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Magnetic structures of the $TbCuSb_2$ compound

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Abstract

Results of neutron diffraction measurements carried out for the $TbCuSb_2$ compound are reported. This compound crystallizes in the tetragonal $ZrCuSi_2$-type crystal structure and is an antiferromagnet below 9 K. The magnetic order at T=1.4 K is collinear, described by the propagation vector $\mathbf{k}$=(1/2, 0, 0). With an increasing temperature, near T_t=5 K the magnetic structure changes to a collinear one with $\mathbf{k}$=(0, 1/4, 1/2). Near the temperature of the phase transition, $T_t \approx 5$ K the new phase which is probably sine wave modulated described by the propagation vector $\mathbf{k}$=(0.423(1), 0, 0).

Keywords: Rare earth compounds; Magnetically ordered materials; Crystal structure; Neutron diffraction

1. Introduction

In the course of a systematic research of ternary $RTSb_2$ (R=rare earth, T=nd-electron metal) intermetallic compounds we present results of neutron diffraction measurements of the $TbCuSb_2$ compound.

X-ray data indicate that this compound crystallizes in the tetragonal $ZrCuSi_2$-type of structure (space group *P4/nmm*) [1]. According to results of magnetic measurement $TbCuSb_2$ is an antiferromagnet with a Néel temperature of 9 K.

2. Experimental

The $TbCuSb_2$ compound, with a total mass of 7 g, was synthetized by arc melting of element ingots starting from the nominal composition $TbCuSb_2$. The sample was subsequently annealed in vacuum for 100 h at 800°C and quenched in water. The examination of the X-ray pattern confirmed that the main phase is tetragonal with a small concentration of another phase. The lattice parameters were determined and found to be in fair agreement with those reported before [1].

The neutron powder diffraction experiments were performed on the polycrystalline samples at Saclay (Orphée reactor, Laboratoire Léon Brillouin) with the G4.1 two-axis diffractometer (λ=2.4249 Å). The neutron powder data were analyzed using the Rietveld technique with the FULLPROF program [2]. Scattering lengths were taken from Sears [3] and the magnetic form factor of Tb^{3+} was calculated in the dipolar approximation, taken from Freeman and Desclaux [4].

3. Crystal structure

Strong intensity peaks observed in the neutron powder diffraction pattern of $TbCuSb_2$ in the paramagnetic state (above T_N) (see Fig. 1) are consistent with the *P4/nmm* space group. An analysis of the nuclear intensities clearly shows that the crystal structure of this compound is of the $ZrCuSi_2$-type; the atoms are located in the following positions:

Tb atoms in 2(c): 1/4, 1/4, z_R.
Cu atoms in 2(a): 3/4, 1/4, 0.
Sb atoms in 2(b): 3/4, 1/4, 1/4 and 2(c): 1/4, 1/4, z_{sb}.
The refined parameters: a, c, z_R and z_{Sb}, are listed in Table 1.

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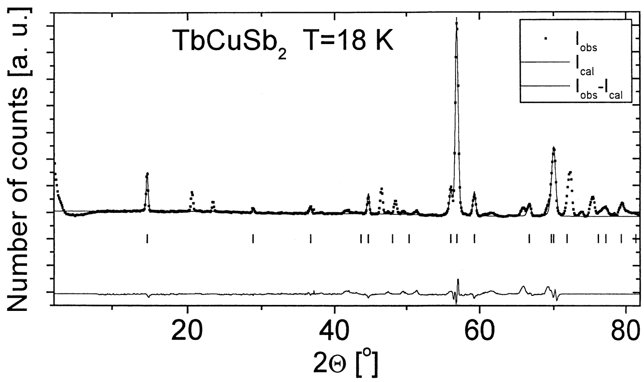

Fig. 1. Observed and calculated neutron diffraction pattern of $TbCuSb_2$ ($T=18$ K). The squares are for the observed points, the solid lines represent a calculated profile and the difference between observed and calculated data (below). The bars indicate the nuclear Bragg peaks.

