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Nature of magnetic phase transitions in $TbCu_2X_2$ (X = Si, Ge) and $HoCu_2Si_2$ compounds

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ABSTRACT

Physical properties of $TbCu_2X_2$ (X = Si, Ge) and $HoCu_2Si_2$, crystallizing with the tetragonal $ThCr_2Si_2$-type crystal structure, were investigated by means of neutron diffraction as well as by magnetic and calorimetric measurements. All compounds exhibit antiferromagnetic ordering below T_N equal to 12 K for $TbCu_2Si_2$, 13 K for $TbCu_2Ge_2$ and 6.4 K for $HoCu_2Si_2$. Neutron diffraction data indicate collinear antiferromagnetic structure described by the propagation vector $\vec{k} = [(1/2), 0, (1/2)]$ at low temperatures. While increasing temperature the direction of the Tb magnetic moment changes from [1 1 0] to [0 1 0] at T_t = 8.5 K for $TbCu_2Si_2$ and 9.7 K for $TbCu_2Ge_2$. In $HoCu_2Si_2$ a change of the magnetic structure from the collinear to a modulated one described by the propagation vector $\vec{k} = [k_x, 0, k_z]$ was found at T_t = 4.7 K.
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1. Introduction

The intermetallic compounds of the RCu_2X_2 series (R – rare earth element, X = Si, Ge) have recently attracted new attention due to new experimental data indicating magnetic phase transitions of order–order type. All these compounds crystallize in the tetragonal structure of the $ThCr_2Si_2$-type (space group I4/mmm) [1,2]. This type of structure forms a natural multilayer system where the planes of the rare earth ions are separated from the transition metal layers (Cu) by the sheets of p-metal atoms (X), resulting in R–X–T–X–R stacking of respective basal planes along the *c*-axis. This layered structure frequently leads to a strong uniaxial anisotropy in these compounds with *c*-axis being an anisotropy axis. Magnetic data indicate that the compounds with the heavy rare earth elements are antiferromagnets at low temperatures with the Néel temperature equal, for example, to 12.5 K [2] or 12 [3] for $TbCu_2Si_2$, 15 K for $TbCu_2Ge_2$ [4] and 7.7 K [2] or 8 K [5] for $HoCu_2Si_2$. Neutron diffraction experiments carried out on polycrystalline samples revealed the presence of an antiferromagnetic ordering of the AFIV-type in $TbCu_2Si_2$ [6–8], $HoCu_2Si_2$ [6,7] and $TbCu_2Ge_2$ [6,9]. The temperature dependence of magnetic peak intensities indicated that this type of the magnetic ordering was stable up to the Néel temperature [6–9].

The new investigations were performed on single crystal samples. The magnetic and specific heat data showed anomalies at T_N = 11.9 K and T_t = 9.2 K in $TbCu_2Si_2$, 5.8 and 4.7 K in $HoCu_2Si_2$ [10–14] and 12.3 and 9.6 K in $TbCu_2Ge_2$ [15,16]. The neutron diffraction studies revealed the presence of an anomaly in ((1/2) 0 (1/2)) peak intensity at T_t = 8.2 K for $TbCu_2Si_2$ [17] and a change of magnetic structure from commensurate to incommensurate for $HoCu_2Si_2$ [18].

The resonant and nonresonant X-ray scattering performed on the $TbCu_2Ge_2$ sample indicated a reorientation of direction of magnetic moment from [1 1 0] below T_t to [0 1 0] for $T_t < T < T_N$ [15].

In the present work the nature of the phase transitions in $TbCu_2X_2$ (X = Si, Ge) and $HoCu_2Si_2$ have been investigated by the magnetic, heat capacity and neutron diffraction measurements on polycrystalline samples. These data have allowed to determine:

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Table 1
Lattice parameters a and c, a/c ratio, unit cell volume V, Si or Ge positional parameter z, magnetic moment μ and angle ϕ between magnetic moment and the a-axis for $TbCu_2Si_2$, $TbCu_2Ge_2$ and $HoCu_2Si_2$ compounds as derived from the neutron diffraction data. The lower index c in μ_c and R_c refers to a commensurate magnetic structure while the index m in μ_m and R_m refers to an incommensurate modulated magnetic structure.

