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2000 J. Phys.: Condens. Matter 12 7455

(http://iopscience.iop.org/0953-8984/12/33/312)

J. Phys.: Condens. Matter **12** (2000) 7455–7462. Printed in the UK PII: S0953-8984(00)13385-5

Neutron study of magnetic phase transitions in $TbCo_2Si_2$ and $DyCo_2Si_2$

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Received 19 April 2000, in final form 19 June 2000

Abstract. Neutron diffraction and magnetic measurements reveal a phase transition in $TbCo_2Si_2$ and $DyCo_2Si_2$ from a collinear antiferromagnetic AFI type order with the $\boldsymbol{k}$-vector [001] to an incommensurate sine-modulated magnetic structure described by the wavevector $\boldsymbol{k} = (0, 0, 1-k_z)$. The transition above occurs directly below the Néel temperature and k_z is equal to 0.042(1) for $TbCo_2Si_2$ and 0.049(1) for $DyCo_2Si_2$. In both phases magnetic moments localized on rare earth ions are parallel to the c-axis.

1. Introduction

In the last two decades there has been a growing interest in investigations of the RT_2X_2 group compounds, where R is a rare earth metal, T is a transition nd atom and X is a p-electron atom. These compounds crystallize in the body-centred tetragonal structure (space group $I4/mmm$) [1, 2]. RCo_2X_2 (X = Si, Ge) compounds belong to this structural type [3, 4]. Their magnetic properties have been studied by different groups. Magnetic and neutron diffraction data indicate that these compounds are antiferromagnets [5, 6]. Recently, our neutron diffraction investigation of $TbCo_2Ge_2$ [7] discovered the change of the magnetic structure from collinear to the sine modulated one taking place below the Néel temperature.

In this paper, new magnetic and neutron diffraction studies of the $TbCo_2Si_2$ and $DyCo_2Si_2$ compounds are reported. The previous investigations [6, 8, 9] show that these compounds are antiferromagnets with Néel temperature equal to 46 K for $TbCo_2Si_2$ and 21.4 K for $DyCo_2Si_2$ [6]. From neutron diffraction measurements carried out for polycrystalline samples of $TbCo_2Si_2$ [10] and $DyCo_2Si_2$ [11] the type of antiferromagnetic order has been determined. Since these works have been performed using instruments with rather low resolution, we have collected new data on the E6 diffractometer at the BERII reactor in the Berlin Neutron Scattering Centre. This instrument, apart from a better incident neutron intensity, offers excellent resolution.

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0953-8984/00/337455+08$30.00

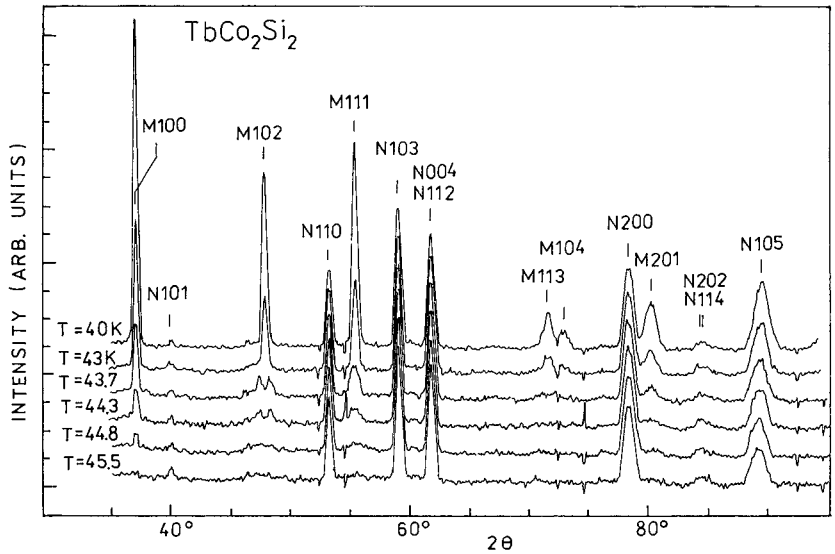

Figure 1. Neutron diffraction patterns of $TbCo_2Si_2$ taken at different temperatures (shown).