Table 1
$TbCuSb_2$ compound, diffraction results, crystal structure, *P4/nmm* space group, neutron

Compound	$TbCuSb_2$
T (K)	18
a (Å)	4.2525(7)
c (Å)	9.8791(32)
V (Å^3)	178.65(12)
c/a	2.3231(12)
z_R	0.7448(14)
z_{Sb}	0.1645(17)
R_{Bragg} (%)	7.92
$R_{prof.}$ (%)	9.16

4. Magnetic structure

Fig. 2 shows the neutron diffraction patterns obtained for the $TbCuSb_2$ sample in the temperature range from 1.4 K (top) to 18 K (bottom).

With an increase of the temperature to $T=4.4$ K, a decrease of the intensities corresponding to one group of peaks and at the same time an increase of additional peaks are observed.

This results indicate a change of the magnetic structure with temperatures which is discussed below.

The magnetic peaks observed in the neutron diffraction pattern of $TbCuSb_2$ taken at $T=1.4$ K (Fig. 3a) are indexed with the propagation vector $\mathbf{k}=(1/2, 0, 0)$ which corresponds to a magnetic ordering scheme in which the magnetic moments localized on the Tb^{3+} ions form a collinear magnetic structure. As there are four Tb magnetic moments localized at the following sites in the magnetic unit cell: $\boldsymbol{\mu}_1(1/8, 1/4, z_R)$, $\boldsymbol{\mu}_2(3/8, 3/4, \bar{z}_R)$, $\boldsymbol{\mu}_3(5/8, 1/4, z_R)$ and $\boldsymbol{\mu}_4(7/8, 3/4, \bar{z}_R)$ three different collinear antiferromagnetic structures are possible $\mathbf{A}=\boldsymbol{\mu}_1-\boldsymbol{\mu}_2-\boldsymbol{\mu}_3+\boldsymbol{\mu}_4$, $\mathbf{C}=\boldsymbol{\mu}_1+\boldsymbol{\mu}_2-\boldsymbol{\mu}_3-\boldsymbol{\mu}_4$ and $\mathbf{G}=\boldsymbol{\mu}_1-\boldsymbol{\mu}_2+\boldsymbol{\mu}_3-\boldsymbol{\mu}_4$. The best fit to the experimental results was obtained for the **A** model. The magnetic moments of Tb, equal to 7.80(5), μ_B are parallel to the [110] direction ($\mathbf{R}_M=5.78\%$) (see Fig. 4a).

An analysis of the neutron diffraction pattern measured at 4.7 K (Fig. 3b) indicates that three magnetic phases coexist:

