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Neutron diffraction studies of the magnetic structures of HoAuGe and ErAuGe

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Abstract

The magnetic structures of HoAuGe and ErAuGe, both crystallizing in the hexagonal LiGeGa-type structure, have been investigated by high resolution neutron diffractometry in the temperature range between 1.5 and 7.7 K. For ErAuGe, additional low temperature diffraction experiments have been performed between 40 mK and 1.4 K. Both compounds order antiferromagnetically at low temperatures. The magnetic structure of HoAuGe at 1.5 K is described by a propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$. The low temperature diffraction pattern of ErAuGe is similar to that obtained for HoAuGe, however, some magnetic reflections of ErAuGe show a significant broadening. This broadening is due to a magnetic domain size effect. Transversal sine wave incommensurate magnetic structures appear close to the Néel temperatures. These structures can be described by a propagation vector $\boldsymbol{k} = [0.4461(5), 0, 0]$ at 4.5 K for HoAuGe and $\boldsymbol{k} = [0.4185(40), 0, 0]$ at 3.0 K for ErAuGe.

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1. Introduction

Ternary RAuGe (R = rare earth element) alloys have been thoroughly examined in the past years [1–5]. These compounds crystallize in the hexagonal LiGeGa-type structure [1–3]. So for investigations have revealed controversial results concerning crystal structure and magnetic properties of these compounds [2–5].

The macroscopic measurements (temperature dependences of magnetic susceptibility χ and specific heat c_P) showed anomalies at different ordering temperatures and further anomalies at

- the Néel temperature T_N which equals 6(1) K (χ), 5.6(2) K (c_P) [2,5] or 7.6 K (χ) [4] and additional anomalies below T_N at $T_1 = 4(1)$ K (χ) or 3.5(2) K (c_P) and $T_2 = 2(1)$ K (χ) or 2.4(2) (c_P) [2,5] for HoAuGe,
- the Néel temperature T_N which equals 4.3(1) K (χ, c_P) [2] or 5.7 K (χ) [4] and additional phase transition at 3.0(1) K (χ, c_P) [2] for ErAuGe.

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Low resolution neutron diffraction measurements performed on the D1B diffractometer at ILL (Grenoble) and the E6 diffractometer at HMI (Berlin) gave the following results:

- the low temperature ILL data indicate that the crystal structure of the investigated compounds is, of the LiGeGa-type [2] while the HMI data suggest a distortion of hexagonal structure [3],
- magnetic order in both compounds at $T = 1.5$ K is described by the propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$. For ErAuGe some Bragg peaks of magnetic origin are broadened when compared with the equivalent HoAuGe peaks. This phenomenon was observed for both ILL and HMI data,
- just below the Néel temperature an incommensurate magnetic order was found to exist in both compounds. However, different magnetic structure models were suggested in Refs. [2,3]

In this paper, we present the new diffraction data obtained on a high resolution diffractometer in order to explain the controversy concerning the crystal and magnetic structure of the investigated compounds. Also the temperature dependence of neutron diffraction patterns is analyzed.

2. Experiment

The samples were obtained by arc melting in an argon atmosphere of the respective elements (minimum purity 3N), and annealing at 800°C for 1 week. X-ray diffraction (Cu K_α radiation) confirmed that the samples crystallize in the LiGeGa-type structure. The determined lattice parameters were in reasonable agreement with the data published previously [1].

Neutron diffraction patterns were recorded on the high resolution diffractometer E9 at the Berlin Neutron Scattering Center. The incident neutron wavelength was 2.4795 Å. Data were collected between 1.5 and 7.7 K. The diffractometer E6 was used to perform neutron diffraction for ErAuGe between 40 mK and 1.4 K using $\lambda_n = 2.44$ Å. In the latter case a ^{3}He/^{4}He dilution cryostat insert ("Dilution Stick") was adopted.

The neutron diffraction data were analyzed using the Rietveld program FULLPROF [6]. Peaks were fitted assuming a Thompson–Cox–Hastings pseudo-Voigt peak shape function (parameter NPROF = 7). This shape function is a mixture of both lorentzian and Gaussian peak shape functions.