Compound	$TbCu_2Si_2$		$TbCu_2Ge_2$		$HoCu_2Si_2$		
T [K]	1.6	18.0	1.4	15.1	1.8	5.3	12.0
a [Å]	3.9751(3)	3.9750(16)	4.0291(5)	4.0308(9)	3.9659(3)	3.9656(3)	3.9668(3)
c [Å]	9.9304(43)	9.9375(60)	10.2741(15)	10.2777(28)	10.0419(9)	10.0420(8)	10.0419(10)
a/c	0.4003(3)	0.4000(4)	0.3922(2)	0.3922(2)	0.3949(1)	0.3949(1)	0.3950(1)
V [Å^3]	156.91(10)	157.02(14)	166.79(6)	166.99(12)	157.94(4)	157.92(4)	158.01(4)
z	0.3833(14)	0.3893(12)	0.3812(5)	0.3809(5)	0.3833(5)	0.3839(3)	0.3831(4)
R_{Bragg} [%]	10.7	11.1	6.1	6.7	4.8	4.5	5.9
$R_{profile}$ [%]	5.8	6.5	3.6	4.7	4.2	3.5	5.8
$\mu[\mu_B]$	8.74(12)		8.72(6)		6.92(3)	$\mu_c = 2.69(4)\mu_m = 2.60(11)$	
$\phi[^\circ]$	42.2(1.2)		48.8(6)		47.7(1.5)	47.7(1.5)	
R_{magn} [%]	10.4		5.8		6.8	$R_c = 10.6$ $R_m = 14.3$	

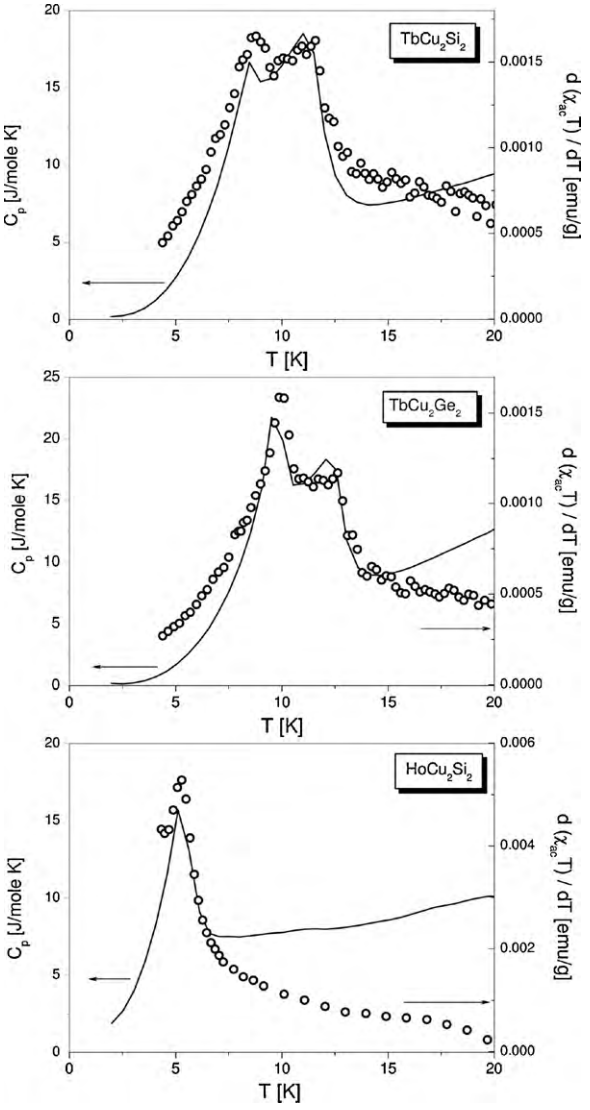

Fig. 1. Temperature dependence of specific heat (solid line/left scale) and $d(\chi_{ac}T)/dT$ (open circles/right scale) for $TbCu_2Si_2$, $TbCu_2e_2$and $HoCu_2i_2$.

