Study of Condensed Matter by Neutron Scattering and Complementary Methods

Magnetic Structures of $Ho_5Rh_4Ge_{10}$

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A powder diffraction measurement of $Ho_5Rh_4Ge_{10}$ is reported. This compound crystallizes in the tetragonal $Sc_5Co_4Si_{10}$-type structure (space group $P4/mbm$) in which the Ho atoms occupy three different sites. The neutron diffraction measurements indicate antiferromagnetic order with the Néel temperature $T_N = 7$ K. Below T_N an additional phase transition at 4.5 K connected with the change of the magnetic structure is observed. The Ho moments in 4(h) site form collinear order up to T_N while moments at 2(a) site form sine modulated structure. Determined experimentally magnetic structures are compared to the results of symmetry analysis.

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1. Introduction

Ternary $R_5Rh_4Ge_{10}$ compounds, where R = rare earth, crystallize in the tetragonal $Sc_5Co_4Si_{10}$-type structure in which the rare earth atoms occupy three nonequivalent crystallographic positions [1]. Magnetic data indicate that these compounds for R = Gd–Tm are antiferromagnets with the Néel temperatures between 14 K (Gd) and 5.5 K (Er). For the investigated in this work $Ho_5Rh_4Ge_{10}$ compound magnetic data give the Néel temperature 6 K [2] or 6.6 K [3] and additional anomaly near 5 K [3]. Neutron diffraction data of compounds with R = Tb [4], Er [5] and Tm [6] confirm antiferromagnetic ordering. For $Ho_5Rh_4Ge_{10}$ compound preliminary neutron diffraction data give model of the magnetic structure with the very low values of the Ho magnetic moments in 4(h) sites [4].

In this work a new analysis of the neutron diffraction data for $Ho_5Rh_4Ge_{10}$ is presented. As the rare earth atoms in this compound occupy three different sublattices in order to obtain certain results concerning the magnetic structures the analysis of the neutron diffraction data is supported by the symmetry analysis (SA). The numerical calculations of the different models proposed by SA are compared with the experimental data. The results adequate to the minimum values of the agreement factors are presented in the work.

2. Experimental details

The sample was obtained by arc melting of the constituent elements (purity 3N in the case of holmium metal and 4N in the case of rhodium and germanium) in an arc furnace in the Ti-gettered argon atmosphere. The sample was annealed in vacuum for 1 week at 800 °C. The sample was identified by their powder X-ray diffractogram that indicates that the sample has the tetragonal $Sc_5Co_4Si_{10}$--type structure and the derived lattice constants are in good agreement with those reported in Ref. [2].

Neutron diffraction patterns were recorded using the E6 diffractometer at the BERII reactor at the Hahn–Meitner Institute, Berlin ($\lambda = 2.4436$ Å; $1.5 < T < 8$ K). The diffraction data were analyzed using the program package FULLPROF [7].

3. Results and discussion

3.1. Crystal structure

Neutron diffraction pattern collected in the paramagnetic state at 9.5 K (Fig. 1) confirmed that the sample exhibits the tetragonal $Sc_5Co_4Si_{10}$-type structure. In this structure (see Fig. 2) the holmium atoms occupy three nonequivalent positions: Ho1 at 2(a): 0, 0, 0; and Ho2 and Ho3 at 4(h): x, $1/2+x$, $1/2$ with different values of the x parameter, Rh atoms located at 8(i): x, y, 0 and 4(g): x, $1/2+x$, 0 and Ge atoms at 4(g): x, $1/2+x$, 0; 8(i): x, y, 0 and 8(j): x, y, $1/2$ with different values of the x and y parameters for individual atoms.

The values of x_i and y_i parameters giving the best agreement between observed and calculated neutron intensities are listed in Table together with the determined lattice parameters.

3.2. Magnetic structure

The neutron diffraction pattern of $Ho_5Rh_4Ge_{10}$ collected at 1.5 K is shown in Fig. 1. The analysis of this pattern is supported by the symmetry analysis method which is based on the theory of representations of space groups proposed by Bertaut [8] and Izyumov et al. [9, 10]. In this work the computer program MODY [11] was used to calculate the models of the magnetic structures.

