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Magnetic ordering in $Tm_5Ni_2In_4$

A. Szytuła[1], S. Baran[1], D. Kaczorowski[2], W. Sikora[3], A. Hoser[4]

[1] *Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland*

[2] *Institute of Low Temperature and Structural Research PAS, P.O.Box 1410, 50-950 Wrocław, Poland*

[3] *AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Mickiewicza 30, 30-059 Kraków, Poland*

[4] *Helmholtz-Zentrum Berlin für Materialen und Energie GmbH, Hahn-Meitner Platz 1, D-14 109 Berlin, Germany*

Abstract. Physical properties of the $Tm_5Ni_2In_4$ compound have been investigated by means of magnetometric, calorimetric as well as neutron diffraction measurements. The compound crystallizes in the orthorhombic $Lu_5Ni_2In_4$-type crystal structure (space group Pbam, No. 55). The reported results indicate that the sample exhibits an antiferromagnetic ordering below T_N = 4.1 K. The Tm^{3+} ions occupy three crystal positions within unit cell: one 2a site and two 4g sites. Analysis of neutron diffraction data collected at T = 1.5 K, together with group theory symmetry analysis predictions show that Tm magnetic moments form a non-collinear magnetic structure described by the propagation vector **k** = [0, ½, ½]. The magnetic moments lie in the (001) plane.

Keywords: A. rare-earth alloys and compounds, A. magnetically ordered materials, C. magnetisation, C. thermodynamic properties, D. neutron diffraction

1. Introduction.

Rare earth $R_5Ni_2In_4$ (R = Sc, Y, Tb - Tm, Lu) intermetallics crystallize in an orthorhombic crystal structure of the $Lu_5Ni_2In_4$-type [1-4]. In this structure the rare earth atoms occupy three nonequivalent crystallographic positions. Magnetometric measurements indicate an existence of magnetic ordering below 103, 30, 18.5 and 4.2 K for Dy [4], Ho [5], Er [6] and Tm [7], respectively. Below these temperatures additional phase transitions at 12 and 8 K for R = Dy [4] and 2 K for R = Er [6] compounds, respectively, are observed. Magnetic ac and dc as well as calorimetric data of $Tm_5Ni_2In_4$ indicate antiferromagnetic properties below $T_N = 4.2$ K [7].

In this paper we revise low-temperature properties of $Tm_5Ni_2In_4$ by means of magnetic susceptibility, magnetization, specific heat and neutron diffraction measurements. The specific heat measurements have been performed at temperatures down to 0.35 K with the main aim of attesting the existence of additional magnetic phase transition at low temperatures.

2. Experimental details

Polycrystalline sample of $Tm_5Ni_2In_4$ was prepared by arc melting of high purity elemental constituents (Tm: 99.9 wt%; Ni and In: 99.99 wt%) under titanium–gettered argon atmosphere. To ensure good homogeneity, the sample was re-melted several times. Then the product was annealed in evacuated silica tube at 870 K for 1 week.

Sample quality was checked by X-ray powder diffraction at room temperature using an XPERT-PRO PANalytical diffractometer with CuK_α radiation. The XPERT HighScore Plus program package was used for phase determination and Rietveld analysis of collected data set. It has been confirmed that the $Tm_5Ni_2In_4$ sample crystallizes in an orthorhombic structure of the $Lu_5Ni_2In_4$-type with lattice parameters a = 17.6545(5) Å, b = 7.8337(2) Å and c = 3.5405(2) Å.

Magnetic measurements were carried out within temperature range 1.72 – 400 K, in magnetic fields up to 5 T, using a Quantum Design MPMS-5 SQUID magnetometer. Specific heat was taken by relaxation method in temperature range 0.35 – 8 K using a Quantum Design PPMS platform.

Powder diffraction patterns were collected using the E6 diffractometer installed at BERII reactor (Helmholtz-Zentrum Berlin) with incident neutron wavelengths equal to

2.447 Å. The data were collected between 1.5 and 5.9 K. They were analyzed using a Rietveld-type program FullProf [8].

3. Results

3.1. Magnetic properties

The magnetic data of $Tm_5Ni_2In_4$ are summarized in Fig. 1. Above about 70 K, the inverse magnetic susceptibility obeys the Curie-Weiss law with effective magnetic moment μ_{eff} = 7.74 μ_B and paramagnetic Curie temperature θ_p = +11 K. At low temperatures some small departure from the straight line behavior is observed, which can be attributed to crystal electric field (CEF) effect. The determined value of μ_{eff} is slightly higher than the one expected for Tm^{3+} free ion (7.56 μ_B). Slightly higher value of 7.92 μ_B was reported in Ref. [7]. On the other hand a negative value θ_p = -47 K was given in Ref. [7]. The latter discrepancy indicates that the magnetic properties of $Tm_5Ni_2In_4$ are strongly anisotropic, and polycrystalline specimens do not represent an averaged susceptibility because of in-built preferred orientation of grains.