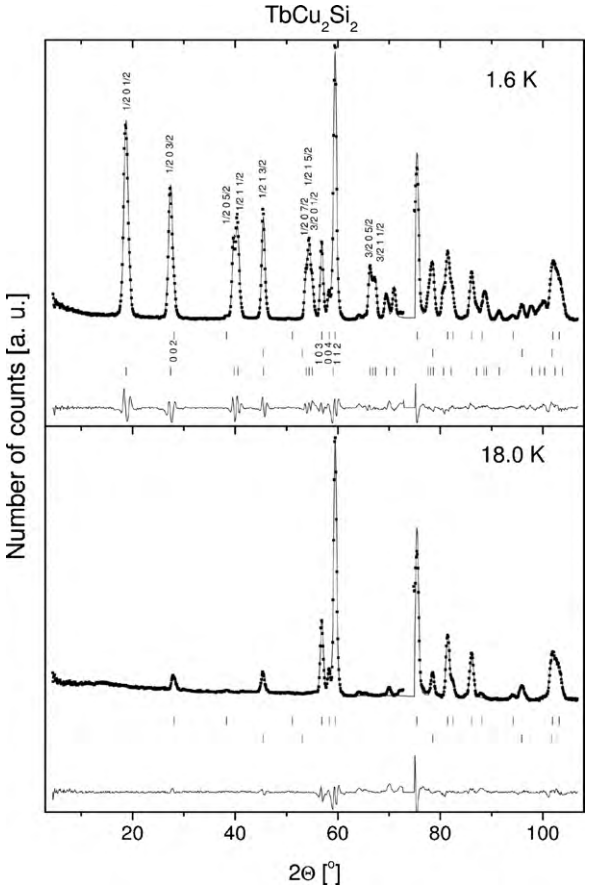

Fig. 2. $TbCu_2Si_2$ Neutron diffraction patterns collected at 1.6 and 18.0 K. The symbols represent the experimental data while the solid lines are calculated profiles for the crystal and magnetic structure models (see the main text). The difference between the observed and calculated intensities is shown at the bottom of each diagram. The vertical bars indicate the positions of the Bragg peaks of nuclear and magnetic origin: the first row refers to nuclear peaks, the second one to impurity phase of Si and the third one to magnetic structure. The region between $2\theta = 73^\circ$ and 75° was excluded from refinement because it contains reflections originating from cryostat shielding.

temperatures of magnetic phase transitions and changes of magnetic strutures.

2. Experimental details

Polycrystalline samples of $TbCu_2X_2$ (X = Si, Ge) and $HoCu_2Si_2$ were synthesized by arc melting high-purity elements (Tb, Ho: 3N; Cu: 4 N; Si, Ge: 5 N) under titanium-gettered argon atmosphere. The $LaCu_2Si_2$ compound was also synthesized as a reference sample for specific heat measurements. In order to ensure appropriate homogeneity the resulting ingots were turned over and remelted several times. Afterwards, the samples were annealed in evacuated quartz ampules at 600 °C for one week.

The product quality was examined by X-ray powder diffraction at room temperature on a Philips PW-3710 X'PERT diffractometer using CuKα radiation. The results confirmed the tetragonal $ThCr_2Si_2$-type crystal structure and indicated almost single-phase character of the prepared samples.

The dc and ac magnetic susceptibilities were measured in the temperature range 4.2–30 K using 7225 Lake Shore instrument. The frequency of ac measurement was $f = 125$ Hz.