2. Experimental details

Samples of $TbCo_2Si_2$ and $DyCo_2Si_2$ compounds were made by melting the individual constituents (taken in stoichiometric proportions) in an arc furnace under high-purity argon atmosphere. The purity of rare earths and of cobalt was 3 N, whereas the purity of Si was 5 N. The samples were then annealed in a quartz tube at 800 °C for 100 h and cooled to room temperature. Powder samples were examined by x-ray diffraction using Co Kα radiation. The powder patterns could be indexed on the basis of the $I4/mmm$ body-centred tetragonal type structure.

AC magnetic susceptibility $\chi_{AC} = \chi' - \mathrm{i}\chi''$, where χ' is the real and χ'' the imaginary component, was measured by means of the Lake Shore 7225 AC susceptometer with the frequency of the driving field set to 125 Hz, and the amplitude equal to 1 Oe or 5 Oe. Temperature dependences of χ_{AC} for the investigated compounds were recorded upon heating with the temperature sweep rate equal to 0.1 and 0.2 K min^{-1}.

Neutron data were collected at a number of temperatures in the temperature range between 1.5 K and Néel points T_N. The neutron wavelength was 2.44 Å. All data processing was done using the FullProf program [12].

3. Results

3.1. Crystal structure

Neutron diffraction patterns recorded above the Néel points (see figures 1 and 2, lower curves) show that both compounds crystallize in the body-centred tetragonal lattice of the $ThCr_2Si_2$ type (space group $I4/mmm$), with an ordered distribution of Tb (Dy) atoms at 2(a): 0, 0, 0; 1/2, 1/2, 1/2; Co atoms at 4(d): 0, 1/2, 1/4; 0, 1/2, 3/4; 1/2, 0, 1/4; 1/2, 0, 3/4 and Si atoms at 4(e): 0, 0, z; 0, 0, $-z$; 1/2, 1/2, 1/2 + z; 1/2, 1/2, 1/2 − z. The determined lattice parameters and z values are given in table 1.

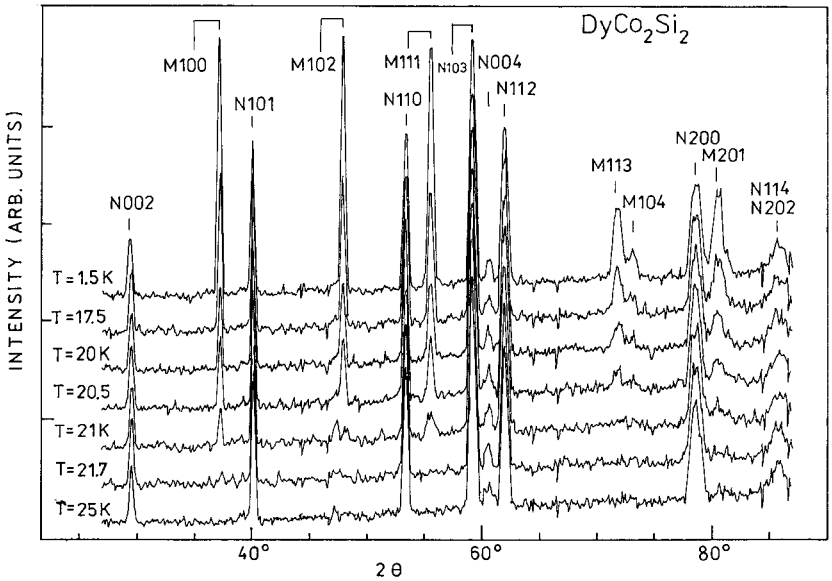

Figure 2. Neutron diffraction patterns of $DyCo_2Si_2$ taken at different temperatures between 1.5 and 25 K.

Table 1. Crystal structure parameters of $TbCo_2Si_2$ and $DyCo_2Si_2$ derived from neutron diffraction data.