3. Crystal structure

Previous X-ray [1] and neutron diffraction studies [2,3] revealed that the parent compounds exhibit the hexagonal LiGeGa-type crystal structure (space group $P6_3mc$) with atoms at the following sites:

2 R atoms at 2(a) site	$0, 0, z_R$	$0, 0, \frac{1}{2} + z_R$
2 Au atoms at 2(b) site	$\frac{1}{3}, \frac{2}{3}, z_{Au}$	$\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z_{Au}$
2 Ge atoms at 2(b) site	$\frac{1}{3}, \frac{2}{3}, z_{Ge}$	$\frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z_{Ge}$

The parameter z_R was fixed to be $\frac{1}{4}$ in order to define the origin of the coordinate system. The high resolution diffractometry allowed to determine very precisely the lattice parameters at temperatures below 10 K. The values of the refined positional parameters and lattice constants obtained from the neutron data collected above the ordering temperature are listed in Table 1. The neutron diffraction patterns of HoAuGe at 7.7 K and ErAuGe at 6.0 K are shown in Figs. 1a and 2a, respectively.

Table 1
Structural parameters of HoAuGe and ErAuGe and residuals for profile and integrated intensities from refinement. Standard deviations were multiplied by correlated residuals [7,8]

	HoAuGe	ErAuGe
T (K)	7.7	6.0
a (Å)	4.3991(2)	4.3913(3)
c (Å)	7.2001(5)	7.1608(9)
c/a	1.6367(1)	1.6307(2)
V (Å^3)	120.669(14)	119.586(22)
z_{Au}	0.040(25)	0.057(9)
z_{Ge}	0.459(24)	0.475(10)
R_{prof}	4.61	4.48
R_{Bragg}	5.98	4.10

