values, except R = Er, of paramagnetic Curie temperatures suggest the antiferromagnetic order. This confirms the neutron diffraction data [4, 5] which also indicate that the magnetic moment is localized on the rare-earth atoms. In $R_5Rh_4Ge_{10}$ compounds the rare-earth atoms occupy three nonequivalent crystallographic positions. The neutron diffraction data indicate the different values of the magnetic moment at individual sites.

Results presented in the work indicated the complex magnetic properties in order state. Particularly interesting results are obtained for $Tb_5Rh_4Ge_{10}$ compound. The dc and ac magnetic susceptibility data indicate three anomalies at 11.5, 5.5 and 3.0 K. Previous results [3] indicate in the temperature dependence of the dc susceptibility the small maximum at 11.5 K and strong at 5.1 K (see inset in Fig. 4 in Ref. [3]). This anomaly confirms the temperature dependence of the specific heat and resistivity (see Table 4 in Ref. [3]).

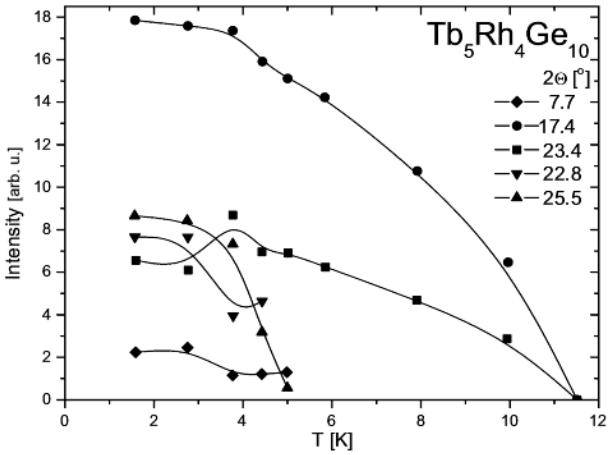

Fig. 9. Temperature dependence of the intensities of the some magnetic peaks on the neutron diffraction patterns for $Tb_5Rh_4Ge_{10}$. The data base on the experimental results measurement previously.

Comparison of these results with the neutron diffraction data reported previously (see Fig. 9) clearly shows that in 11.5 K there is a disappearance of the long-range magnetic order. The analysis of the magnetic intensities gives below T_N the complex antiferromagnetic order similar to those observed in isostructural $Er_5Ir_4Si_{10}$ [6]. Below the 5 K the additional peaks of the magnetic ordering are observed, but the basic magnetic structure is not determined [4]. The small intensity peaks observed below 3 K is connected with the impurity phase TbO_2 [7].

For $Dy_5Rh_4Ge_{10}$ only one anomaly in temperature dependence of the dc and a magnetic susceptibility at 6.9 K is observed. Also magnetic, heat capacity and resistivity data reported in Ref. [3] give similar result. Absence of the neutron diffraction data makes impossible determining of the temperature dependence of the magnetic order.

For $Ho_5Rh_4Ge_{10}$ the temperature dependence of the dc magnetic susceptibility gives the strong anomaly at 4.7 K and difference between ZFC and FC curves below 6.6 K (see inset in Fig. 4). The $\chi_{ac}(T)$ gives strong anomaly at 5 K and small at 6.6 K (see Fig. 5). The data reported in Ref. [3] give the anomaly at 4.5 K (ρ), 6 K (χ) and 6.3 K (C_p). The neutron diffraction data give the critical temperature of magnetic order equal to 7 K and anomaly at 4.5 K [8].

For $Er_5Rh_4Ge_{10}$ the dc and ac magnetic susceptibilities give the distinct maximum at 4.2 K. These results are in contradiction with the results reported in Ref. [3] which give the anomalies at 5 K (χ), 5.5 K (ρ) and 5.6 and 4.2 K (C_p). The change of the magnetic order is clearly visible in the neutron diffraction experiment of $Er_5Rh_4Ge_{10}$ in which, with the increase of the temperature at 4.2 K, the sine wave modulated ordering described by the propagation vector $\boldsymbol{k} = (k_x, k_x, 0)$ changes from $k_x = 1/4$ at low temperature to $k_x = 1/3$ near the Néel temperature equal to 5.5 K [4].

For $Tm_5Rh_4Ge_{10}$ compounds the dc data give the anomaly at 6 K. This is in good agreement with the previous data; from resistivity at 6 K, specific heat at 6 and 6.9 K [3] and neutron diffraction at 6.9 K [5]. For isostructural $Gd_5Rh_4Ge_{10}$ compounds the temperature dependence of the magnetic susceptibility resistivity and specific heat give four transition temperatures at ≈ 6.7, ≈ 8.5, ≈ 11.5, and 14 K [3, 9]. The complex crystal structures in which the rare-earth atoms with localized magnetic moments occupy three equivalent sites indicate that the interactions between the moments at different sublattices lead to different magnetic orderings at different temperature region.

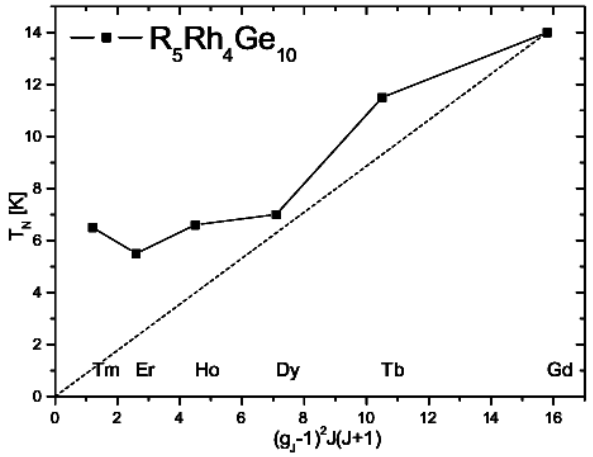

Fig. 10. The Néel temperatures versus de Gennes factor $(g_J-1)^2J(J+1)$ for $R_5Rh_4Ge_{10}$ (R = Gd–Tm). The breaking line corresponding to the de Gennes function normalized for Gd-compound.

The observed in the neutron diffraction experiments the modulated magnetic order, metallic character of the electrical conductivity [3], and the large interatomic R–R distance (≈ 4 Å) suggest that the magnetic interaction between the localized rare earth moments is probably via conduction electrons (the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction). In this model the critical temperature of the magnetic order is a function of the de Gennes factor $(g_J-1)^2J(J+1)$ [10], where g_J is the Landé splitting factor and J is the total angular momentum of the corresponding magnetic ion. The de Gennes scaling is not fulfilled in these compounds in particular for those

with R = Ho, Er, and Tm (see Fig. 10) which means that another mechanism influences on the stability of their magnetic ordering. The observed reorientation processes indicate an influence of various R–R bonds or the crystal electric field.

Acknowledgments

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