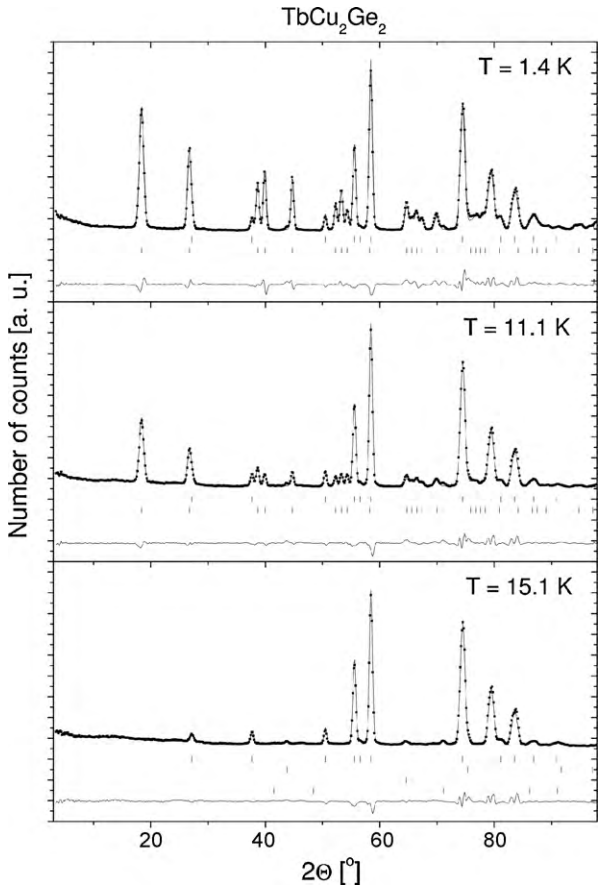

Fig. 3. Neutron diffractions patterns of $TbCu_2Ge_2$ at 1.4, 11.1 and 15.1 K. The symbols represent the experimental data while the solid lines are calculated profiles for the crystal and magnetic structure models (see the main text). The difference between the observed and calculated intensities is shown at the bottom of each diagram. The first row of vertical bars indicates the positions of the Bragg peaks of nuclear origin while the second one refers to those originating form magnetic structure. Small peaks correspond to Ge ($2\theta = 43.8^\circ$), Al cryostat shielding (64.5°) and Cu (71.4°).

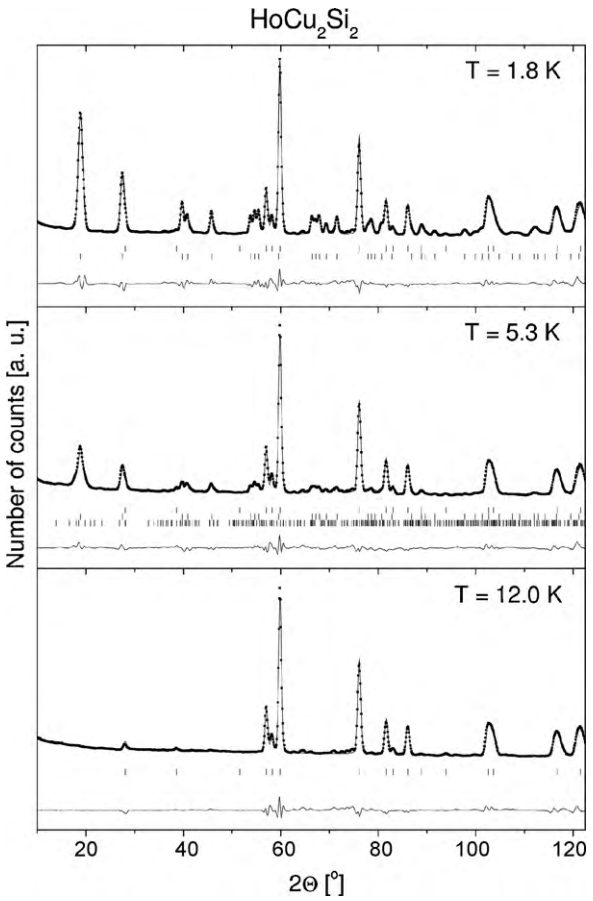

Fig. 4. Neutron diffractions patterns of $HoCu_2Si_2$ at 1.8, 5.3 and 12.0 K. The symbols represent the experimental data while the solid lines are calculated profiles for the crystal and magnetic structure models (see the main text). The difference between the observed and calculated intensities is shown at the bottom of each diagram. The first row of vertical bars indicates the positions of the Bragg peaks of nuclear origin while the second and third ones refer to those originating form commensurate and incommensurate magnetic structures, respectively. Small peaks seen at $2\theta = 61$–75° correspond to an unknown impurity phase.

