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Magnetic order in RAgGe (R=Gd–Er) intermetallic compounds

S. Baran[a], M. Hofmann[b], J. Leciejewicz[c], B. Penc[a], M. Ślaski[d], A. Szytuła[a,]*

[a]Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Kraków, Poland
[b]Berlin Neutron Scattering Centre, Hahn-Meitner Institut, Berlin, Germany
[c]Institute of of Nuclear Chemistry and Technology, Warsaw, Poland
[d]School of Physics and Space Research, University of Birmingham, Edgbaston, Birmingham, UK

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Abstract

Polycrystalline samples of the ternary intermetallics RAgGe (R=Tb–Er) were investigated by means of magnetization and neutron diffraction measurements. For GdAgGe compounds only magnetic measurements were performed. They crystallize in the hexagonal ZrNiAl-type structure. Magnetic measurements show antiferromagnetic ordering at Néel temperatures between 15.6 K for R–Gd and 3.6 K for R=Er. For TbAgGe the neutron diffraction data reveal a complicated sine modulated magnetic structure which is affected by temperature changes. For DyAgGe and HoAgGe the square modulated magnetic ordering is described by the wave vector $k=(\frac{1}{3}\frac{1}{3}\ 0)$ while for ErAgGe by $k=(\frac{1}{2}\frac{1}{2}\ 0)$. With increasing number of 4f-electrons one observes a change of the direction of magnetic moment from parallel to the c-axis for R=Tb via one which forms an angle φ with the c-axis for R=Dy, to one which lies in the basal plane for R=Ho and Er.

Rare earth intermetallic compounds; Rare earth silver germanides; Magnetic structure; Neutron diffraction; Magnetic properties

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1. Introduction

In recent years the investigation of the magnetic properties of the rare earth intermetallic compounds have been a subject of intensive research. The RTX compounds, where R is a rare earth element, T is a transition nd element and X is a p-electron metal, crystallize in more than 30 different structure types [1]. Our investigations are concentrated on RTX compounds where T=Cu, Ag, Au and X=Sn and Ge. Except for RAgSi and RAgGe all these compounds crystallize in the hexagonal LiGeGa-type of crystal structure. The X-Ray data for powder [2,3] and single crystal [4] RAgGe samples indicate that these compounds crystallize in hexagonal ZrNiAl-type structure (Fe_2P order). Magnetic susceptibility measurements show antiferromagnetic ordering at Néel temperatures of 13.0(2) and 3.3(1) K for GdAgGe and ErAgGe respectively and ferromagnetic ordering at $T_C=14.0(2)$ K for DyAgGe [4].

In this paper the neutron diffraction and magnetic data are presented for RAgGe (R=Gd–Er). The crystal and magnetic structures of these compounds are determined.

2. Experimental

The samples, each of a total weight of 7 g, were synthesized by argon arc melting of the elements with 3 N minimum purity. Annealing was carried out at 970 K for ten days.

After annealing, the samples were examined by powder X-ray diffraction using a DRON 3 diffractometer with CoKα radiation. The indexing of the diffraction lines was verified by computing intensities using the data from ref. [2–4]. The determined lattice constants are in good agreement with the data published earlier by Zanicchi et al. [3]. Several observed small intensity reflections were ascribed to an impurity phase.

The magnetic susceptibility and magnetization of polycrystaline samples were determined with a Cryogenics S100 SQUID susceptometer that operates in magnetic fields up to 1000 Oe and with an Oxford Instruments VSM

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*Corresponding author. E-mail: szytula@if.uj.edu.pl

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12T magnetometer in magnetic fields up to 120 kOe between 4.2 and 300 K.

For the RAgGe (R = Tb–Er) compounds the neutron diffraction measurements were carried out in the BER II reactor at the Hahn-Meitner Institut in Berlin. The neutron wavelength was 2.378 Å. Additional measurements with the wave length $\lambda = 4.36$ Å were performed for the TbAgGe compound. The observed neutron diffraction intensities were processed using the FULLPROF program [5]. Neutron scattering length values were taken from Ref. [6]. The form-factors for the R^{3+} ions were taken as $f = <\gamma_0> + c_2 <\gamma_2>$ in the dipolar approximation according to Ref. [7].