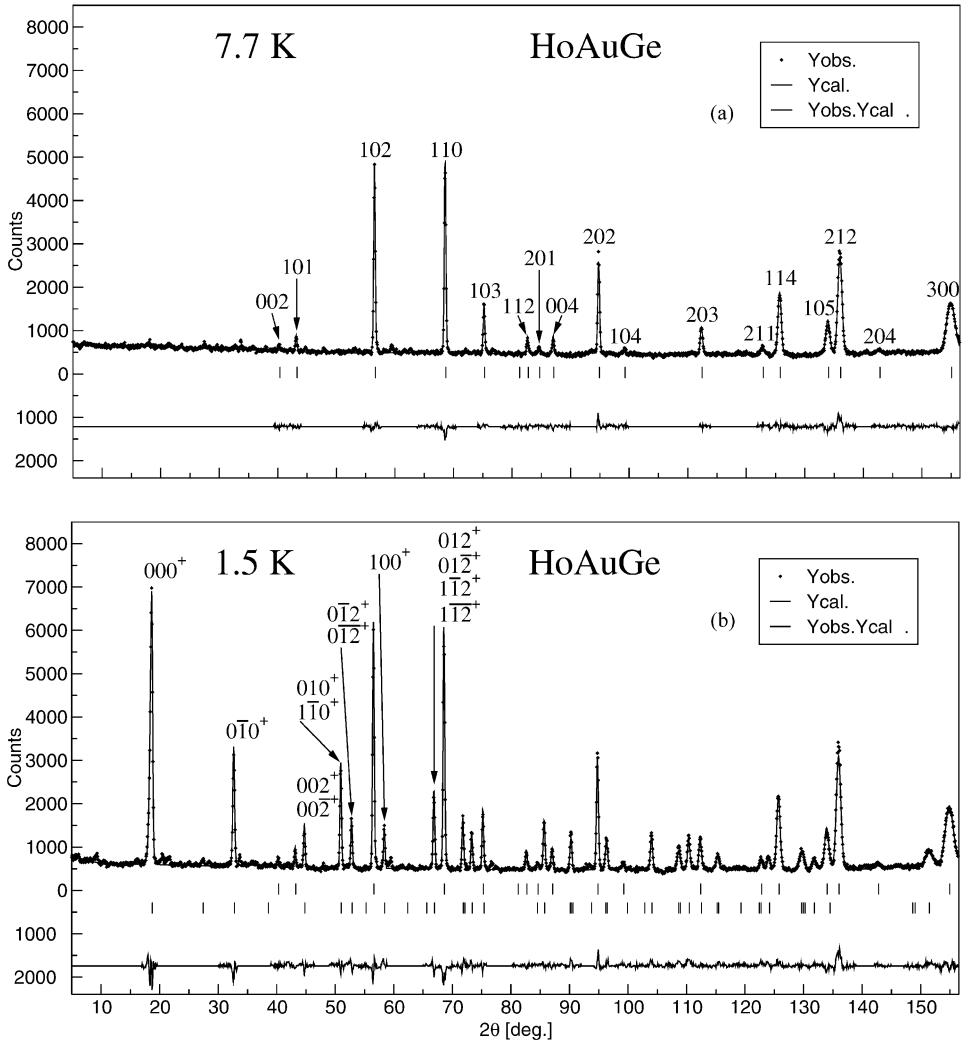

Fig. 1. Neutron diffraction patterns of HoAuGe at 7.7 K (a) and 1.5 K (b) together with Rietveld fits and difference plots. Vertical ticks indicate the positions of nuclear and magnetic reflections. Due to the large number of reflections only magnetic reflections below $2\theta = 70^\circ$ are indexed.

4. Magnetic structures

The neutron diffractogram of HoAuGe recorded at 1.5 K is shown in Fig. 1b. All magnetic reflections could be indexed assuming an antiferromagnetic order described by a propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$. The best fit was obtained for a collinear magnetic structure with magnetic moments inclined by an angle of $\varphi_c = 26^\circ(2)$ in the plane (1 0 0) with respect to the c-axis ($R_{magn} = 8.44\%$). The corresponding orthorhombic magnetic unit cell is presented in Fig. 3. The lattice parameters of the orthorhombic magnetic unit cell are related to the lattice parameters of the crystal unit cell by: $a_{ortho} = \sqrt{3}a_{hex}$, $b_{ortho} = a_{hex}$ and $c_{ortho} = c_{hex}$. The Ho magnetic moment is equal to $6.75(70)\,\mu_B$. Refinements with the magnetic moment confined parallel to the c-axis yielded a residual $R_{magn} = 11.7\%$.