two collinear ones with the propagation vectors $\mathbf{k}_1=$

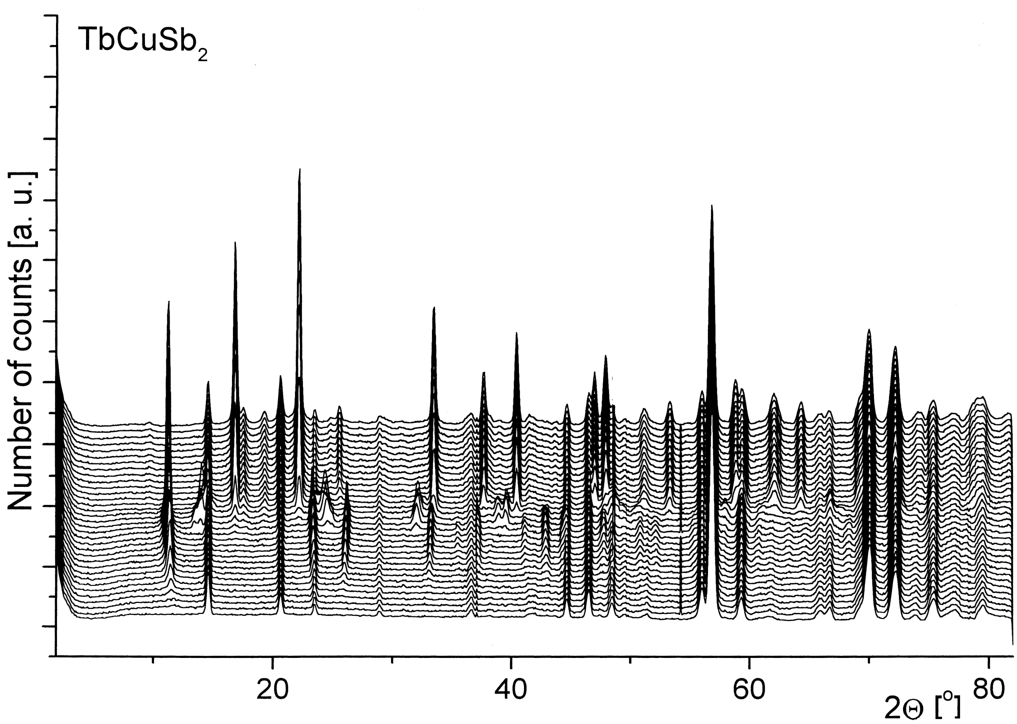

Fig. 2. Neutron diffraction patterns of the $TbCuSb_2$ sample at temperatures from 1.4 K (top) to 18 K (bottom).

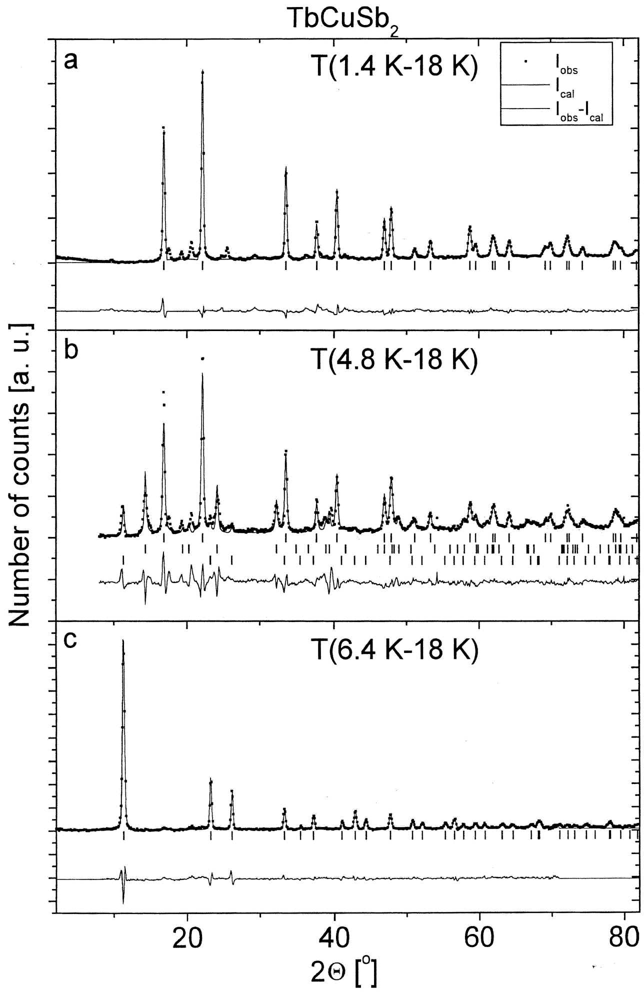

Fig. 3. Observed and calculated neutron powder diffraction patterns of $TbCuSb_2$ (a) ($T=1.4$–18 K), (b) (4.8–18 K), (c) (6.4–18 K). The squares represent the experimental points, solid lines the calculated profiles. The lower pattern shows the difference between the experimental and calculated patterns. Vertical bars are for magnetic peak positions corresponding to different magnetic structures (see text).