Specific heat studies were carried out by relaxation method using the Quantum Design PPMS-9 platform. These measurements were carried out in the 2–20 K temperature range.

The neutron powder diffraction patterns were collected on the E6 diffractometer installed at the BERII reactor (Helmholtz-Zentrum Berlin) within the temperature range from 1.4 to 18 K. The incident neutron wavelength was 2.452 Å. The neutron diffraction data were analyzed using the Rietveld-type program FullProf [19].

3. Results

The X-ray diffraction data, collected at room temperature, as well as the neutron diffraction data, obtained in both magnetically ordered and paramagnetic state, confirmed unambiguously the tetragonal $ThCr_2Si_2$-type structure (space group I4/mmm; space group no. 139) with the atoms occupying the following sites:

2 Tb or Ho atoms at 2(a) site	0,0,0	
4 Cu atoms at 4(d) site	$0, \frac{1}{2}, \frac{1}{4}$;	$\frac{1}{2}, 0, \frac{1}{4}$
4 Si or Ge atoms at 4(e) site	$0,0,z$	$0, 0, \bar{z}$
	+ body centering translation.	

The values of the lattice parameters and the free positional parameter z, derived from the neutron diffraction pattern, are listed in Table 1.

The temperature dependences of specific heat and $d(\chi_{ac}T)/dT$ (χ_{ac} is a real part of ac magnetic susceptibility) for all three compounds are presented in Fig. 1. In these dependences two maxima typical of a phase transition are observed for compounds containing Tb. The transition temperatures equal 8.2 and 11.0 K for $TbCu_2Si_2$ and 9.5 and 12.0 K for $TbCu_2Ge_2$. Only one maximum at 5.0 K is present for $HoCu_2Si_2$.

The neutron diffraction patterns of all investigated compounds taken below the Néel temperatures clearly reveal the presence of some additional reflections due to the magnetic ordering (see Figs. 2–4). The reflections of magnetic origin found in the patterns measured at low temperatures (close to 1.5 K) can be indexed using the propagation vector $\vec{k} = [(1/2), 0, (1/2)]$. These patterns are similar to those reported in previous papers [6–9]. The corresponding magnetic ordering can be described as ferromagnetic (1 0 1) layers stacked antiferromagnetically.

In case of compounds containing therbium element the best fits were obtained for Tb magnetic moments lying close to the [1 1 0] direction. The values of Tb magnetic moments equal $8.74(12)\mu_B$ and $8.70(6)\mu_B$ for $TbCu_2Si_2$ and $TbCu_2Ge_2$, respectively. These values are in agreement with previously published data [6–9] and they are close to $9.0\mu_B$ which is the free Tb^{3+} value. The temperature dependencies of the magnetic peak intensities provide the Néel temperatures equal to 12 and 13 K for $TbCu_2Si_2$ and $TbCu_2Ge_2$, respectively (see Figs. 5a and 6a).

Figs. 5b and 6b show temperature dependences of the $I((1/2)\,0\,(5/2))/I((1/2)\,1\,(1/2))$ intensity ratio for $TbCu_2Si_2$ and $TbCu_2Ge_2$. The change of this ratio is connected with the reorientation of Tb magnetic moments. For both compounds the value of the above defined ratio increases about T_t. Numerical analyses

