Magnetic Ordering in $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$ Compounds

B. PENC^a, A. ARULRAJ^b, D. KACZOROWSKI^c, A. SZYTULA^{a,*} AND E. WAWRZYŃSKA^a

^aM. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland

^bBENSCH, Hahn–Meitner-Institute, Glienicker Str. 100, 14109 Berlin-Wannsee, Germany

^cW. Trzebiatowski Institute of Low Temperatures and Structure Research, Polish Academy of Sciences
P.O. Box 1410, 50-950 Wrocław, Poland

The magnetic ordering in $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$ compounds crystallizing in the orthorhombic structure of the CeNiSi_2 -type has been investigated by neutron diffraction and magnetic measurements. The Er magnetic moments have been found to order antiferromagnetically below 2.5 K in $\text{ErFe}_{0.3}\text{Ge}_2$ and 2.3 K in $\text{ErNi}_{0.65}\text{Ge}_2$. The magnetic structure of the former compound can be described by the propagation vector $\mathbf{k} = (0.044(1), 0, 0.384(1))$. The Er magnetic moments are aligned along the a -axis and alternate with the sequence $++--$ in the unit cell. At 1.5 K they are equal to $5.9(1) \mu_B$. In contrast, the magnetic unit cell of $\text{ErNi}_{0.65}\text{Ge}_2$ has been established to be equal to the chemical one. The magnetic moments in this compound are arranged in a collinear manner pointing along the a -axis with the sequence $+-+-$. The Er moment value measured at 1.5 K is $2.90(8) \mu_B$.

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1. Introduction

Ternary rare earth (R) ternaries of composition RTX_2 , where T is a $3d$ element and X is a metalloid (Si, Ge, Sn), constitute a large family of compounds with interesting magnetic properties [1]. Most of them crystallize with the orthorhombic CeNiSi_2 -type of structure (space group $Cmcm$) [2]. The silicides exist as stoichiometric phases, while the germanides and the stannides exhibit distinct nonstoichiometry [3].

The hitherto performed investigations focused on the compounds with T = Mn, Co, Ni and Cu. For example, for the series RNiGe_2 (R = Gd, Tb, Dy and Ho) and RNi_xGe_2 (R = Tb, Ho, Er) antiferromagnetic ordering has been found at low temperatures [4–7]. From the germanides with T = Fe the magnetic properties have been determined for $\text{CeFe}_{0.63}\text{Ge}_2$ and $\text{HoFe}_{0.33}\text{Ge}_2$. The former compound is a Curie–Weiss paramagnet above 100 K and remains nonmagnetic down to low temperatures [8, 9], whereas the other one orders antiferromagnetically below 8 K [10].

As a continuation of our systematic studies of the RTX_2 phases, we performed recently neutron diffraction and magnetic measurements on polycrystalline samples of $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$. Here, we report on the crystal and magnetic structures of the two compounds.

2. Experiment

Polycrystalline samples of $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$ were obtained by arc melting the respective elements

(purity better than 99.9 wt%) in high-purity argon atmosphere. Subsequently, the buttons were annealed at 800 °C for 1 week. Quality of the products was examined by X-ray powder diffraction.

The magnetic susceptibility and magnetization data were collected in the temperature range from 1.7 to 300 K and in external magnetic field up to 5 T employing a Quantum Design MPMS-5 SQUID magnetometer.

Neutron diffraction measurements were carried out at several temperatures from the temperature interval from 1.5 to 10 K with the incident neutron wavelength 0.2445 nm using the E6 diffractometer installed at the BER II reactor (Hahn–Meitner-Institute, Berlin). The diffractograms were analyzed with the use of the Rietveld program FULLPROF [11].

3. Bulk magnetic data

The magnetic behavior of $\text{ErFe}_{0.3}\text{Ge}_2$ is presented in Fig. 1. A clear maximum in the temperature dependence of the magnetic susceptibility marks an onset of the antiferromagnetic state below $T_N = 2.5$ K. The magnetization measured at $T = 1.7$ K is a linear function of external magnetic field up to 1.5 T and saturates in stronger fields. The magnetic moment determined in a field of 5 T is equal to $5.9 \mu_B$. In the paramagnetic region, the reciprocal magnetic susceptibility obeys the Curie–Weiss law with the paramagnetic Curie temperature close to zero ($\theta_p = -0.2$ K) and the effective magnetic moment nearly equal to the free Er^{3+} ion value ($\mu_{\text{eff}} = 9.54 \mu_B$ versus $g[J(J+1)]^{1/2} = 9.58$).