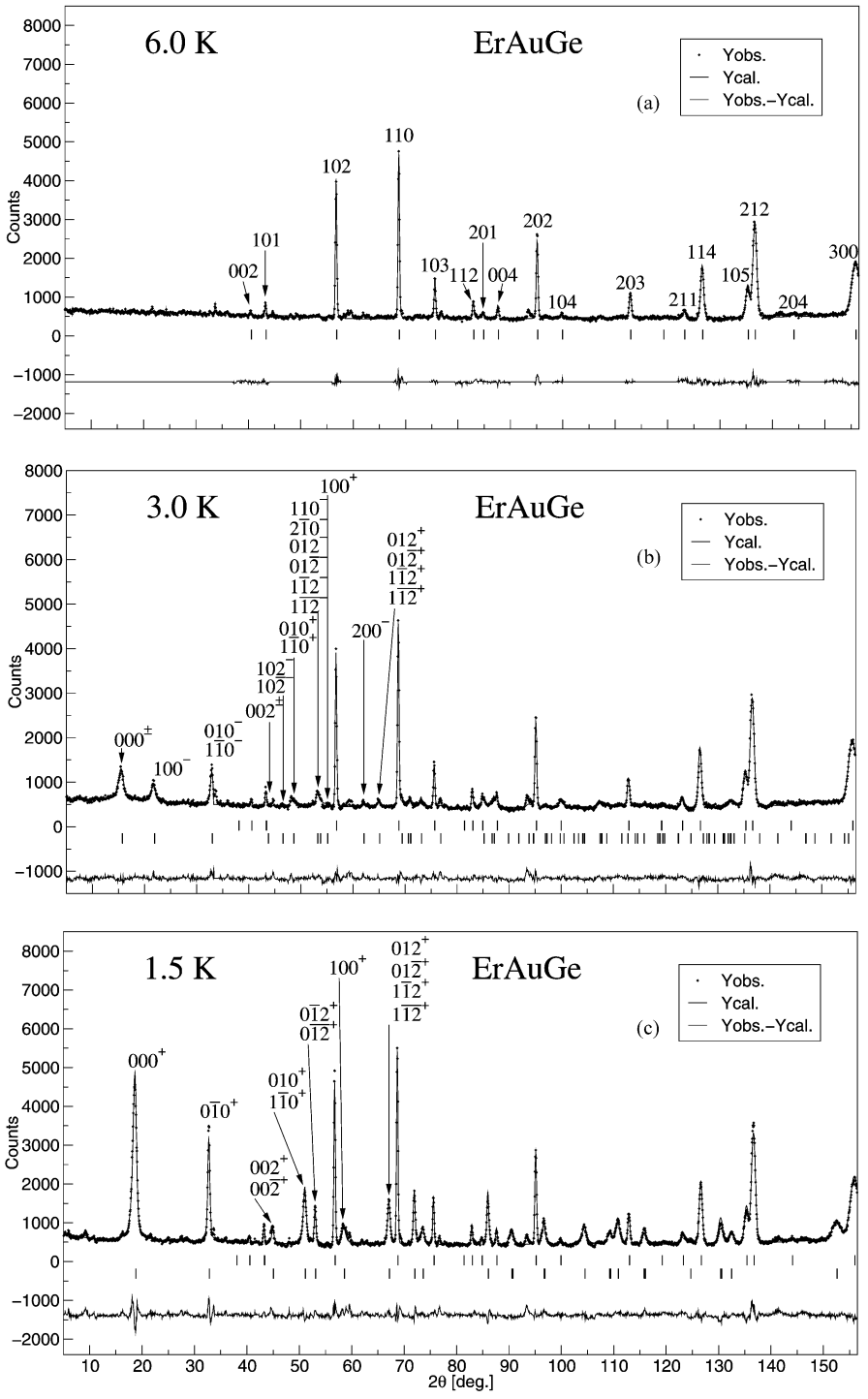

Fig. 2. Neutron diffraction patterns of ErAuGe at 6.0 (a), 3.0 (b) and 1.5 (c) K, Rietveld fits and difference plots. Vertical ticks indicate the positions of nuclear and magnetic reflections. Only magnetic reflections below $2\theta = 70^\circ$ are indexed.

The size of the Ho magnetic moment obtained at $T = 1.5$ K is equal to 6.75(70) μ_B and is close to the value of 6.88 μ_B per Ho atom determined from the neutron diffraction data [2], 7.2 μ_B determined from the magnetization measurements at $H_{ext} = 70$ kOe and $T = 2$ K [2] or 6.9 μ_B per Ho atom at $H_{ext} = 120$ kOe and $T = 4.2$ K [4]. All values are significantly lower than the theoretically calculated moment $g_J J = 10\,\mu_B$ for the Ho^{+3} free ion.

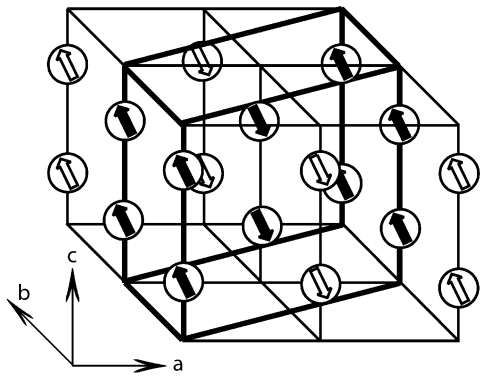

Fig. 3. Magnetic order in HoAuGe at 1.5 K. Arrows indicate Ho magnetic moments which belong to four crystal unit cells. The arrows marked in black indicate Ho magnetic moments which belong to one orthorhombic magnetic unit cell.

The difference of neutron diffraction patterns of HoAuGe collected at 4.5 and 7.7 K is shown in Fig. 4. The magnetic reflections may be divided into two groups. The first group can be related to the structure with a propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$ and the second group with $\boldsymbol{k}_1 = [0.4461(5), 0, 0]$. The best results were obtained assuming a transversal sine-wave modulated incommensurate magnetic structure with no phase factor between the R atoms in the unit cell. The statistics was not sufficient to determine the orientation of the magnetic moment. Therefore, the magnetic moment was confined to be parallel to the c-axis during the refinements. The obtained magnetic structure parameters of HoAuGe are summarized in Table 2.