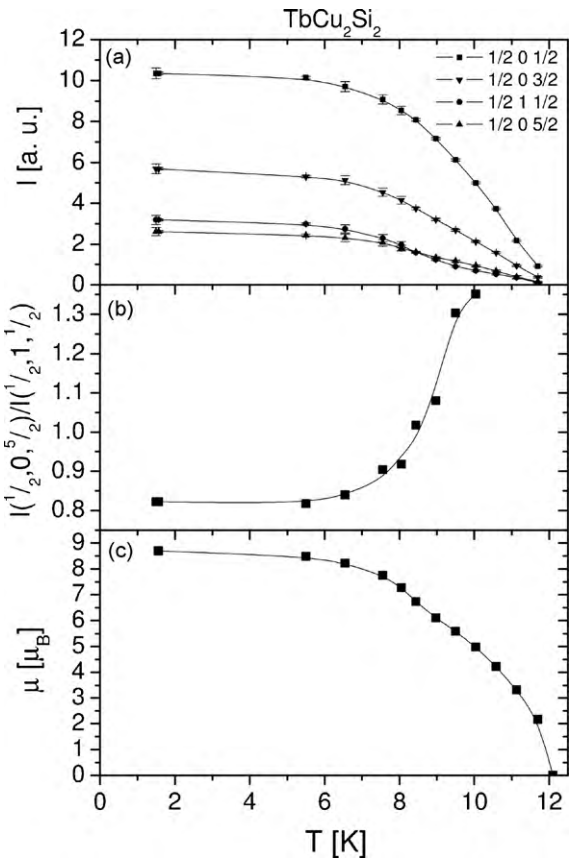

Fig. 5. $TbCu_2Si_2$ temperature dependence of: (a) some magnetic peak intensities, (b) $I((1/2)\,0\,(5/2))/I((1/2)\,1\,(1/2))$ intensity ratio, (c) Tb magnetic moment.

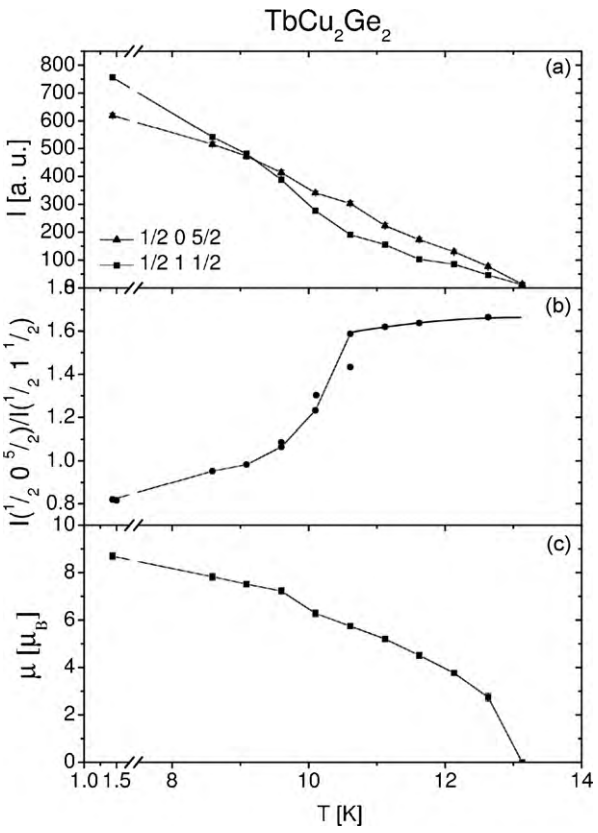

Fig. 6. $TbCu_2Ge_2$ temperature dependences of: (a) intesities of $I((1/2)\,0\,(5/2))$ and $I((1/2)\,1\,(1/2))$ Bragg reflections of magnetic origin, (b) $I((1/2)\,0\,(5/2))/I((1/2)\,1\,(1/2))$ magnetic peak intensity ratio, (c) Tb magnetic moment.

of the magnetic peak intensities indicate a change of the ϕ angle, between magnetic moment and the a-axis, from about 45° to 90°. This change of the ϕ angle corresponds to the change of direction of magnetic moments from [1 1 0] to [0 1 0] close to 8.5 and 9.7 K for $TbCu_2Si_2$ and $TbCu_2Ge_2$, respectively. At the same temperatures one may also notice some small anomalies in the temperature dependencies of the magnetic moment magnitude (see Figs. 5c and 6cFigs. 5 and 6).