The low-temperature dependence of the magnetic susceptibility exhibits a distinct maximum near T_N = 4.1 K, typical of antiferro- to paramagnetic transition (see upper inset in Fig. 1). Furthermore, below 3.1 K, an upturn in χ(T) is seen, signaling more complex magnetic behavior. The isothermal magnetization curve measured at 1.72 K increases with increasing external magnetic field with a small step near 0.3 T (see lower inset in Fig. 1). Near 5 T, the magnetization nearly saturates at a value that corresponds to the magnetic moment of 4.15 μ_B/Tm atom, notably smaller than the free Tm^{3+} ion value (7.0 μ_B).

The low-temperature specific heat of $Tm_5Ni_2In_4$, presented in Fig. 2, shows two peaks at 3.95 and 4.05 K. While the latter one can be associated with the onset of the antiferromagnetic state, the former one has an unclear origin. No anomaly in C(T) is observed near 3.1 K, where the upturn in χ(T) was found. Below about 0.7 K a small increase of the specific heat is seen that can be related to nuclear contribution.

3.2. Crystal structure

Neutron diffraction pattern, collected in paramagnetic state at 5.9 K (Fig. 3a), confirms that the sample exhibits the orthorhombic $Lu_5Ni_2In_4$-type structure (space group Pbam, No. 55). In this structure the thulium atoms occupy three nonequivalent positions: Tm at 2a site: 0, 0, 0; Tm' and Tm'' at 4g site: x, y, 0 with different values of x and y parameters. The Ni atoms

are located at 4h site: x, y, ½, while the In atoms form two sublattices (In1 and In2) of the 4h site: x, y, ½ with different values of x and y. The determined positional parameters are collected in Table 1. They are in good agreement with previously reported ones that were obtained from x-ray diffraction measurements at room temperature [1, 7].

3.3. Magnetic structure

The neutron diffraction patterns of $Tm_5Ni_2In_4$, taken below the Néel temperature, clearly reveal the presence of some additional reflections originating from magnetic ordering. The low temperature magnetic contribution can be easily extracted by making differential patterns like that shown in Fig. 3b (1.5–5.9 K). The observed reflections were indexed using a cell with dimensions a x 2b x 2c corresponding to a magnetic propagation vector **k** = [0, ½, ½].

In the crystallographic unit cell of $Tm_5Ni_2In_4$, the Tm atoms occupy ten positions:

- in 2a sublattice (Wyckoff notation): Tm1 (0, 0, 0) and Tm2 (½, ½, 0);
- in 4g sublattice with x = 0.2208(12), y = 0.2486(40): Tm'1 (x, y, 0), Tm'2 (1-x, 1-y, 0), Tm'3 (½-x, ½+y, 0) and Tm'4 (½+x, ½-y, 0);
- in 4g sublattice with x = 0.4151(13), y = 0.1212(27): Tm"1 (x, y, 0), Tm"2 (1-x, 1-y, 0), Tm"3 (½-x, ½+y, 0) and Tm"4 (½+x, ½-y, 0).

The diffraction patterns can be evaluated using the symmetry analysis (SA) method that is based on the theory of representation of space groups formulated by Bertaut [9] and Izymov et al. [10]. According to this formalism a magnetic structure given by **S** can be expressed in a coordinate system formed by the basis of irreducible representation of group G. The symmetry analysis reported in this work is based on a computer program basireps [11] which was used to calculate possible magnetic structure models.

Symmetry analysis shows for Pbam (No. 55) space group and propagation vector **k** = [0, ½, ½] that in each 4g sublattice the (x, y, 0) site stays coupled with the (1-x, 1-y, 0) one through the same basisvectors. The same is true for the (½-x, ½+y, 0) and (½+x, ½-y, 0) sites. Both the pairs are independent from each other. Also independent are the pairs belonging to different 4g sublattices. Magnetic moment components within one pair are of the same magnitude but can have either the same or opposite signs.

Numerical analysis of the neutron diffraction pattern measured at 1.5 K gives a complex noncollinear magnetic structure with magnetic moment lying in the a-b plane as presented in Fig. 4. Magnetic moments in each pair show ferromagnetic coupling and have

unique value and orientation as it is allowed by symmetry. The refined parameters of the structure are listed in Table 2.

In purpose to explain the nature of the magnetic susceptibility anomaly observed at 3.1 K and the heat capacity anomaly found at 3.95 K, additional neutron diffraction experiments were performed in limited angle ($15° < 2\theta < 45°$) and temperature ($2.90\ K < T < 4.24\ K$ with $\Delta T \approx 0.05\ K$) range (see Fig. 5). The data do not show any temperature-induced changes in the magnetic structure. The Néel temperature found from the neutron diffraction is close to 4.1 K.