The inset in Fig. 4 shows the temperature dependence of the integrated intensities for the strongest magnetic reflections $M\,000^+$ and $M_1\,000^\pm$ originating from the commensurate and

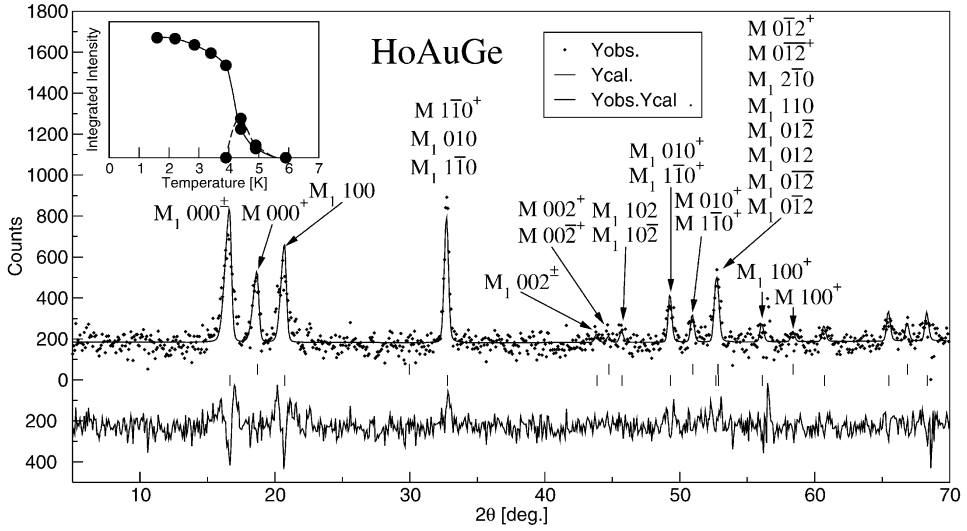

Fig. 4. Difference plot of neutron diffraction patterns of HoAuGe collected at 4.5 and 7.7 K. The upper row of vertical ticks indicate magnetic reflections indexed by the propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$ while the lower ticks indicate those indexed by the propagation vector $\boldsymbol{k}_1 = [0.4461(5), 0, 0]$. Due to the large number of reflections only magnetic reflections below $2\theta = 60^\circ$ are indexed. The inset shows the temperature dependence of the integrated intensity of the strongest magnetic reflection which are $M\,000^+$ and $M_1\,000^\pm$. The black circles refer to the reflection indexed by $\boldsymbol{k}$ while the grey circles refer to the reflection indexed by $\boldsymbol{k}_1$.

Table 2
Parameters of magnetic structure of HoAuGe. Standard deviations were multiplied by correlated residuals [7,8]

	HoAuGe		
Temperature (K)	1.5	4.5	
$\boldsymbol{k}$	$[\frac{1}{2}, 0, 0]$	$[\frac{1}{2}, 0, 0]$	[0.4461(5), 0, 0]
$\mu(\mu_B)$ (amplitude of modulation)	6.75(70)	1.67(12)	4.26(13)
Orientation of magnetic moment[a]	$\varphi_c = 26^\circ(2)$	$\|\boldsymbol{c}$	
R_{magn} (%)	8.44	22.4	24.7

[a] See main text for details

Table 3
Parameters of magnetic structure for ErAuGe. Standard deviations were multiplied by correlated residuals [7,8]

	ErAuGe	
Temperature (K)	1.5	3.0
$\boldsymbol{k}$	$[\frac{1}{2}, 0, 0]$	[0.4185(40), 0, 0]
$\mu(\mu_B)$ (amplitude of modulation)	8.8(5)	8.3(8)
Orientation of magnetic moment	$\|\boldsymbol{c}$	
R_{magn}(%)	8.74	16.8

incommensurate magnetic structure, respectively. Close to 4 K a transition from one phase to another is observed. The transition temperature is in good agreement with the anomalies observed in the magnetic susceptibility and specific heat at 4 and 3.5 K, respectively [5]. Our neutron diffraction data indicate no change in the magnetic structure at 2 K.

The neutron diffraction pattern of ErAuGe collected at 1.5 K (Fig. 2c) is similar to that measured for HoAuGe (Fig. 1b). A significant broadening of some magnetic reflections (for instance those at $2\theta = 18.7^\circ$ and $2\theta = 50.1^\circ$) is observed for ErAuGe. It was found that the width of the magnetic reflection at $2\theta = 18.7^\circ$ increases with decreasing temperature down to 1.5 K. An additional neutron diffraction experiment performed at 40 mK gave the same results as that performed at 1.5 K. The broadening of some magnetic reflections was still present at ultra-low temperature range. The peak shape of broadened reflections have been analyzed between 3 K and 40 mK. The diffraction pattern at 1.5 K obtained on a high resolution diffractometer was used for a Rietveld refinement.