	$TbCo_2Si_2$ $T = 45.5$ K	$DyCo_2Si_2$ $T = 25$ K
a (Å)	3.8960(13)	3.8970(14)
c (Å)	9.8005(36)	9.7987(45)
z	0.3778(8)	0.3779(25)
R_{Bragg} (%)	3.44	10.6
$R_{prof.}$ (%)	3.04	7.8

3.2. Magnetic susceptibility

Temperature dependences of χ' for investigated compounds are displayed in figures 3 and 4. Results for the two temperature sweep rates coincide. As expected for the antiferromagnetic structure, χ'' is near zero. In the figures, the temperature derivative of χ' and the $\chi'T$ product (in arbitrary units) are also shown. The temperature T_N is marked on the $d\chi'/dT$ curve as the centre of a well defined fall-down and is equal to 45 K for $TbCo_2Si_2$ and 21.9 K for $DyCo_2Si_2$, which is close to the results of [6] cited in the introduction. It appears that for both compounds below T_N an anomaly in the $d\chi'/dT$ curve is seen, which may be connected with some change in the magnetic structure. Spin reorientation should be excluded since such transitions are usually clearly seen in the χ'–T dependences, which is not the case here. Thus, the observed anomalies come probably from the transitions from the antiferromagnetic collinear ordering to the incommensurate structure. The anomalous behaviour of $d\chi'/dT$ starts at $T_t = 42$ K for $TbCo_2Si_2$ and 20 K for $DyCo_2Si_2$. In this way, the temperature range $\Delta T = T_N - T_t$ of the existence of the incommensurate phase covers 0.067 and 0.087 of the magnetically ordered state, respectively. It should be mentioned that analysis of the derivative of the $\chi'T$ curve (not shown) gives the same result.

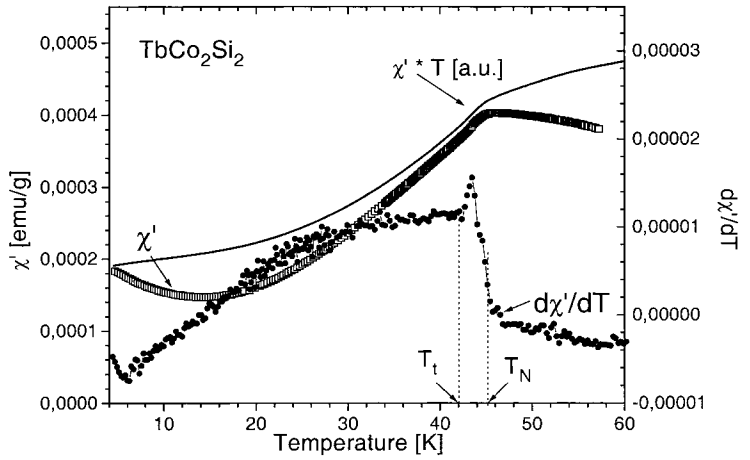

Figure 3. Temperature dependence of the AC magnetic susceptibility χ' and of the related values $\chi'T$ and $\mathrm{d}\chi'/\mathrm{d}T$ (in arbitrary units) for $TbCo_2Si_2$.

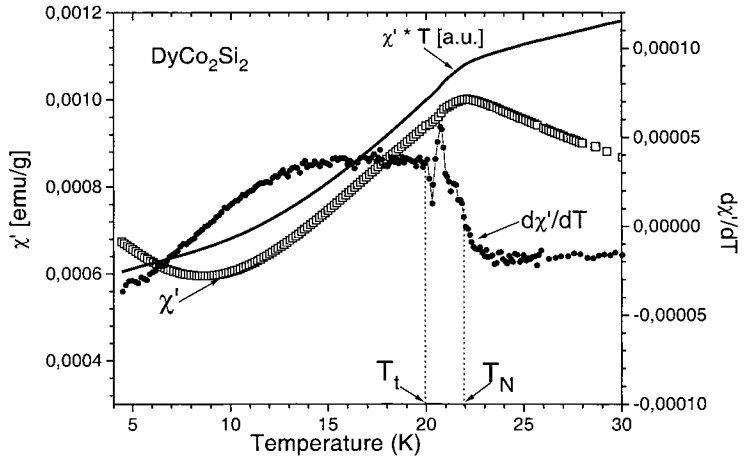

Figure 4. Temperature dependence of the AC magnetic susceptibility χ' and of the related values of $\chi'T$ and $\mathrm{d}\chi'/\mathrm{d}T$ for $DyCo_2Si_2$.