3. Results

3.1. Crystal structure

Neutron diffraction peaks observed in the patterns of RAgGe (R = Tb–Er) compounds at the temperatures above the respective Néel points correspond to the hexagonal structure of the ZrNiAl-type (space group $P\bar{6}2m$). The atoms occupy the following positions:

3 R atoms at 3(*g*):	$x, 0, 0;$	$0, x, 0;$	$\bar{x}, \bar{x}, 0;$
3 Ge atoms at 3(*f*):	$y, 0, \frac{1}{2};$	$0, y, \frac{1}{2};$	$\bar{y}, \bar{y}, \frac{1}{2};$
2 Ag atoms at 2(*c*);	$\frac{1}{3}, \frac{2}{3}, \frac{1}{2};$	$\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$	
1 Ag atom at 1(*b*):	0,0,0		

The values of the *x* and *y* parameters corresponding to the minimum of the reliability factors are listed in Table 1. The obtained parameters are in good agreement with those published in Ref. [4].

3.2. Magnetic properties

In Fig. 1 the temperature dependence of the magnetic susceptibility and reciprocal magnetic susceptibility of the RAgGe compounds within the temperature range 4.2–300 K are shown. In the low temperature range, for the RAgGe (R = Gd–Ho) compounds, a maximum characteristic of an antiferro- to paramagnetic transition is observed. The determined values of the Néel temperatures are listed in Table 2. The magnetic susceptibility of ErAgGe has a paramagnetic character up to 4.2 K. In the temperature dependence of the magnetic susceptibility two additional anomalies at 6 and 20 K for TbAgGe and one at 11 K for DyAgGe are observed. We measured both the ZFC (zero field cooled) and FC (field cooled) magnetization curves with monotonically increasing temperature. In the data for the RAgGe (R = Gd–Ho) compounds considerable differences between the ZFC and FC branches are found. The ZFC curves are lower. This effect is due to magnetic domains and the motion of domain walls [8].

Table 1
Crystal data for RAgGe compounds (R = Tb–Er)

R	Tb	Dy	Ho	Er
T (K)	50	20	15	5
a (Å)	7.1221(38)	7.1140(46)	7.0862(44)	7.0634(39)
c (Å)	4.1221(22)	4.2058(25)	4.1864(26)	4.1727(23)
c/*a*	0.5788	0.5912	0.5908	0.5907
V (A^3)	181.07	184.33	182.05	180.29
x_1	0.5867(17)	0.5845(17)	0.5828(17)	0.5856(15)
x_2	0.2467(34)	0.2471(92)	0.2459(39)	0.2428(37)
R_{Bragg}(%)	7.82	6.48	8.3()	7.39
$R_{\mathrm{prof.}}$(%)	7.10	8.66	6.70	7.00

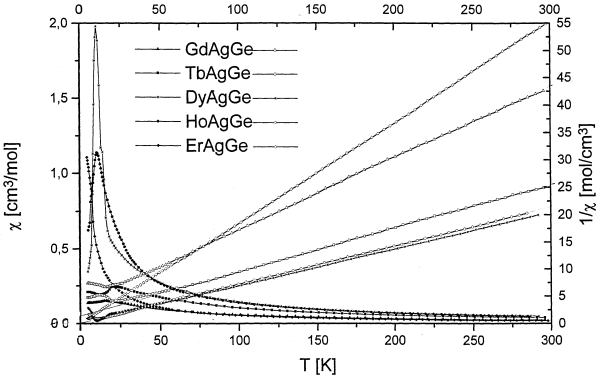

Fig. 1. Temperature dependence of the magnetic susceptibility and reciprocal magnetic susceptibility of RAgGe (R = Gd–Er) compounds.

Above 50 K the reciprocal magnetic susceptibility curves of all samples obey the Curie-Weiss law:

$$\chi(T) = \frac{n\mu_{\mathrm{eff}}^2}{3k_B(T - \theta_p)}.$$

From the numerical fits to the experimental data give the paramagnetic Curie temperatures θ_p were derived, which change from negative values for R = Gd, Tb and Dy to positive values for R = Er. The negative values of paramagnetic Curie temperature suggest antiferromagnetic order in rare earth sublattice. The effective magnetic moments are found to be close to the R^{3+} free ion values (see Table 2).