For $HoCu_2Si_2$ the Bragg peaks of magnetic origin are described by the propagation vector $\vec{k} = [(1/2), 0, (1/2)]$ at $T = 1.8$ K (Fig. 4). The Ho magnetic moment equals 6.92(3) μ_B ($R_{magn} = 6.8\%$) and it lies within the basal plane forming the angle $\phi = 47.7(1.5)°$ with the a-axis. This type of magnetic order is stable up to 4.6 K. At 4.9 K a broadening of the ((1/2), 0, (1/2)) magnetic reflection ($2\theta = 18.8°$) is observed. This broadening indicates an appearence of the new modulated structure described by the propagation vector $\vec{k} = [k_x, 0, k_z]$. In the temperature range from 4.9 K to T_N the coexistence of two magnetic structures: the collinear one and the modulated one, occurs. The k_x component of the propagation vector equals 0.524(1) at $T = 4.9$ K and is temperature independent while the k_z component, equal to 0.52(1) at $T = 4.9$ K, increases to 0.532(4) at $T = 5.2$ K and then decreases to 0.501(8) at $T = 6.1$ K (see Fig. 7a). In case of a modulated magnetic structure the magnetic moment magnitude on particular atom is given by the formula $\mu = \mu_A \sin(\vec{k} \cdot \vec{r} + \Phi)$ where μ_A denotes an amplitude of modulation, $\vec{k}$ is a propagation vector, $\vec{r}$ is a vector pointing from the beginning of the coordinate system to the atom and Φ is a phase. The best fit to the diffraction data collected at 5.3 K is presented in Fig. 4 while the magnetic structure parameters are summarized in Table 1. The temperature dependences of the magnetic moment of the commensurate structure, the amplitude of modulation of

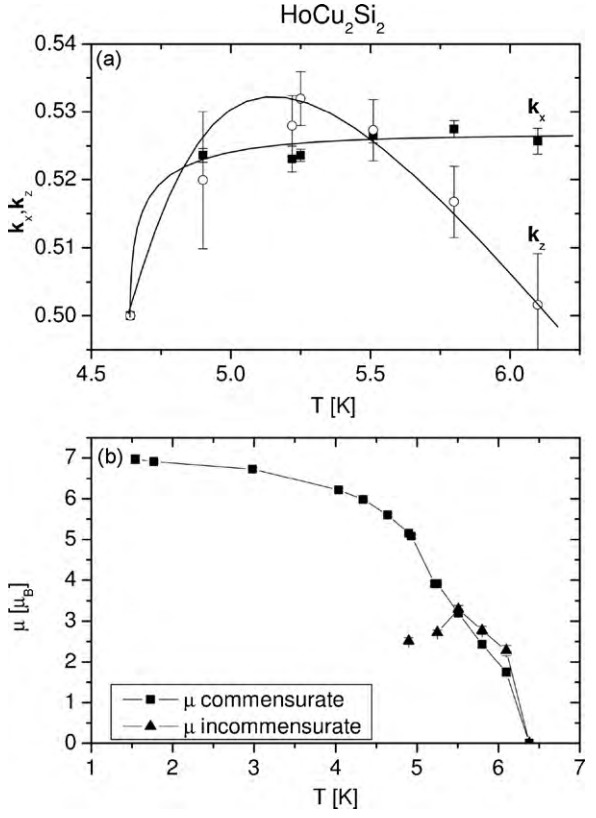

Fig. 7. $HoCu_2Si_2$ temperature dependences of (a) k_x and k_z components of the propagation vector $\vec{k}$ and (b) Ho magnetic moment in commensurate and incommensurate magnetic phase.

