Magnetic Properties and Magnetic Structure of $DyCoSi_2$ Compound

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The results of new magnetic dc and neutron diffraction measurements of $DyCoSi_2$ compound are presented. Below T_N equal to 10.9 K the Dy moments form collinear G-type structure with the moment parallel to the c-axis. The value of Dy-moment equal to 5.5(2) μ_B are smaller than free Dy^{3+} ion value (10.0 μ_B). These and the three-step magnetization process indicate the strong influence of the crystal electric field on the stability of the magnetic order. Increase of the values of the lattice parameters at 1.5 K in reference of these at 20 K indicate magnetostriction effect at low temperatures.

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1. Introduction

Ternary rare-earth compounds of composition $RCoSi_2$ where R is rare-earth element, crystallize in the orthorhombic $CeNiSi_2$-type structure (space group *Cmcm*, No. 63) [1, 2]. In this structure each kind of an atom i.e. R, Co, Si1, and Si2 occupies the 4c positions $0, y, 1/4$ with different values of y parameters. These atoms are arranged in alternating layers (parallel to the b-axis) stacked in the sequence R–Co–Si2–Co–R–Si1–R–Co–Si2–Co–R. Magnetic measurements indicate that the compounds with R = Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm are antiferromagnets at low temperatures [3]. Investigated in this work $DyCoSi_2$ has the Néel temperature equal to 10.5 K and contrary to other, these compounds have a positive value of the paramagnetic Curie temperature. Preliminary neutron diffraction experiment for $DyCoSi_2$ is performed in temperature 4.2 K for which the ratio T/T_N is equal to 0.4 [4] gives the small value of the magnetic moment localized on the Dy atoms equal to 5.74(18) μ_B. The Dy moments form collinear antiferromagnetic structure (see text below) and lying in the a–c plane making an angle of 27° with the c-axis. In this experiment the data were collected using an instrument with power resolution. Now the study of the magnetic properties and the magnetic structure of $DyCoSi_2$ have been reported.

2. Experiment

The $DyCoSi_2$ polycrystalline sample was synthesized from high-purity (3N for Dy and Co and 5 N for Si) elements by arc melting under argon atmosphere. In order to obtain a homogeneous material, the sample was annealed at 800 °C for 1 week.

The X-ray diffraction studies were performed at room temperature using a PANalytical X'PERT diffractometer (Cu K_α radiation). The dc magnetic measurements were carried out with the use of vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform. Three types of magnetic measurements were performed: cooling at low temperatures at zero magnetic field (ZFC) and at field (FC) equal to $H = 50$ Oe (to determine the phase transition temperature), the scanning from 1.9 K up to 350 K in a magnetic field of 1 kOe (to determine the values of the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p) and finally measuring the magnetization curves up to 90 kOe at 1.9 K (to determine the values of the magnetic moment in the ordered state).

Neutron diffraction data were collected with the E6 powder diffractometer located at the BERII reactor in Helmholtz-Zentrum Berlin. This instrument offers excellent resolution and is equipped with multichannel detectors. The sample with the mass about 5 g was encapsulated in a vanadium container. Neutron diffraction patterns were collected at 1.5 and 20 K with the incident wavelength of 2.447 Å. Refinements of neutron data were made using the Rietveld-type FullProf program [5].

3. Results

3.1. Crystal structure

The X-ray diffraction data at room temperature and neutron diffraction data at 1.5 and 20 K indicate that $DyCoSi_2$ crystallize in the orthorhombic $CeNiSi_2$-type structure (*Cmcm* space group). The unit cell constants are in good agreement with the previously reported data [1, 3]. The atoms occupy 4c Wyckoff position $(0, y, 1/4)$ with different y positional parameters.

The refinement parameters of the crystal structure from the pattern taken at 1.5 and 20 K are listed in Table I. Comparing these parameters, the increase of the values determined at 1.5 K are observed. This result suggests the magnetostriction effect at low temperatures.

3.2. Magnetic properties

The temperature dependence of the dc magnetic susceptibility has a distinct maximum at 10.9 K typical for antiferro- to paramagnetic transition (see Fig. 1a).

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TABLE I

Crystal structure parameters of $DyCoSi_2$ derived from the neutron diffraction patterns collected at 1.5 and 20 K.