3.3. Magnetic structure

Figure 1 shows neutron diffraction patterns of $TbCo_2Si_2$ at different temperatures. In the patterns measured at 40 K and 43 K a number of additional reflections of magnetic origin over those obtained at low temperatures [5] with indices obeying the $h + k + l$ odd condition are observed. This corresponds to the AFI-type magnetic structure in which Tb magnetic moments in the (0, 0, 0) and (1/2, 1/2, 1/2) positions are coupled antiparallely. On the other hand, from the zero intensity of the $00l$ magnetic line it can be assumed that these moments are parallel to the c-axis. Cobalt seems to carry no magnetic moment, similarly to the other compounds of that type. Similar magnetic structure is observed at low temperatures [6].

Neutron patterns obtained at 43.7, 44.3 and 44.8 K reveal two satellite reflections around the magnetic peak M102. The above effect indicates that a transition to a new incommensurate magnetic phase with a wavevector along the c-axis takes place. If an in-plane wavevector

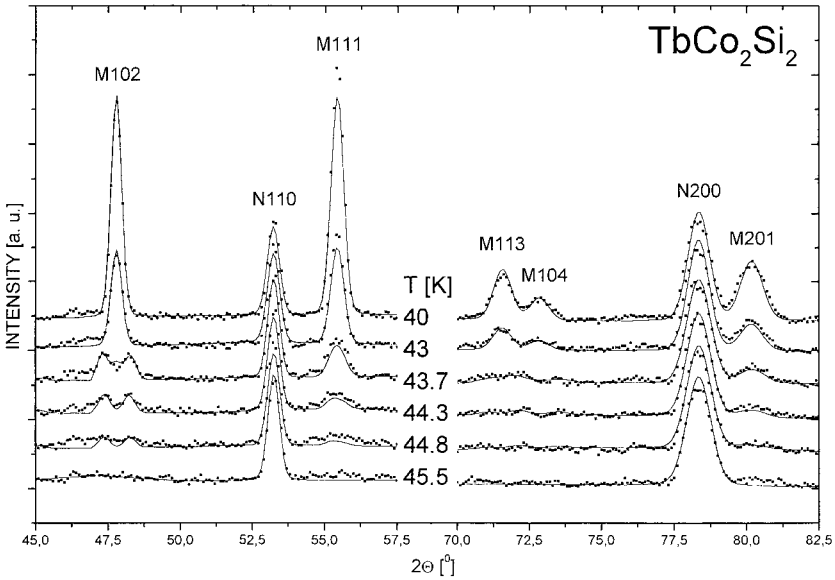

Figure 5. Two parts of the neutron diffraction patterns of $TbCo_2Si_2$ collected at several temperatures between 40 and 45.5 K. Open squares represent the experimental points, solid lines the calculated profiles.

Table 2. The positions of the satellite reflections in the incommensurate phase of the $TbCo_2Si_2$ compound at $T = 43.7$ K.

hkl	$2\theta^-$	$2\theta^+$	$\Delta(2\theta)$[a]
102	46.8	47.6	0.8
111	54.6	55.0	0.4
103	70.3	71.3	1.0
104	71.4	72.7	1.3

[a] $\Delta(2\theta) = 2\theta^+ - 2\theta^-$.

component had been present, it would have led to a splitting of the (100) reflection, too. The positions of the satellite reflections are described by the wavevector $\boldsymbol{k} = (0, 0, 1 - k_z)$ with the refined value of wavevector component k_z equal to 0.042 at 43.7 K. k_z increases with increase of temperature up to 0.045 at 44.8 K (see figure 5). These values correspond, with a good approximation, to a $24c$ and $22c$ enlargement of the unit cell, respectively.