The magnetic properties of $\text{ErNi}_{0.65}\text{Ge}_2$ were reported in Ref. [5]. The compound was found to order antiferromagnetically below the Néel temperature of 2.3 K. In

* corresponding author; e-mail: szytula@if.uj.edu.pl

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of $\text{ErFe}_{0.3}\text{Ge}_2$. The solid line represents the Curie–Weiss law fit. Upper inset: low-temperature dependence of the magnetic susceptibility. Lower inset: magnetic field variation of the magnetization taken at $T = 1.7$ K with increasing (full symbols) and decreasing (open symbols) magnetic field.

the paramagnetic state the magnetic susceptibility exhibits the Curie–Weiss behavior with the effective magnetic moment of $9.69 \mu_B$ and the paramagnetic Curie temperature of -2 K.

4. Crystal and magnetic structure

The X-ray diffraction patterns taken at room temperature (RT) and the neutron patterns recorded at $T = 5$ K for $\text{ErFe}_{0.3}\text{Ge}_2$ (see Fig. 2) and $T = 10$ K for $\text{ErNi}_{0.65}\text{Ge}_2$ (see Fig. 3) confirmed the orthorhombic structure of the CeNiSi_2 -type, which was reported previously for both compounds [3]. Moreover, the lattice parameters determined at RT are in good agreement with those given in Ref. [3]. In the CeNiSi_2 -type unit cell all the atoms occupy the $4c$ position $(0, y, 1/4)$ with different values of the free parameter y (space group $Cmcm$). The refined values of the lattice parameters and the positional parameters y , derived from the neutron diffraction data, are listed in Table I, together with the corresponding final reliability factors. A few spurious peaks of small intensities indicated the presence in the specimens studied of little admixtures of elemental Ge and another indefinite phase in $\text{ErFe}_{0.3}\text{Ge}_2$ and some tiny amount of ErNi_2Ge_2 in $\text{ErNi}_{0.65}\text{Ge}_2$.

The Bragg peaks of magnetic origin, present in the neutron diffraction pattern of $\text{ErFe}_{0.3}\text{Ge}_2$ collected at 1.5 K (*cf.* Fig. 2), can be indexed with the use of the propagation vector $\mathbf{k} = [0.044(1), 0, 0.384(1)]$. For the Er atoms located at the $4c$ site of the $Cmcm$ space group, three antiferromagnetic models are possible: $\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4$; $\mathbf{C} = \mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4$ and $\mathbf{G} = \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4$, where the positive and negative signs of $\mathbf{S}_{1...4}$ refer to the spin direction of the Er

Fig. 2. Neutron diffraction pattern of $\text{ErFe}_{0.3}\text{Ge}_2$ taken at 5 K (bottom part) and the difference between the patterns measured at 1.5 K and 5 K (upper part), together with the Rietveld fits described in the text (solid lines) and the difference plots. The vertical ticks indicate positions of the magnetic Bragg reflections (upper part) and the Bragg peaks of nuclear origin (bottom part). The second row ticks mark the Ge impurity contribution. The small peaks at $2\theta = 60^\circ$ and 81° correspond to an unidentified phase.

magnetic moments located at the $0, y, 1/4$ ($\mathbf{S}_1$); $0, \bar{y}, 3/3$ ($\mathbf{S}_2$); $1/2, 1/2 + y, 1/4$ ($\mathbf{S}_3$) and $1/2, 1/2 - y, 3/4$ ($\mathbf{S}_4$) site. The minimum of the reliability factor was obtained for the sequence $++--$ of the magnetic moments in the elementary unit cell ($\mathbf{C}$ -mode) being oriented along the a -axis. The refined value of the moment at 1.5 K was $5.9(1) \mu_B$, in excellent agreement with the bulk magnetization data (see above). From the temperature evolution of the magnetic peak intensities the Néel temperature of 2.5 K can be derived, again in accord with the afore-discussed magnetic susceptibility results. As displayed in Fig. 4, the temperature variations of the lattice parameters and the unit cell volume exhibit remarkable changes at the magnetic phase transition, thus signaling strong magnetostriction effect in $\text{ErFe}_{0.3}\text{Ge}_2$.

In the case of $\text{ErNi}_{0.65}\text{Ge}_2$ the proper description of the neutron diffraction pattern collected at 1.5 K has been obtained assuming the magnetic unit cell equal to the chemical one. The best agreement between the theoretical model and the experimental data has been reached for a collinear antiferromagnetic structure corresponding to the $\mathbf{G} = \mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4$ mode with the magnetic moments aligned along the a -axis. The Er moments found at 1.5 K amount to $2.90(8) \mu_B$. From the temperature

Fig. 3. Neutron diffraction patterns of $\text{ErNi}_{0.65}\text{Ge}_2$ collected at 1.5 and 10 K. The solid curves are the calculated profiles for the crystal and magnetic structures described in the text and the difference between the observed and calculated intensities (bottom of each diagram). The vertical bars indicate the Bragg peaks of nuclear and magnetic origin. The second row ticks correspond to the ErNi_2Ge_2 impurity phase. The peak at $2\theta = 55^\circ$ belongs to an unknown phase. Inset: temperature variation of the (020) magnetic peak intensity.