T [K]	1.5	20
a [Å]	4.0122(18)	3.990(3)
b [Å]	16.3597(84)	16.323(13)
c [Å]	3.9575(17)	3.952(3)
V [Å^3]	259.76(37)	257.39(59)
y_{Dy}	0.1078(17)	0.1052(8)
y_{Co}	0.337(5)	0.338(4)
y_{Si1}	0.454(4)	0.457(3)
y_{Si2}	0.761(4)	0.757(3)
R_{Bragg} [%]	10.1	8.2
R_{prof} [%]	11.4	11.6

Above 50 K the reciprocal magnetic susceptibility obeys the Curie–Weiss law with paramagnetic Curie temperature equal to 22 K and effective magnetic moment equal to 10.6(1) μ_{B} which is close to the free Dy^{3+} ion value equal to 10.65 μ_{B}. The magnetization curve vs. magnetic field has a metamagnetic character with critical fields equal to 18, 27.5, and 32.5 kOe (Fig. 1b and c). The critical field values, corresponding to the metamagnetic transition were found from the field dependence of $\mathrm{d}M/\mathrm{d}H$ (see Fig. 1c). The magnetic moment at the maximal applied magnetic field equal to 90 kOe not saturated and equals 6.0(1) μ_{B} which is significantly smaller than the free Dy^{3+} ion value (10.0 μ_{B}).

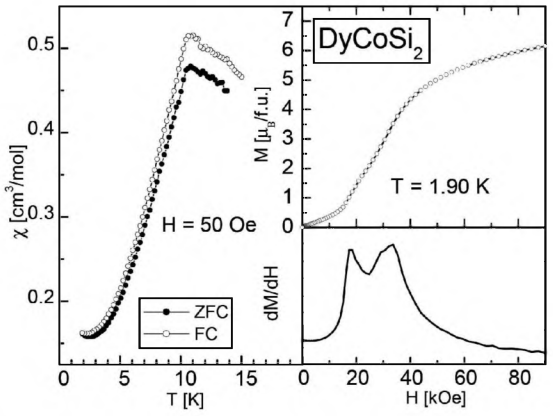

Fig. 1. Magnetic data for $DyCoSi_2$: (a) temperature dependence of the magnetic susceptibilities: ZFC (lower curve and FC (upper curve) and (b) magnetized moment μ, and (c) derivative $\frac{\mathrm{d}M}{\mathrm{d}H}$ versus intensity of the applied magnetic field up to 90 kOe at 1.9 K.

3.3. Magnetic structure

The neutron diffraction pattern collected at 1.5 K contains a number of additional Bragg reflections originating from magnetic order (see Fig. 2). All these reflections corresponding to the magnetic unit cell which have the same dimensions at crystallographic one. In this cell the Dy moments occupy the following positions: $\boldsymbol{\mu}_1(0, y, 1/2)$, $\boldsymbol{\mu}_2(0, \bar{y}, 3/4)$, $\boldsymbol{\mu}_3(1/2, 1/2 + y, 1/4)$ and $\boldsymbol{\mu}_4(1/2, 1/2 - y, 3/4)$.

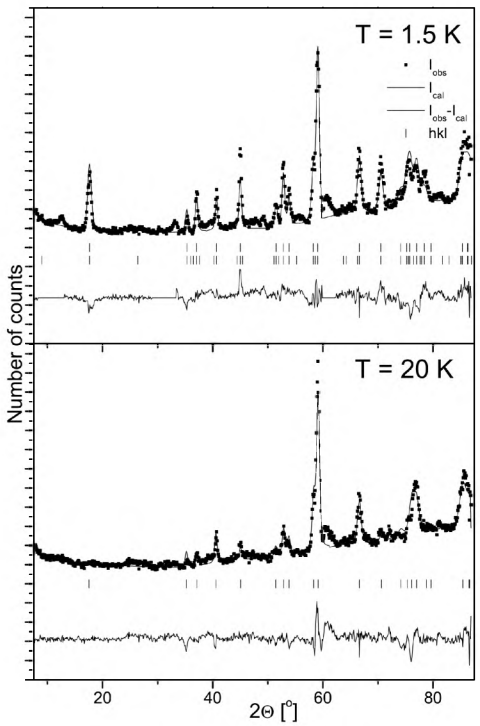

Fig. 2. Neutron diffraction patterns of $DyCoSi_2$ at 1.5 and 20 K. The symbols represent the experimental data while the solid line denotes the calculated profile. The difference between the observed and calculated intensities is shown at the bottom of each diagram. The vertical bars indicate the positions of the Bragg peaks, first row nuclear and second magnetic one.