The magnetization curves at different temperatures in external magnetic fields up to 120 kOe are shown in Fig. 2. For GdAgGe the magnetization increases almost linearly with increasing external magnetic field. A similar dependence is observed at $T = 15$ and 30 K.

For TbAgGe and DyAgGe the magnetization curves at $T = 4.2$ K have a metamagnetic character with four critical magnetic fields. With increasing temperature the low-field metamagnetic phase transition vanishes. In the magnetization curve of HoAgGe at $T = 4.2$ K only one metamagnetic phase transition is observed while the magnetization curve of ErAgGe at $T = 4.2$ K is typical of paramagnetic materials.

The values of the critical field H_C decrease with

Table 2
Magnetic properties of RAgGe compounds (R = Gd–Er)

R	T_N (K)		T_t (K)		θ_p (K)	μ_{eff} (μ_B)		μ_s (μ_B)			H_{Cr} (kOe)
	M	ND	M	ND		Exp.	Theor.	Exp.		Theor.	
								M*	ND		
Gd	15.6				-31.4	7.88	7.94	2.9		7	
	13^b				-23^b	7.1^b				9	
Tb	25	27	20	20.5	-14.6	9.97	9.72	5.6			2.4,16,35,105
Dy	14.5	14.5	11		0	10.86	10.63	8.0	9.9	10	2.1,15,20.5,48.6
	14^b				-11^b	10.3^b					
Ho	10.3	10.3			0	10.73	10.61	8.2	10.0	10	0.6,11.5
Fr	3.3^b	3.6			$+6.4$	9.54	9.58	7.4^a	4.37	9	
					-1^b	$9/1^b$					

M: magnetic susceptibility measurements in $H = 10$ Oe.
M*: magnetization measurements in $H = 120$ kOe and $T = 4.2$ K.
ND: neutron diffraction experiment in $H = 0$ and $T = 1.6$ K.
[a] Data in the paramagnetic state
[b] Ref. [4].

increasing number of 4f electrons. The values of the magnetic moments at $T = 4.2$ K and $H = 120$ kOe are smaller than the free R^{3+} ion values (see Table 2).

3.3. Magnetic structures

The comparison of the neutron diffraction patterns of the RAgGe compounds, recorded in the paramagnetic state, with the neutron diffraction patterns recorded below the Néel temperatures shows the presence of additional peaks resulting from the onset of magnetic order. For TbAgGe the magnetic reflections in the neutron diffraction pattern at $T = 1.6$ K (see Fig. 3a) could be indexed by assuming a magnetic structure with two different schemes of the propagation vectors:

first, $k_1 = (0.3791(9),\ 0.3791(9),\ 0)$ and $k_2 = (0.3116(36),\ 0.1361(48),\ 0.2060(33))$ and
second, $k_1 = 0.3794(27),\ 0.2417(18),\ 0)$ and $k_2 = (0.3116(36),\ 0.1361(48),\ 0.2060(33)$.

The magnetic ordering corresponding to these wave vectors is sine modulated. In the magnetic structure described by both the k_1 wave vectors the magnetic moments which equal 7.83(36) μ_B are parallel to the c-axis. For both models of the magnetic structure the same values of the reliability factor $R_m = 14.3\%$ are obtained. The magnetic structure described by the wave vector k_2 is also sine modulated with the magnetic moment which equals 5.7(4) μ_B and which forms an angle of $\theta = 38(14)$ 0 with the c-axis.

With increasing temperature the peaks corresponding to the k_1-wave vector vanish at 27 K while those corresponding to the k_2-wave vector vanish at 20.5 K (see inset in Fig. 4a). The existence of two wave vectors is clearly visible in the additional measurements with the longer wavelength, $\lambda = 4.36$ Å (Fig. 4b). The magnetic peaks at $T = 25$ K are described by the wave vector $k_1 = (0.3767(12),\ 0.3767(12),0)$ or $k_2 = (0.3712(27),\ 0.2491(24),0)$. For both wave vectors a similar model of the magnetic structure is obtained: a sine modulated one with the moment equal to 4.57(27) μ_B lying in the 10 plane and forming an angle of 28(10)° with the c-axis.