Due to the fact that only magnetic reflections are broadened, the broadening is probably caused by magnetic domain size effects and not by microstrains (which would affect also the nuclear reflections). To describe domain size effects the size model no. 1 was chosen (parameter IsizeModel = 1) [6]. In the refinement, domains of a plate like shape are assumed. The orientation of the platelet domain is defined by the special vector. The best fit was obtained for a magnetic moment parallel to the c-axis and the vector, defining the domain orientation, to be along the $[2, 1, 0]$ direction. One can notice that vector $[2, 1, 0]$ (in the real space) is parallel to the propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$ (in the reciprocal space). This leads to the conclusion that magnetic domains are significantly shortened along the direction of the propagation vector. The parameters of the magnetic structure of ErAuGe at 1.5 K are listed in Table 3. The determined value of the Er magnetic moment (8.8 μ_B) is close to the free Er^{3+} ion value (9.0 μ_B).

The neutron diffraction pattern of ErAuGe measured at 3.0 K is shown in Fig. 2b. The propagation vector was determined to be $\boldsymbol{k} =$ [0.4183(20), 0, 0]. The magnetic moment was assumed to be parallel to the c-axis. The anisotropic magnetic peak broadening was treated in the same way as for the neutron diffraction pattern at 1.5 K.

Parameters of the magnetic structures for ErAuGe are listed in Table 3.

The neutron diffraction patterns of ErAuGe measured at different temperatures between 1.5 and 3.7 K are displayed in Fig. 5. The inset shows the temperature dependence of the strongest magnetic reflections $M\,000^+$ and $M_1\,000^\pm$ which originate from commensurate and incommensurate magnetic phases respectively. The inset demonstrates also the FWHM (full width at half maximum) of the $M\,000^+$ magnetic reflection. At 3 K the change of the magnetic structure is observed. This result is in good agreement with the macroscopic data in Ref. [5].

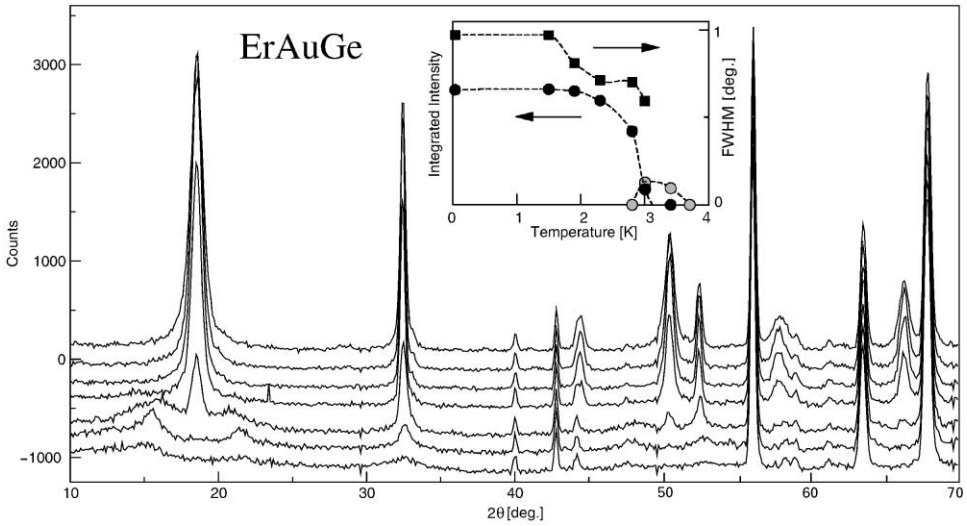

Fig. 5. Neutron diffraction patterns of ErAuGe at 1.5, 1.9, 2.3, 2.8, 3.0, 3.4 and 3.7 K from top to bottom. The inset shows the temperature dependence of the integrated intensity of the strongest magnetic reflections in the temperature range from 0.04 up to 3.7 K. The black circles refer to the reflection M 000^{+} of commensurate magnetic structure while the grey circles refer to the reflection $M_1000^{\pm}$ of incommensurate magnetic structure. The black squares refer to FWHM of the reflection M 000^{+}. The Bragg reflection at $2\theta = 63.5^{\circ}$ originate from Al sample container.