The effect of the splitting into the satellites is clearly visible only for the M102 reflection because this peak has large intensity and the difference $\Delta(2\theta) = 2\theta^+ - 2\theta^-$ in positions of the 102^+ ($2\theta^+$) and 102^- ($2\theta^-$) reflections is 0.8° (see table 2). The next strongest intensity magnetic peak 111 has a small value of $\Delta(2\theta)$ equal to 0.4°. Two other two peaks 113 and 104 which have a large value of $\Delta(2\theta)$ have small intensity near the Néel temperature (see figure 5).

A similar dependence of intensities of the magnetic peaks is observed for $DyCo_2Si_2$ (see figure 2). Reflections observed in the patterns measured at 1.5, 17.5, 20, 20.5 K correspond to the collinear AFI-type magnetic structure. The satellites of the M102 reflection in the patterns measured at $T = 21$ and 21.7 K correspond to the modulated structure with k_z equal 0.049. This value corresponds to a $20.4c$ enlargement of the unit cell.

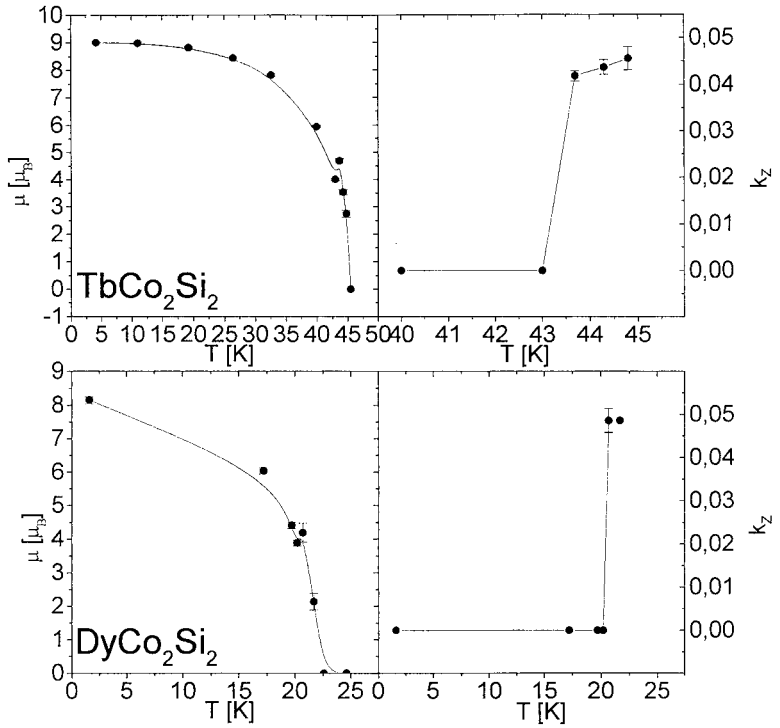

Figure 6. Temperature dependence of the rare earth magnetic moments and k_z component of the wavevector for $TbCo_2Si_2$ and $DyCo_2Si_2$. Low temperature data for $TbCo_2Si_2$ are from [5].

Both investigated compounds are antiferromagnets; for that reason, in order to explain the splitting two types of magnetic structure can be considered:

- an amplitude modulated structure,
- a helicoidal order.

Analysis of the intensity of the magnetic reflections for incommensurate structure indicates that a slightly better value of the reliability factor is obtained for both compounds for an amplitude modulated structure. In such a structure the moment value μ_{nj} of the jth atom in the nth cell may be derived from the moment value in the zeroth cell:

$$\mu_{nj} = \mu_{0j} z \cos(2\pi\rho R_n + \phi_j)$$

where z is a unit vector of the varying moment component, μ_{0j} the amplitude of the sinusoidal variation and ?$_j$ a phase factor of the jth atom relative to the origin of the wave usually taken at atom 1.

A similar type of magnetic structure is observed in the isostructural $TbCo_2Ge_2$ compound [7].

For both compounds in the temperature dependence of the values of the rare earth magnetic moments a small anomaly is observed (see figure 6) accompanying the commensurate to modulated structure transition. From figure 7 it follows that the lattice parameters a and c also behave in a discontinuous way.