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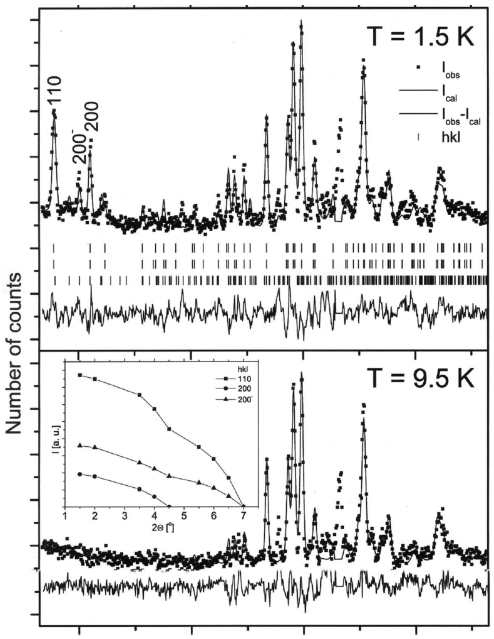

Fig. 1. Neutron diffractograms of $Ho_5Rh_4Ge_{10}$ obtained at 1.5 and 9.5 K. Squares represent the experimental data, solid lines — the calculated profile. The difference between the observed and calculated data is shown at the bottom of each diffractogram. Vertical bars indicate the angular positions of nuclear peaks (upper row) and magnetic peaks correspond to the collinear and modulated structures (lower rows), respectively. Inset shows the temperature dependence of the magnetic intensities of the reflections (110), (200) and (200^{-}).

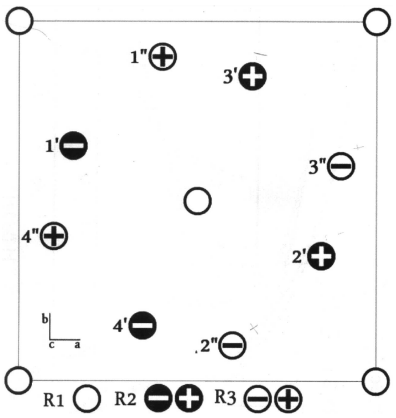

Fig. 2. Magnetic structure of $Ho_5Rh_4Ge_{10}$. Projection on the a–a plane. Signs + or − indicate the direction of the magnetic moment along c-axis in 4(h) sites.

The temperature dependence of the magnetic peak intensities indicate that the 110 and 200 peaks at 2θ equal to 15.6° and 22.1° exist up to the Néel temperature equal to 7 K where the peak of the small intensities probably connected with the impurity phase at $2\theta = 19.9°$ decreases to zero at $T = 4.5$ K. The values of the Bragg peaks of the magnetic reflections indicate that a magnetic structure corresponds to a magnetic unit cell equal to the crystal unit cell. These peaks are connected with the Ho moments in 4(h) site. For the Ho moments in 4(h) sites the magnetic order is described by the propagation vector $\boldsymbol{k}_1 = (0,\ 0,\ 0)$; the symmetry analysis gives the two models of antiferromagnetic orderings of magnetic moments parallel to the c-axis by two irreducible representations:

TABLE

$Ho_5Rh_4Ge_{10}$ compounds crystal structure, $P4/mbm$ space group, neutron powder diffraction results.

T [K]	9.5
a [Å]	12.881(7)
c [Å]	4.240(2)
x_{1R}(4h)	0.1537(2)
x_{2R}(4h)	0.3976(18)
x_{Rh}(8i)	0.2645(16)
y_{Rh}(8i)	0.5217(23)
x_{Ge}(4g)	0.0663(16)
x_{Ge}(8i)	0.1635(14)
y_{Ge}(8i)	0.2035(13)
x_{Ge}(8j)	0.1621(18)
y_{Ge}(8j)	0.0089(15)
R_{Bragg} [%]	9.5
$R_{prof.}$ [%]	1.5

— one-dimensional τ_5 $S-1$: (0, 0, c); 2: (0, 0, c); 3″ (0, 0, $-c$); 4: (0, 0, $-c$) and

— two-dimensional τ_{10} $S-1$: (0, 0, c'); 2: (0, 0, $-c'$); 3: (0, 0, $-c'$); 4: (0, 0, c').