5. Discussion

The results of the high resolution neutron diffraction indicate that both investigated compounds crystallize in the LiGeGa-type structure down to 1.5 K for HoAuGe and 0.04 K for ErAuGe. The splitting of some Bragg reflections reported in Ref. [3] which suggested the distortion of the crystal structure was not confirmed by the high resolution data. That is why the splitting observed previously was probably due to some instrumental effect.

The magnetic structures of both compounds at low temperatures are described by a propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$. The same propagation vector is observed for isostructural compounds with compositions: RCuSn [9], RAgSn [10] and RAuSn [11,12] (R = Tb–Er). In HoAuGe the magnetic moment is inclined by an angle of 26° with respect to the *c*-axis in the plane (1 0 0) while in ErAuGe the magnetic moment is parallel to this axis. The difference in the direction of the magnetic moment is probably caused by the influence of the CEF. According to the data presented in Ref. [2] the direction of the magnetic moment changes with the increase of the number of 4f electrons. The rare earth magnetic moment is inclined at an angle of 65° to the *c*-axis in TbAuGe, 49° in DyAuGe and 18° in HoAuGe. The orientation of the magnetic moment in ErAuGe was not determined in Ref. [2]. The above mentioned results indicate the change of crystal electric field parameters with the increase of the number of 4f electrons.

With increasing temperature a change of the magnetic structure from a commensurate collinear antiferromagnetic to an incommensurate sine-modulated at 4.0 K for HoAuGe and at 3.0 K for ErAuGe is observed. For HoAuGe in the temperature range between 4.0 K and $T_N = 5.5$ K, the commensurate and incommensurate magnetic phases coexist while for ErAuGe between $T = 3.0$ K and $T_N = 3.7$ K, only incommensurate magnetic phase exists. For HoAuGe, neutron diffraction data do not indicate any change of magnetic structure at temperature T_2 which was detected from magnetic susceptbility and specific heat mesurements (see Section 1). An incommensurate magnetic phase was also found to exist in a

number of isostructural compounds. The phenomenon of an incommensurate magnetic ordering appearing close to the Néel temperature is explained in Ref. [13]. The authors consider it to be the result of a free energy temperature dependence for different propagation vectors.

The specific heat of HoAuGe shows at $T = 3.5$ K an anomaly characteristic of a first order transition (Fig. 2 in Ref. [5]). This explains the observed coexistence of commensurate and incommensurate magnetic phases in temperatures close to the temperature of the magnetic phase transition. The coexistence phenomenon is probably also due to possible temperature distribution in our samples.

The magnetic structure of HoAuGe was investigated by Gibson [2] who, for the low temperature magnetic phase at $T = 1.5$ K, applied the magnetic structure model with the moments parallel to the c-axis. For the temperature range where the commensurate and incommensurate magnetic phases coexist, he proposed a model where the moments are parallel to the c-axis for commensurate magnetic phase while for the incommensurate magnetic phase the moments lay in the (0 0 1) plane and are perpendicular to the propagation vector. When we applied Gibson model to our experimental data we obtained $R_{\mathrm{magn}} \approx 37\%$, which is much worse than for the model reported in Table 2.

Fig. 6 shows the dependence of FWHM (full width at half maximum) in the function of Bragg angle 2θ for HoAuGe and ErAuGe. The data from Rietveld fit to the neutron diffractograms collected at 1.5 K are presented. Both nuclear and magnetic peaks are taken into account.

FWHM of Thompson–Cox–Hastings pseudo-Voigt peak shape function is described in the following way:

$$H_{\mathrm{G}}^2 = (U + D_{\mathrm{ST}}^2)\tan^2\theta + V\tan\theta + W + \frac{I_{\mathrm{G}}}{\cos^2\theta}, \tag{1}$$

$$H_{\mathrm{L}} = X\tan\theta + \frac{Y + F(S_{\mathrm{Z}})}{\cos\theta} \tag{2}$$

where H_{G} and H_{L} refer to the FWHM of Gaussian and Lorentzian components, respectively, U, V, W are half-width parameters chracterizing the instrumental resolution function, D_{ST} is an