In the case in which the magnetic unit cell coincides with the crystallographic one, four collinear ordering schemes are possible: three antiferromagnetic and one ferromagnetic. The possible magnetic structures can be described by sets of four vectors [6]:

$$\boldsymbol{F} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2 + \boldsymbol{\mu}_3 + \boldsymbol{\mu}_4,$$
$$\boldsymbol{G} = \boldsymbol{\mu}_1 - \boldsymbol{\mu}_2 + \boldsymbol{\mu}_3 - \boldsymbol{\mu}_4,$$
$$\boldsymbol{C} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2 - \boldsymbol{\mu}_3 - \boldsymbol{\mu}_4,$$
$$\boldsymbol{A} = \boldsymbol{\mu}_1 - \boldsymbol{\mu}_2 - \boldsymbol{\mu}_3 + \boldsymbol{\mu}_4,$$

which constitute the basis of the irreducible representation of spin transformation for the 4c sites in the space group $Cmcm$. The positive and negative signs refer to the moment direction of Dy atoms located at μ_1, μ_2, μ_3, and μ_4. Analysis of magnetic peak intensities indicates that the magnetic order corresponding to the G-mode in which the moments located on the plane with $z = 1/4$ and $z = 3/4$ are coupled ferromagnetically but the coupling between adjacent planes is antiferromagnetic. The Dy moments are parallel to the c-axis and equal to 5.5(2) μ_{B} which is smaller than the free ion value (10.0 μ_{B}).

4. Discussion

The data presented in this work confirm antiferromagnetic properties of $DyCoSi_2$ compound at low tempera-

tures (see Table II). The magnetic and neutron diffraction data indicate that magnetic moments are localized on the Dy atoms and form magnetic order of the G-type [6] with the moments parallel to the c-axis. Observed ordering is similar to this detected in the large number of isostructural compounds (see Table 6.5 in Ref. [7]). The direction of the Dy magnetic moment is determined by sign of the B_2^0 parameter of the crystal electric field. In the series of $RCoSi_2$ compounds the rare earth moment for R = Tb [8] and R = Ho [4] is parallel to the c-axis where for R = Er [9] lie in the a–c plane. This is in agreement with the change of the Stevens factor α_J from the negative values for R = Tb–Ho to positive for R = Er–Yb [10]. The data do not confirm the localized magnetic moment on the Co atoms.

TABLE II

Magnetic properties of $DyCoSi_2$: the Néel temperature (T_N), the paramagnetic Curie temperature (θ_p), experimental (exp.) and the theoretical (theor.) values of the effective magnetic moment (μ_{eff}) and the moment in the ordered state (μ) and the magnetic critical field (H_{cr}). Experimental methods: M — magnetic, ND — neutron diffraction.

T_N	θ_p	μ_{eff} [μ_B]		μ [μ_B]		H_{cr} [kOe]	References
[K]	[K]	Exp.	Theor.	M	ND		
10.5	8	10.7(2)	10.65				[3]
10.9	22	10.6(1)		6.0(1)	5.5(2)	18, 27.5, 32.5	this work
10.4				7.2		15, 30	[15]
					5.74(18)		[4]

The isostructural $YCoSi_2$ compound is the Pauli paramagnet [3]. The magnetic field dependence of the magnetization is similar to those observed for $DyCo_2Si_2$ [11]. With increase of the magnetic field the three-step metamagnetic transition is observed. Both compounds have the simple antiferromagnetic ordering with the sequence $+-+-$ at $H = 0$, which is stable up to H_{c1}. External magnetic field indicate the ferri- or noncollinear structures. These are results of the competition of three interactions: exchange interactions, crystalline electric field, and magnetostatic energy. The value of the critical temperature of the magnetic order indicates that the exchange energy is weak. Additionally these values do not obey the de Gennes site [12] which suggests the strong influence of the crystal electric field [13]. The determined values of the Dy moments equal to 6.0(1) at 90 kOe and 7.2 μ_B [14] at 140 kOe from the magnetization and 5.5(2) μ_B from neutron diffraction data respectively are smaller than free Dy^{3+} ion value (10.0 μ_B). These data indicate strong influence of the crystal electric field which caused that the direction of Dy moments is parallel to the c-axis. This is in agreement with the crystal field parameters [15].

The positive values of the paramagnetic Curie temperature determined in this work and presented in Ref. [3] are typical for the antiferromagnet with the layer magnetic structure. This is in agreement with the observed magnetic structure where the Dy moments parallel to the c-axis order ferromagnetically in plane $z = 1/4$ and $z = 3/4$ and antiferromagnetically between plane.

5. Summary

Reported in the work data confirm that $DyCoSi_2$ is collinear antiferromagnet. The magnetic moment is localized on the Dy atoms and is parallel to the c-axis. This and lower value of the moment as well as the three step magnetization process indicate the strong influence of the crystal electric field.

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