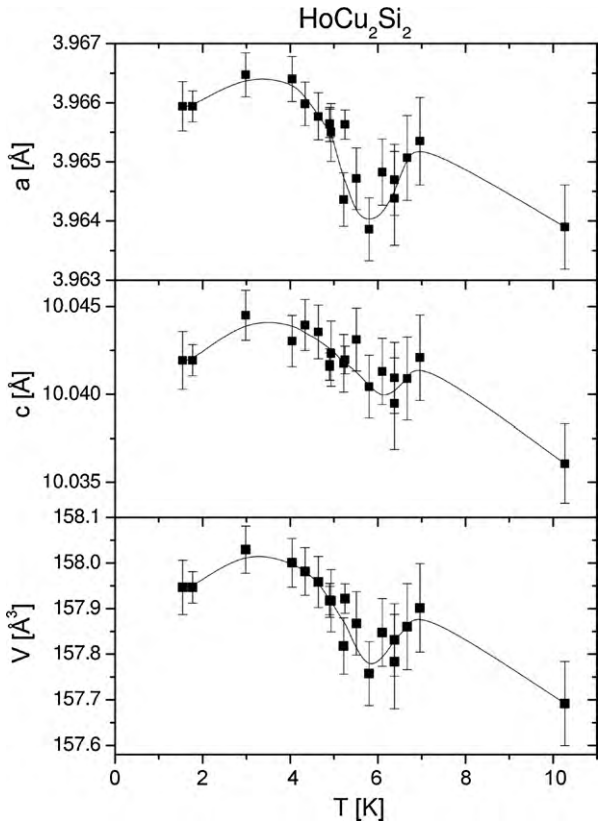

Fig. 8. Temperature dependences of the lattice parameters a and c and the unit cell volume V for $HoCu_2Si_2$.

the modulated structure and both the k_x and k_z components of the propagation vector are presented in Fig. 7.

Fig. 8 shows temperature dependences of the lattice parameters a and c and unit cell volume V for $HoCu_2Si_2$. These dependences have distinct anomalies at the T_t and T_N temperatures.

4. Discussion and conclusion remarks

The investigated $TbCu_2X_2$ (X = Si, Ge) and $HoCu_2Si_2$ compounds crystallize in the tetragonal $ThCr_2Si_2$-type crystal structure. They are antiferromagnets below the Néel temperatures equal to 12.0 K for $TbCu_2Si_2$, 13.0 K for $TbCu_2Ge_2$ and 6.4 K for $HoCu_2Si_2$. The presented results of magnetic susceptibility, specific heat and neutron diffraction measurements confirm the complex magnetic structures at low temperatures. The magnetic ordering of all compounds is described by the propagation vector $\vec{k} = [(1/2), 0, (1/2)]$ at temperatures close to 1.5 K. For the $TbCu_2X_2$ (X = Si, Ge) compounds this vector is stable up to the Néel temperature. A change of direction of the Tb magnetic moment from [1 1 0] to [0 1 0] takes place at T_t equal to 8.5 K for $TbCu_2Si_2$ and 9.7 K for $TbCu_2Ge_2$. The data for $TbCu_2Ge_2$ are in good agreement with results obtained from resonant and nonresonant magnetic X-ray scattering [15] while the data for $TbCu_2Si_2$ are the first experimental results that connect the anomaly at T_t with a change of direction of magnetic moment.

In $HoCu_2Si_2$ the magnetic order described by the propagation vector $\vec{k} = [(1/2), 0, (1/2)]$ is stable up to 4.6 K while above this temperature the coexistence of two magnetic structures: the commensurate one with $\vec{k} = [(1/2), 0, (1/2)]$ and the modulated one with $\vec{k} = [k_x, 0, k_z]$, is observed. Similar change of a magnetic order is observed in isostructural $ErCu_2Ge_2$ [20].

The presented data indicate a different nature of the magnetic phase transitions in ordered state in different compounds. In $TbCu_2X_2$ (X = Si, Ge) this transition is related to a change of direction of magnetic moment within the basal plane. This change may arise from crystalline electric field and/or a change of anisotropy. In case of $HoCu_2Si_2$ the phase transition consists on an appearance of a modulated incommensurate magnetic structure which coexists with a commensurate one up to the Néel temperaure. Such a transition is observed in a large number of the rare earth intermetallics including also the 1:2:2 phases [20–22]. The appearance of the incommensurate magnetic structure is a results of a long range exchange interaction of R^{3+} moments in presence of magnetocrystalline anisotropy [23].

In all investigated compounds the magnetic moments lie in the basal plane which is in agreement with a positive sign of the crystal electric field parameter B_2^0 [14].

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