Analysis of the peak intensities indicates an antiferromagnetic collinear ordering of the Ho-moments with the magnetic unit cell equal to the crystal unit cell. The holmium moments in crystal unit cell in 4(h) positions described above order with the sequence $-++-$ for $4(h_1)$ (Ho2 site) and $+--+$ $4(h_2)$ (Ho3 site) with the following values of the moments: $\mu(4h_1) = 8.7(5)\ \mu_B$ and $\mu(4h_2) = 4.2(6)\ \mu_B$ ($R_{mag} = 15.7\%$). Projection of the magnetic order in 4(h) sites on the a–a plane is shown in Fig. 2. This model of the magnetic order is in agreement with the two-dimensional model from the symmetry analysis.

For position 2(a) with the Ho moments at (1: (0, 0, 0); 2: (1/2, 1/2, 0)) and the ordering along the c axis with propagation vector $\boldsymbol{k} = (k_x,\ k_x,\ 0)$ ($k_x = 0.178$) is in one orbit and may belong to one of the following two representations:

$$\begin{aligned}
\tau_1\ S^a &= 1+\boldsymbol{t}\text{: } (0,\ 0,\ a\cos(2\pi(n+m)k_x)),\\
&\quad 2+\boldsymbol{t}\text{: } (0,\ 0,\ a\cos(2\pi(n+m)k_x)),\\
\tau_3\ S^a &= 1+\boldsymbol{t}\text{: } (0,\ 0,\ a\cos(2\pi(n+m)k_x)),\\
&\quad 2+\boldsymbol{t}\text{: } (0,\ 0,\ -a\cos(2\pi(n+m)k_x)),
\end{aligned}$$

where $\boldsymbol{t} = n\boldsymbol{a}_1 + m\boldsymbol{a}_2 + p\boldsymbol{a}_3$ are the lattice translations.

The model belonging to τ_1 representation gives the best agreement to the experimental data from the neutron diffraction measurements.

The magnetic moments in 2(a) site form a sine-wave modulated structure with the moment equal to 8.3(4) μ_B ($R_{mag} = 16.5\%$). The magnetic moments in all sites are aligned parallel to the c-axis.

The temperature dependence of the intensities of the first group of the magnetic peaks corresponding to the collinear structure give a Néel temperature $T_N = 7$ K which is in good agreement with magnetic data presented in this work and Ref. [3]. Intensity of 200^- peak decreases to zero at 4.5 K (see inset in Fig. 1).

4. Conclusions

Reported in this work results of the neutron diffraction confirm that $Ho_5Rh_4Ge_{10}$ compound crystallizes in the tetragonal $Sc_5Co_4Si_4$-type structure. For this compound the magnetic ordering is determined by the localized $4f$ electrons of the rare earth ions. The Ho moments in 4(h) sites order below a Néel temperature equal to ≈ 7 K and form a collinear antiferromagnetic structure, while those in 2(a) order below 4.5 K and form sine-wave modulated structure. Similar two-step magnetic ordering was observed in $Er_5Ni_2In_4$ [12]. In this compound the Er moments occupy two 4(g) sites and one 2(a) site. Below the Néel temperature equal to 18.5 K order the moments in 4(g) sites while the moments in 2(a) site order below 2 K. The Ho moments in all sites is parallel to the c-axis which is in good agreement with the sign of the Stevens factor and confirm the influence of CEF.

The values of the Ho moments at three sublattices are different and are smaller than the free Ho^{3+} ion value (10 μ_B), because the values of the effective magnetic moment are near to the free Ho^{3+} ion values [2, 3], the reduction of the magnetic moment in order state is probably the influence of the crystal electric field (CEF). This prediction supported the difference between the experimental and theoretical based on the Ruderman–Kittel–Kasuya–Yosida (RKKY) theory values of the Néel temperatures (see Fig. 3 in Ref. [5]) [13, 14].

Presented in the work results included the investigated compounds up to new series of compounds in which the rare earth atoms occupy two or three nonequivalent sites in which rare earth moments at different sites ordered independently at different temperatures with different structures.

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