Below and above the Néel temperature near the $000^{\pm}$ reflection ($2\theta = 12°$) a diffuse peak is observed, indicative of short range order.

The magnetic peaks observed in the neutron diffraction pattern of DyAgGe at T = 1.5 K are indexed with the wave vectors $k = (\frac{1}{3}, \frac{1}{3}, 0)$ and $3k$. The presence of k and $3k$ wave vectors suggests a square modulated magnetic structure. The Dy magnetic moments at the positions: $(x, 0, 0)$ and $(0, x, 0)$ are parallel while at the position $(\bar{x}, \bar{x}, 0)$ they are antiparallel. The magnetic moments equal to 9.9(3) μ_B lie in the b–c plane and form an angle of 50(7)° with the c-axis. The projection of this structure on the a–b plane is shown in Fig. 5a. The change of the $000^{\pm}$ reflection intensity gives a Néel temperature of 14.5 K.

The magnetic peaks in the neutron diffraction pattern of HoAgGe at $T = 1.6$ K are described by the wave vectors $k = (\frac{1}{3}, \frac{1}{3}, 0)$ and $3k$ (see Fig. 6). The magnetic ordering is a non-collinear one with magnetic moments equal to 10.0(3) μ_B lying in the basal plane (see Fig. 5b).

The temperature dependence of the $000^{\pm}$ peak corresponding to wave vector k gives a Néel temperature of 10.3 K.

A different magnetic ordering is observed in ErAgGe. The magnetic peaks observed in the neutron diffraction pattern at $T = 1.6$ K (see Fig. 7) are described by the wave vector $k = (\frac{1}{2}, \frac{1}{2}, 0)$. The Er magnetic moments form a collinear antiferromagnetic structure (see Fig. 5c) with the moments equal to 4.37(15) μ_B and parallel to the b-axis. From the temperature dependence of the $000^{\pm}$ reflection intensity we derive a Néel temperature of 3.6 K.