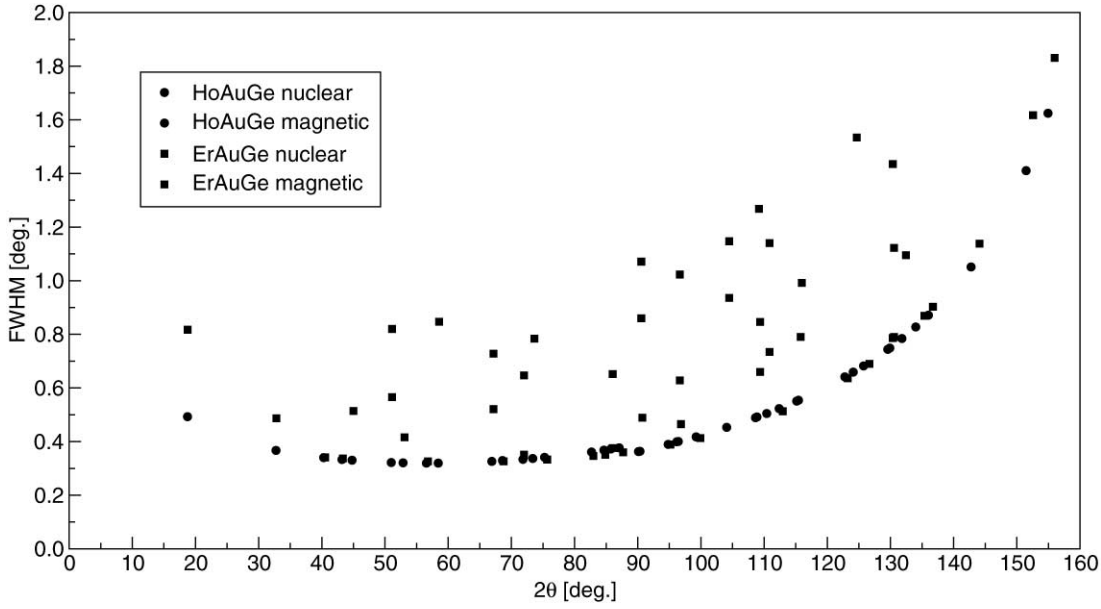

Fig. 6. Angle dependence of FWHM from Rietveld fit to the neutron diffraction data at 1.5 K for HoAuGe and ErAuGe.

anisotropic Gaussian contribution to microstrain, I_G is a Gaussian isotropic size parameter, X is a Lorentzian isotropic strain parameter, Y is a Lorentzian isotropic size parameter and $F(S_Z)$ is an anisotropic Lorentzian contribution of particle size.

In general, Bragg reflection broadening is due to microstrain or size effect. From Figs. 2 and 6 one can easly notice that only magnetic peaks of ErAuGe are broadened and this broadening is of anisotropic character. This fact leads to the conclusion that the broadening of ErAuGe magnetic peaks is due to magnetic domain size effects.

In the refinement, magnetic domains of plate like shape were assumed (size model no. 1, parameter IsizeModel = 1). For this model

$$F(S_Z) = S_Z \cos\phi, \tag{3}$$

where S_Z is a refinable parameter and ϕ is the acute angle between the scattering vector and the vector defining the platelet.

The analysis of the high resolution neutron diffraction pattern of ErAuGe at 1.5 K led us to the conclusion that the magnetic domains of ErAuGe are significantly shortened in the direction of propagation vector, i.e. [1, 0, 0] direction when orthorhombic magnetic unit cell is taken into account, see Section 4.

6. Conclusions

The data presented in this paper indicate that:

- Crystal structure of HoAuGe and ErAuGe is hexagonal and of LiGeGa-type in the broad temperature range from 290 (X-ray studies [1]) down to 1.5 (HoAuGe) and 0.04 K (ErAuGe).
- At low temperatures both rare earth (Ho, Er) magnetic moments form a collinear magnetic structure described by a propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$ or equivalent an orthorhombic magnetic unit cell.
- Close to the Néel temperature a change of the magnetic structure from a collinear commensurate one to a transversal sine-wave modulated incommensurate one is observed for both compounds.
- Anisotropic broadening of ErAuGe magnetic reflections was interpretted on the basis of magnetic domain size effects. Magnetic domains of ErAuGe were found to be significantly shortened in the direction of propagation vector $\boldsymbol{k} = [\frac{1}{2}, 0, 0]$. To study magnetic domain size effects more deeply an experiment on $Er_{1-x}Ho_xAuGe$ and TmAuGe samples is planned.

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