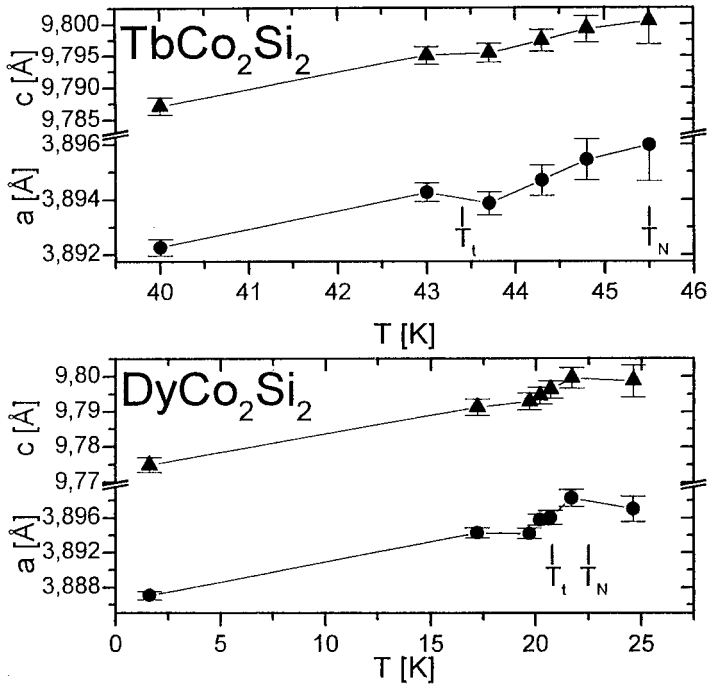

Figure 7. Temperature dependence of the *a*- and *c*-axis lattice constants for $TbCo_2Si_2$ and $DyCo_2Si_2$ compounds.

4. Comment

The results of the presented magnetic and neutron diffraction measurements confirm the existence of a magnetic phase transition in $TbCo_2Si_2$ and $DyCo_2Si_2$ below the Néel point. The collinear antiferromagnetic AFI-type order transforms into an incommensurate, sine-wave modulated structure which exists in a narrow temperature from 42 to 45 K for $TbCo_2Si_2$, 20 to 21.7 K for $DyCo_2Si_2$ and 29 to 34 K for $TbCo_2Ge_2$ [7]. The temperature range of the modulated magnetic phase in $DyCo_2Si_2$ is in good agreement with the specific heat data, which give two anomalies at 20.3 and 21.4 K [17].

The transition from a commensurate magnetic ordering at low temperature to an incommensurate structure in the vicinity of the Néel point has been observed in a large number of RT_2X_2 compounds with $ThCr_2Si_2$-type structure [6, 13], for example in isostructural $PrCo_2Si_2$ [14], $NdCo_2Si_2$ [15] and $NdCo_2Ge_2$ [16]. For these compounds the modulated magnetic structures are observed in broad temperature intervals of 20.1 K, 17 K and 17 K, respectively.

Two factors influence the stability of the experimentally observed magnetic structures in RT_2X_2 compounds: exchange interactions via conduction electrons (RKKY model) and the action of the crystalline electric field (CEF) of 4f electrons. The former factor favours long range oscillatory magnetic structures, the latter uniaxial ordering. The occurrence of the magnetic phase transition from collinear commensurate to an incommensurate, oscillatory structure can be explained in terms of the realistic mean field model, which takes into account the temperature dependence of the periodic exchange field and CEF effect [14]. For $PrCo_2Si_2$ [18] and $NdCo_2Si_2$ [19] the calculations based on the molecular

field model reproduced the magnetic order and the field–temperature magnetic phase diagram. The magnetic transitions observed in these compounds between commensurate and incommensurate phases have been discussed in connection with the wave-dependent molecular field coefficients.

In both phases (collinear and modulated) the magnetic moments are parallel to the *c*-axis. This indicates a strong magnetocrystalline anisotropy. The anomalies of the temperature dependence of the lattice parameters near the transitions are caused by a magnetoelastic effect, as observed for $NdCo_2Si_2$ [20].

Acknowledgments

The kind hospitality and financial support of the Berlin Neutron Scattering Centre HMI to perform neutron experiments is gratefully acknowledged by two authors (BP and AS).

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