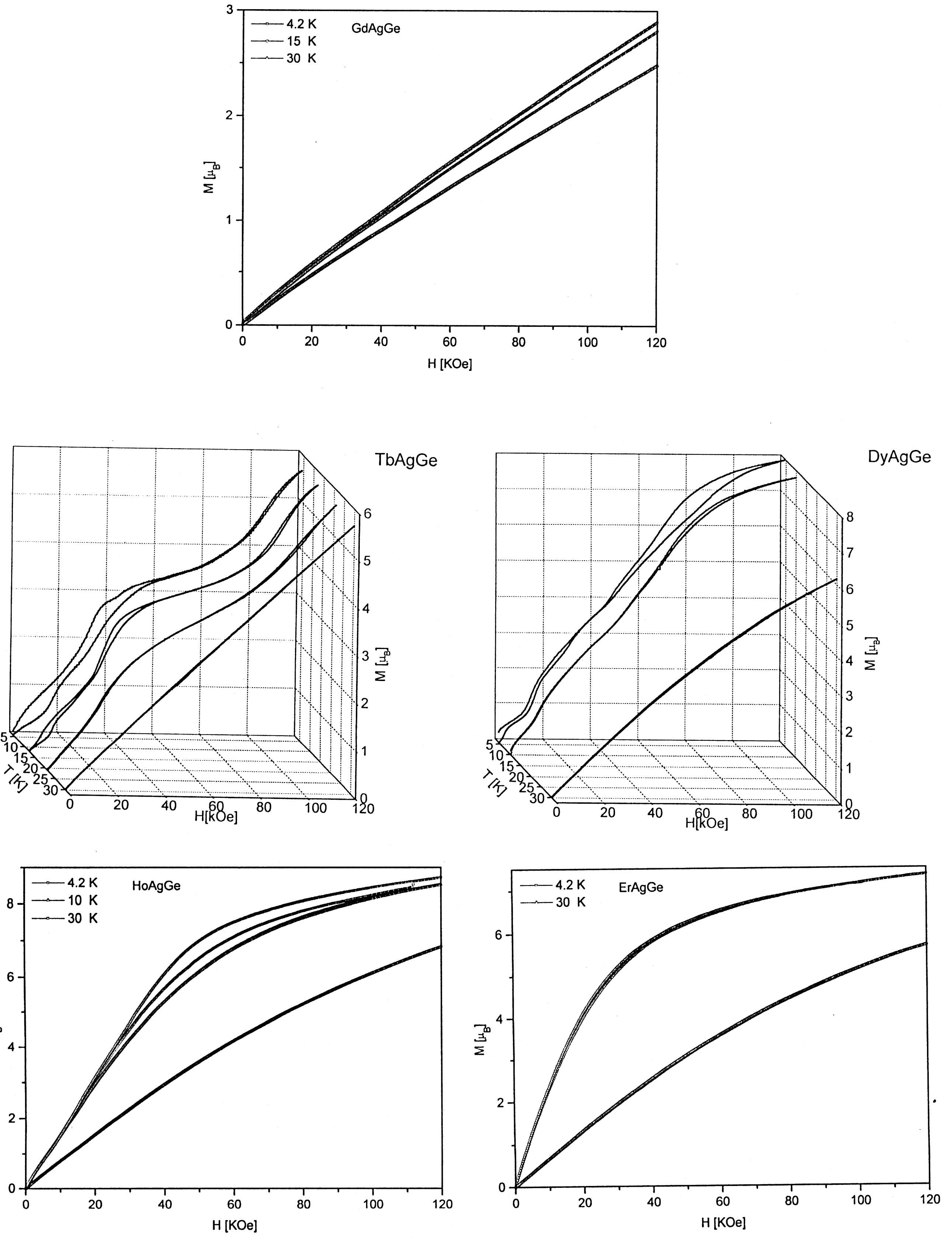

Fig. 2. Magnetization curves at different temperatures for RAgGe (R=Gd–Er).

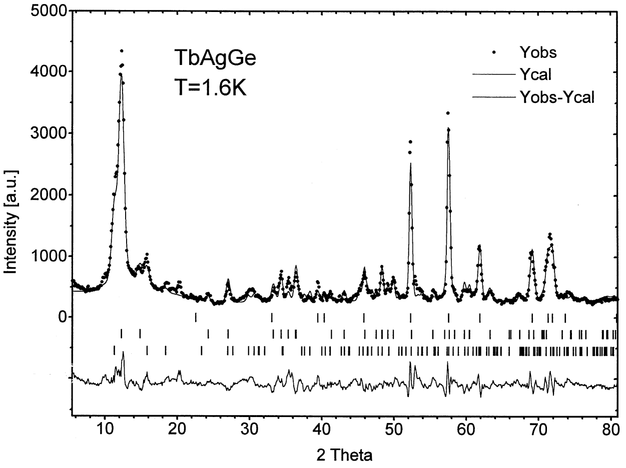

Fig. 3. Observed and calculated neutron diffraction pattern of TbAgGe at $T=1.5$ K. The solid lines represent the profile and the difference between the observed and calculated data (below). The vertical bars indicate the nuclear and magnetic peaks corresponding to the wave vectors k_1 and k_2.

4. Discussion

The RAgGe compounds, investigated in this paper, crystallize in the hexagonal ZrNiAl-type structure. The atomic arrangement leads to two different kinds of layers in the unit cell: Ag–Ge layers at $z=\frac{1}{2}$ and R–Ag layers at $z=0$. The projection of the crystal structure on a basal plane is shown in Fig. 8. The distribution of the rare earth atoms forms a triangle. The interatomic distance between rare earth atoms in the triangle is equal to 3.673 Å in ErAgGe while the distance between centers of triangles is equal to $a=7.063$ Å. Each R atom has four R nearest neighbours in the plane and two next-nearest R neighbours along the c-axis (at the distance of the c lattice constant). This fact suggests that the magnetic properties should be strongly anisotropic.

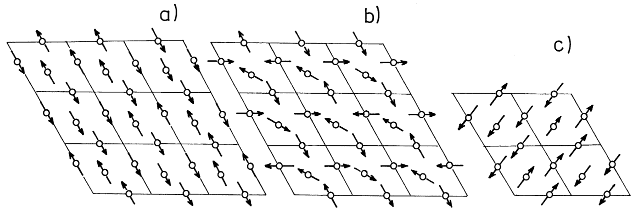

Fig. 5. Magnetic structures of RAgGe compounds. Projection of structures of (a) DyAgGe, (b) HoAgGe (c) ErAgGe on the basal plane.