Fig. 4. Temperature dependences of the lattice parameters a , b and c and the unit cell volume V as well as of the value of the magnetic moment μ of $\text{ErFe}_{0.3}\text{Ge}_2$.

dependence of the (020) magnetic peak intensity the Néel temperature of 2.3 K can be derived, in good agreement with the bulk magnetic data [5].

TABLE I

The lattice parameters (a, b, c) and the positional parameters (y_{Er} , $y_{\text{Fe/Ni}}$, y_{Ge1} , y_{Ge2}) of $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$, determined from the neutron diffraction data collected at 5 and 10 K, respectively. The residual reliability factors for integrated (R_{Bragg}) and profile (R_{profile}) intensities are also listed.

Compound	$\text{ErFe}_{0.3}\text{Ge}_2$	$\text{ErNi}_{0.65}\text{Ge}_2$
T [K]	5	10
a [nm]	0.40818(8)	0.40727(15)
b [nm]	1.56332(40)	1.61179(73)
c [nm]	0.39734(8)	0.39930(15)
y_{Er}	0.1044(7)	0.1035(13)
$y_{\text{Fe/Ni}}$	0.3173(17)	0.3124(12)
y_{Ge1}	0.4464(5)	0.4500(8)
y_{Ge2}	0.7790(7)	0.7784(10)
R_{Bragg} [%]	7.65	11.7
R_{profile} [%]	6.21	8.3

5. Summary

The magnetic behavior of the ErT_xGe_2 ($T = \text{Fe, Ni}$) compounds, crystallizing with the orthorhombic structure of the CeNiSi_2 -type, is governed by the presence of the magnetic moments localized on the rare-earth atoms. In the paramagnetic state the effective magnetic moments are close to the free Er^{3+} ion values. Below $T_N = 2.5$ K for $\text{ErFe}_{0.3}\text{Ge}_2$ and $T_N = 2.3$ K for $\text{ErNi}_{0.65}\text{Ge}_2$ the erbium magnetic moments order antiferromagnetically with the modulated ($\mathbf{k} = [0.044(1), 0, 0.384(1)]$) and collinear structure, respectively. In both compounds the magnetic moments are parallel to the a -axis. The refined values of the ordered moments are equal to $5.9(1) \mu_B$ and $2.90(8) \mu_B$ for $\text{ErFe}_{0.3}\text{Ge}_2$ and $\text{ErNi}_{0.65}\text{Ge}_2$, respectively. The distinct reduction of these values with respect to the free ion value ($9.0 \mu_B$) likely originates from the crystalline electric field effect. However, it should be noted that because the neutron diffraction experiments were performed rather close to the respective temperature T_N , the uncertainty in the derived values of the ordered magnetic moment is relatively large.

TABLE II

Comparison of the Néel temperatures (T_N), the propagation vector components (k_x , k_y , k_z), the ordered magnetic moment values at 1.5 K (μ_o), direction of the moments (DMM) and the magnetic structure type (Mode) determined for several RT_xX_2 germanides and stannides.

Compound	T_N [K]	k_x	k_y	k_z	μ_o (μ_B)	DMM	Mode	Ref.
ErFe _{0.3} Ge ₂	2.5	0.044	0	0.384	5.9(1)	a	C_x	this work
ErNi _{0.65} Ge ₂	2.3	0	0	0	2.90(9)	a	G_x	this work
ErCo _{0.4} Ge ₂	≈ 1.5	0.548	0.548	0	3.3(1)	c	F_z	[12]
ErCu _{0.25} Ge ₂	4.5	0	0	0	7.89(15)	a	G_x	[13]
ErCo _{0.4} Sn ₂	4.5	0	0	.5	6.15(13)	a	C_x	[14]
ErNi _{0.15} Sn ₂	4.0	0	0	0.5	9.16(9)	a	C_x	[14]

Table II summarizes the magnetic data for several ErT_xGe_2 and ErT_xSn_2 compounds. All these phases order antiferromagnetically at low temperatures with the Er magnetic moments aligned along the a -axis, except for $ErCo_{0.4}Ge_2$ that has the moments being oriented parallel to the z -axis [12]. Interestingly, the rare-earth moment direction is different in the corresponding compounds with $R = Tb-Ho$ [1, 13, 14]. This feature indicates strong influence of the crystalline electric field on the magnetic ordering. As is apparent from Table II, the magnetic structures of the ErT_xGe_2 and ErT_xSn_2 phases represent different modes and are describable by different wave vectors, hence implying significant diversity in the magnetic exchange interactions.

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