(1/2, 0, 0) (I) and $\mathbf{k}_2=(0, 1/4, 1/2)$ (II) and probably a sine modulated one with $\mathbf{k}_3=(0.423(1), 0, 0)$ (III). In the first phase the Tb moments are equal to 5.38(6) μ_B and parallel to the [110] direction ($\mathbf{R}_{1mag}=8.3\%$) while for the phase II the Tb moments of 1.99(8) μ_B are parallel to the *a*-axis ($\mathbf{R}_{2mag}=23.0\%$). In the sine-wave modulated phase the magnetic moment are equal to 3.75(9) μ_B and parallel to the [110] direction ($\mathbf{R}_{3mag}=32.5\%$) (Fig. 4b).

A further increase of the temperature causes that only phase II remains. The analysis of the neutron diffraction pattern at 6.4 K (Fig. 3c) shows that the Tb moments are equal to 6.27(8) μ_B and form a collinear magnetic structure described by the propagation vector $\mathbf{k}=(0, 1/4, 1/2)$ ($\mathbf{R}_{mag}=11.3\%$). Magnetic moment is parallel to the *a*-axis (Fig. 4c).

The temperature dependence of the peak intensity leads to a Néel temperature of 9 K (Fig. 5).

5. Discussion

The results of the neutron diffraction measurements presented in this work confirm that the $TbCuSb_2$ compound crystallizes in the tetragonal $ZrCuSi_2$-type of crystal structure. In this structure the $\mathbf{R}^{3+}$ ions are located at positions with of tetragonal point symmetry (4*mm*).

In the $TbCuSb_2$ compound, with increasing the temperature, a change of the magnetic structure from collinear antiferromagnetic described by the propagation vector $\mathbf{k}_1=(1/2, 0, 0)$ at low temperature to a new one described by $\mathbf{k}_2=(0, 1/4, 1/2)$ near the Néel temperature is observed. Near the temperature of the phase transition between these two phases ($T_t\approx5$ K) an incommensurate sine-wave modulated phase is observed. Such a phenomenon is rare in rare earth intermetallic compounds and is a result of a free energy temperature dependence for different propagation vectors [6].

Large **R–R** distances of about ~4 Å in plane and ~5.5 Å between planes and modulated magnetic structures observed in these compounds suggest that the magnetic interactions have a long-range character, probably of the RKKY-type.

The magnetic structure of $TbCuSb_2$ at $T=1.4$ K is similar to that observed in isostructural $TbAgSb_2$ [5]. In $TbAgSb_2$ the magnetic order is stable up to the Néel temperature, equal to 11 K. The change in magnetic structure observed in $TbCuSb_2$ from commensurate at low temperatures through incommensurate to a new collinear phase is similar to that observed in isostructural $HoAgSb_2$ [5]. In $HoAgSb_2$ at 1.4 K the magnetic order is described by the propagation vector $\mathbf{k}=(1/2, 0, 0)$. With an increase of the temperature a change of the magnetic structure to the incommensurate structure described by the propagation vector $\mathbf{k}=(k_x, 0, k_z)$ ($k_x\sim1/8$, $k_z\sim1/2$) is observed. In the $HoAgSb_2$ compound, over a wide temperature range up to the Néel temperature equal to 5.0 K a coexistence of both magnetic phases is observed.

The determined magnetic structures indicate a strong magnetocrystalline anisotropy in the basal plane [7]. In low temperature commensurate and incommensurate phases the Tb magnetic moment is parallel to the [110] direction while in the high temperature phase it lies along the [100] direction.

The second factor which influences the magnetic ordering is the crystal electric field (CEF). The CEF interaction is described by the Hamiltonian:

$$H_{CEF}=\mathbf{B}_2^0\mathbf{O}_2^0+\mathbf{B}_4^0\mathbf{O}_4^0+\mathbf{B}_4^4\mathbf{O}_4^4+\mathbf{B}_6^0\mathbf{O}_6^0+\mathbf{B}_6^4\mathbf{O}_6^4$$

where $\mathbf{O}_n^m$ are the Stevens operators and $\mathbf{B}_n^m$ are CEF parameters as defined by Hutchings [8]. The $\mathbf{B}_n^m$ values determined for the tetragonal RT_2Si_2 compounds indicate that the $\mathbf{B}_2^0$ parameter is dominant [9]. The direction of the magnetic moment with reference to the tetragonal *c*-axis is connected with the sign of the $\mathbf{B}_2^0$ parameter. The magnetic