The large interatomic distances and metallic character of the electric resistivity indicate that the observed magnetic ordering results from indirect coupling via conduction electrons (RKKY model).

In the RKKY model, the ordering temperatures are proportional to the de Gennes factor $(g_J-1)^2J(J+1)$. The dependence of the Néel temperature on the rare earth atom R for RAgGe, when viewed in terms of experimental data and the data resulting from the theory, is shown in Fig. 9. According to the de Gennes scaling T_{N} should have a maximum for the GdAgGe [9]. The maximum of the Néel temperature, for the measured compounds, shifts from Gd to Tb which may result from the crystalline electric field (CEF) effect [10]. The presented results show that a simple

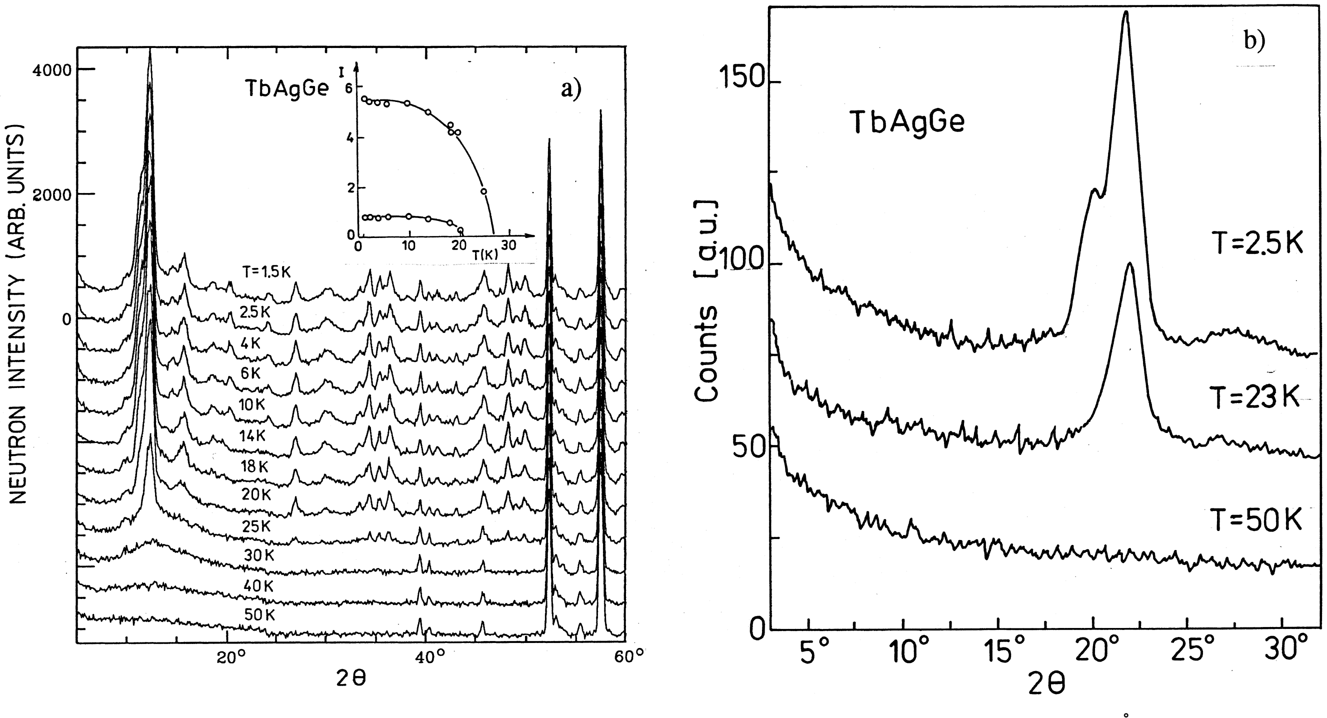

Fig. 4. The neutron diffraction patterns of TbAgGe taken at a (a) number of temperatures between 1.6 and 50 K ($\lambda=2.378$ Å) (the inset shows the integrated intensities of the magnetic peaks corresponding to the k_1 and k_2, wave vectors), (b) at $T=2.5$, 20 and 50 K ($\lambda=4.37$ Å).

