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

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The magnetic ordering in ErFe$_{0.3}$Ge$_2$ and ErNi$_{0.65}$Ge$_2$ compounds crystallizing in the orthorhombic structure of the CeNiSi$_2$-type has been investigated by neutron diffraction and magnetic measurements. The magnetic properties of ErFe$_{0.3}$Ge$_2$ and ErNi$_{0.65}$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].

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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$_2$Ge$_2$ (R = Tb, Ho, Er, Tm, Yb) antiferromagnetic ordering has been found at low temperatures [4–7]. From the R 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) µB. In contrast, the magnetic unit cell of ErNi$_{0.65}$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) µB.

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3. Bulk magnetic data

The magnetic behavior of ErFe$_{0.3}$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 µB. In the paramagnetic region, the reciprocal magnetic susceptibility obeys the Curie–Weiss law $\chi = \frac{C}{T} + \frac{1}{\Theta}$, where $C = 9.5 \mu\text{B} \text{K}^{-1}$ and $\Theta = 5.9$. The magnetic moments in this compound are aligned along the a-axis and alternate with the sequence +−−−. At 1.5 K they are equal to 5.9(1) µB. In contrast, the magnetic unit cell of ErNi$_{0.65}$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) µB.

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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 \( \text{ErNi}_{0.05}\text{Ge}_2 \) (see Fig. 3) confirmed the orthorhombic structure of the \( \text{CeNiSi}_2 \)-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 \( \text{CeNiSi}_2 \)-type unit cell all the atoms occupy the 4c position \((0, y, 1/4)\) with different values of the free parameter \( y \) (space group \( \text{Cmcm} \)). 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 \( \text{Ge} \) and another indefinite phase in \( \text{ErFe}_0.3\text{Ge}_2 \) and some tiny amount of \( \text{ErNi}_{0.05}\text{Ge}_2 \) in \( \text{ErNi}_{0.05}\text{Ge}_2 \).

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 \( \text{Er} \) atoms located at the 4c site of the \( \text{Cmcm} \) 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 \( \text{Er} \) magnetic moments located at the \( 0, y, 1/4 \) \( (S_1) \); \( 0, 3/3 \) \( (S_2) \); \( 1/2, 1/2 + y, 1/4 \) \( (S_3) \) and \( 1/2, 1/2 - y, 3/4 \) \( (S_4) \) site. The minimum of the reliability factor was obtained for the sequence \(+ - - -\) of the magnetic moments in the elementary unit cell (\( \text{C} \)-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 aforementioned 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 \( \text{ErNi}_{0.05}\text{Ge}_2 \) 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 \( \text{Er} \) moments found at 1.5 K amount to 2.90(8) \( \mu_B \). From the temperature...
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Fig. 3. Neutron diffraction patterns of ErNi$_{0.65}$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$_2$Ge$_2$ 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 $\mu$ of ErFe$_{0.3}$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].

5. Summary

The magnetic behavior of the ErT$_x$Ge$_2$ ($T =$ 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 ErFe$_{0.3}$Ge$_2$ and $T_N = 2.3$ K for ErNi$_{0.65}$Ge$_2$ the erbium magnetic moments order antiferromagnetically with the modulated ($k = [0.044(1), 0.384(1)]$) 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 ErFe$_{0.3}$Ge$_2$ and ErNi$_{0.65}$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 I

| Compound | ErFe$_{0.3}$Ge$_2$ | ErNi$_{0.65}$Ge$_2$ |
|----------|------------------|------------------|
| $T$ [K]  |                  |                  |
| $a$ [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)       |
| $y_{Fe/Ni}$| 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 |
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 ($\mu_o$), direction of the moments (DMM) and the magnetic structure type (Mode) determined for several RT$_x$X$_2$ germanides and stannides.

| Compound     | $T_N$ [K] | $k_x$ | $k_y$ | $k_z$ | $\mu_o$ ($\mu_B$) | 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$_2$ | $\approx$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     | 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$_x$Ge$_2$ and ErT$_x$Sn$_2$ 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$_x$Ge$_2$ and ErT$_x$Sn$_2$ phases represent different modes and are describable by different wave vectors, hence implying significant diversity in the magnetic exchange interactions.

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