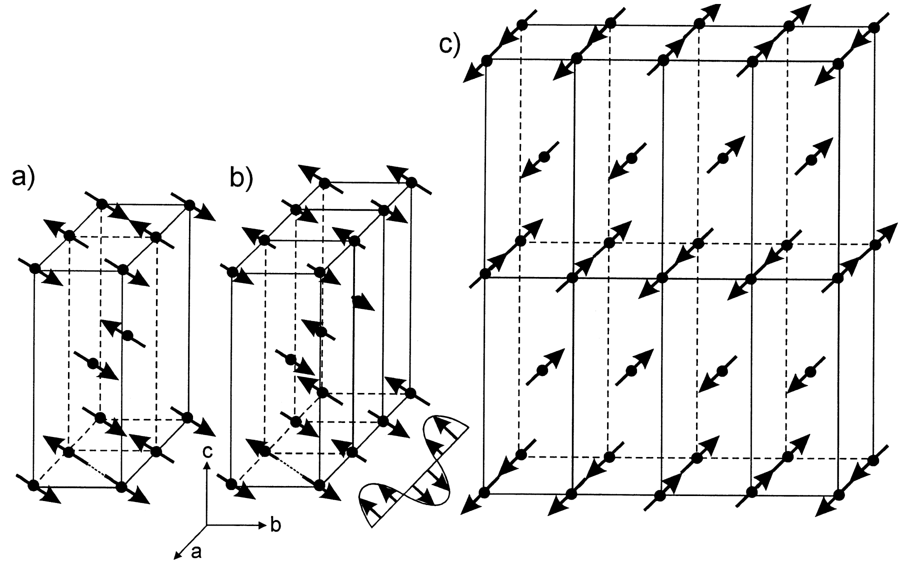

Fig. 4. Magnetic structures of $TbCuSb_2$ in (a) collinear $\mathbf{k}=(1/2, 0, 0)$, (b) modulated $\mathbf{k}=(k_x, 0, 0)$ and collinear $\mathbf{k}=(0, 1/4, 1/2)$ phases.

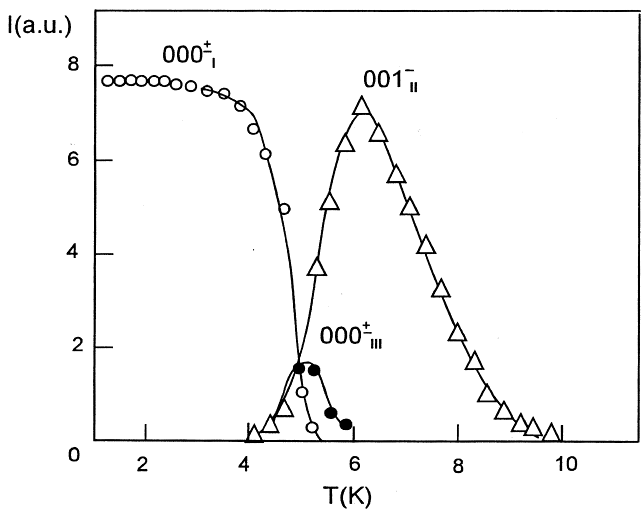

Fig. 5. Temperature dependence of the magnetic peak intensities corresponding to different magnetic phases for $TbCuSb_2$ (reflex (○) $000^{\pm}_{I}$, (△) 001^{-}_{II} and (●) $100^{\pm}_{III}$).

moment is parallel to the *c*-axis if $\mathbf{B}_2^0<0$ and perpendicular to the *c*-axis if $\mathbf{B}_2^0>0$ [10,11]. The obtained data for $TbCuSb_2$ show that $\mathbf{B}_2^0$ is positive. The change of the direction of the magnetic moment with increasing temperature indicates an influence of higher-order terms [8].

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