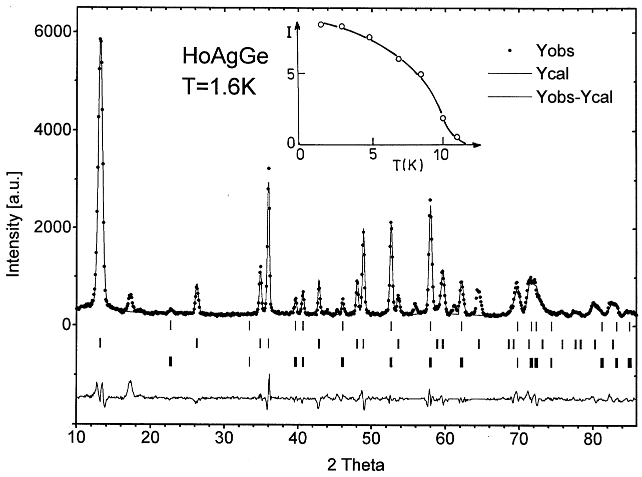

Fig. 6. Neutron diffraction pattern of HoAgGe at $T=1.6$ K and the difference pattern. The solid lines represent the profile and the difference between the observed and calculated data (below). The vertical bars indicate the nuclear and magnetic peaks corresponding to the wave vectors k and $3k$. The inset shows the temperature dependence of the intensity of $000^{\pm}$ peak corresponding to the k wave vector.

RKKY model is not suitable for the description of the magnetic properties of these compounds. It is necessary to include also the influence of the CEF. The neutron diffraction measurements disclose the complicated magnetic ordering as present in these compounds.

As regards TbAgGe at low temperatures this ordering is described by two wave vectors. With increasing temperature the change of the magnetic structure of TbAgGe into one described by one wave vector is observed at $T=20$ K. For the determination of the exact magnetic structure of the discussed compound it is necessary to perform a neutron diffraction experiment on a single crystal.

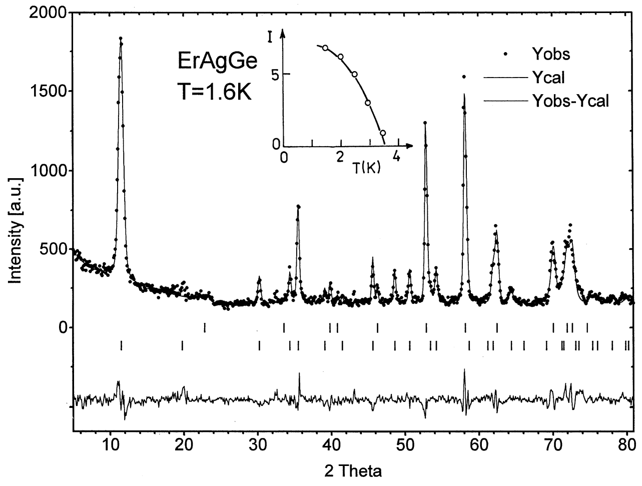

Fig. 7. Neutron diffraction pattern of ErAgGe at $T=1.6$ K and the difference pattern. The solid lines represent the profile and the difference between the observed and calculated data (below). The vertical bars indicate the nuclear and magnetic peaks corresponding to the wave vector k. The inset show the temperature dependence of the intensity of $000^{\pm}$ peak.

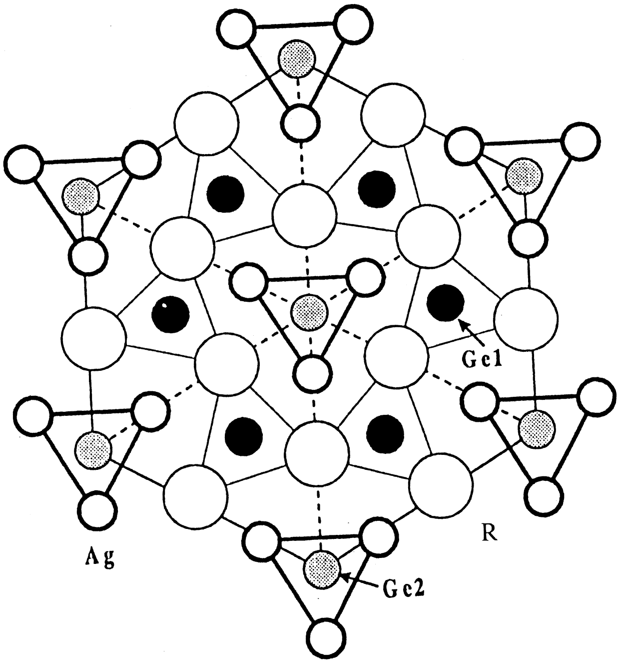

Fig. 8. Projection of the crystal structure of RAgGe compounds on the plane.

In DyAgGe and HoAgGe the magnetic order is described by the wave vector $k=(\frac{1}{3}, \frac{1}{3}, 0)$. The magnetic structure of ErAgGe is collinear and antiferromagnetic with the wave vector $k=(\frac{1}{2}, \frac{1}{2}, 0)$.

With changing number of 4f electrons a change of the magnetic structure from incommensurate for TbAgGe to commensurate for the other compounds is observed. The observed magnetic ordering results from the interactions between the moments in the triangle and from a long range interaction of oscillatory character. The short range interaction is ferromagnetic (ErAgGe), antiferromagnetic (TbAgGe), or has a frustrated character (HoAgGe).

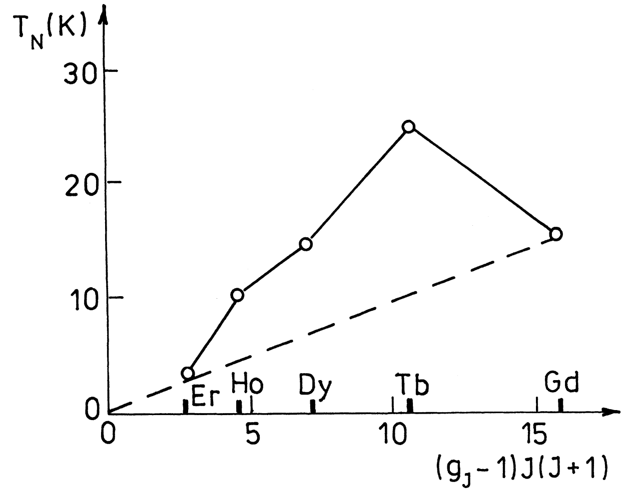

Fig. 9. The dependence of the Néel temperature as found for RAgGe compounds and its relation to the de Gennes function (dashed line).

We also observed a change of the direction of the magnetic moments from parallel to the *c*-axis for TbAgGe, via one which forms an angle φ with the *c*-axis for DyAgGe to one which lies in the basal plane for the HoAgGe and ErAgGe compounds.

In this structure type in which the rare earth atoms are located at the 3f site with the orthorhombic symmetry $C_{2V}(m2m)$ the Hamiltonian of the crystal electric field is represented by

$$H_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6$$

where B_n^m is the CEF parameter and O_n^m is the Stevens operator [11].

The direction of the magnetic moment is connected with the sign of the B_2^0 parameter. The magnetic moment for the negative value of B_2^0 is parallel to the *c*-axis while the magnetic moment for the positive value of B_2^0 is perpendicular to the *c*-axis.

The experimental data presented in this paper indicate that with increasing number of 4f electrons a change of the direction of the magnetic moments is observed from parallel to the *c*-axis for TbAgGe to perpendicular to the *c*-axis for HoAgGe and ErAgGe. The existence of a moment direction 50° away from the *c*-axis in DyAgGe indicates that higher-order terms also play a role in the stability of the magnetic structure.

Powder neutron experiments, however, cannot solve the problem sufficiently due to the limited information which can be arrived at, especially in cases of complex magnetic moment configurations. It is necessary to perform single crystal neutron diffraction experiments for TbAgGe and DyAgGe which would either support or discard the models of the magnetic structures as discussed in this paper.

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