4. Discussion

The compound $Tm_5Ni_2In_4$ crystallizes in the orthorhombic $Lu_5Ni_2In_4$-type structure. The atoms form a two-layered structure along the short c-axis. The first layer is composed of Tm atoms (monoatomic z = 0, 1) while the second one for z = ½ is built of Ni and In atoms. A decrease of the lattice parameters while going from para- (5.9 K) to antiferromagnetic (1.5 K) region is clearly noticeable and related to magnetostriction effect below the Néel temperature. Large values of Δa and Δb and very small one for Δc are in agreement with the proposed model of magnetic structure.

The magnetic susceptibility, specific heat and neutron diffraction data indicate that antiferromagnetic ordering exists below 4.1 K. A complex non-collinear magnetic structure has been determined from neutron diffraction data. The thulium magnetic moments are located at one 2a site and two separate 4g sites with different lattice parameters. The moments lie within the a-b plane and are coupled in five different pairs as allowed by symmetry analysis. Moments in each pair are coupled ferromagnetically and are characterized by their unique value and orientation.. The determined values of magnetic moments at different sites vary from 3.1(4) μ_B up to 7.5(5) μ_B at 1.5 K (see Table 2). The average Tm magnetic moment is of 5.4 μ_B .Magnetic structures with different values of magnetic moments at different sites are observed in other intermetallics, like isostructural $Er_5Ni_2In_4$ [6] or $R_5Rh_4Ge_{10}$ (R = Tb, Ho, Er) [12, 13] and $RIrGe_2$ (R = Tb, Ho) [14]. Large interatomic Tm-Tm distances (about 3.5 Å along the c-axis and 4.35 Å within the a-b plane) indicate indicate indirect magnetic interactions of the RKKY-type.

The deviation of inverse magnetic susceptibility from the Curie-Weiss law at low temperatures together with low value of Tm moment in the ordered state indicates influence of CEF. The average magnetic moment of 5.4 μ_B at 1.5 K, found from neutron diffraction, is

smaller then the free Tm^{3+} ion which equals 7.0 μ_B, however, it is still larger than the values found from magnetization measurements: 4.15 μ_B at B = 5 T and T = 1.72 K. The difference between magnetic moment derived from neutron diffraction and the one determined from magnetization measurements suggests that the full saturation has not been reached under external magnetic field of 5 T and temperature 1.72 K. The magnetic structure derived from neutron diffraction data (see Fig. 4) is a noncollinear one. Thus external magnetic field forces a reorientation of magnetic moments.

The magnetic susceptibility, magnetization and specific heat data revealed a fairly complex character of the ordered magnetic state that could not be accounted for by the neutron diffraction results. Interestingly, the double-peak character of the specific heat of $Tm_5Ni_2In_4$ is very similar to the behavior reported for $TmGa_3$ [15]. For the latter gallide, one maximum in C(T) was related to antiferromagnetic phase transition, while the other one was attributed to quadrupole ordering. A tempting possibility of quadrupolar order in $Tm_5Ni_2In_4$ will be a subject of our further experimental investigation of this interesting material.

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Figure captions

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of $Tm_5Ni_2In_4$. The solid line marks a Curie-Weiss behavior. The upper inset shows low temperature magnetic susceptibility. The lower inset displays the isothermal magnetization measured at 1.72 K with increasing (open symbols) and decreasing (filled symbols) magnetic field.

Fig. 2. Low-temperature dependence of the specific heat of $Tm_5Ni_2In_4$.

Fig. 3. Neutron diffraction patterns of $Tm_5Ni_2In_4$. (a) Data taken in paramagnetic state at T = 5.9 K. The squares represent experimental points. The solid lines are calculated profile of Bragg reflections and difference between the observed and calculated intensities (at the bottom of diagram). The vertical bars indicate the positions of nuclear peaks. (b) Differential neutron diffraction pattern of $Tm_5Ni_2In_4$ together with Rietveld fit and difference plot. The pattern was made as a difference between patterns collected at 1.5 and 5.9 K. The upper row of vertical ticks indicates the positions of nuclear reflections while the lower one indicates the positions of reflections originating from antiferromagnetic order.

Fig. 4. Magnetic unit cell of $Tm_5Ni_2In_4$. The adjacent (001) planes are coupled antiferromagnetically.

Fig. 5. Neutron diffraction patterns of $Tm_5Ni_2In_4$ collected in 2θ range from 15° to 45° at several temperatures between 2.90 and 4.24 K with temperature step of about 0.05 K.

Table 1. Refined crystal structure parameters of $Tm_5Ni_2In_4$ at 5.9 K with reliability factors. Standard deviations are given in parentheses.

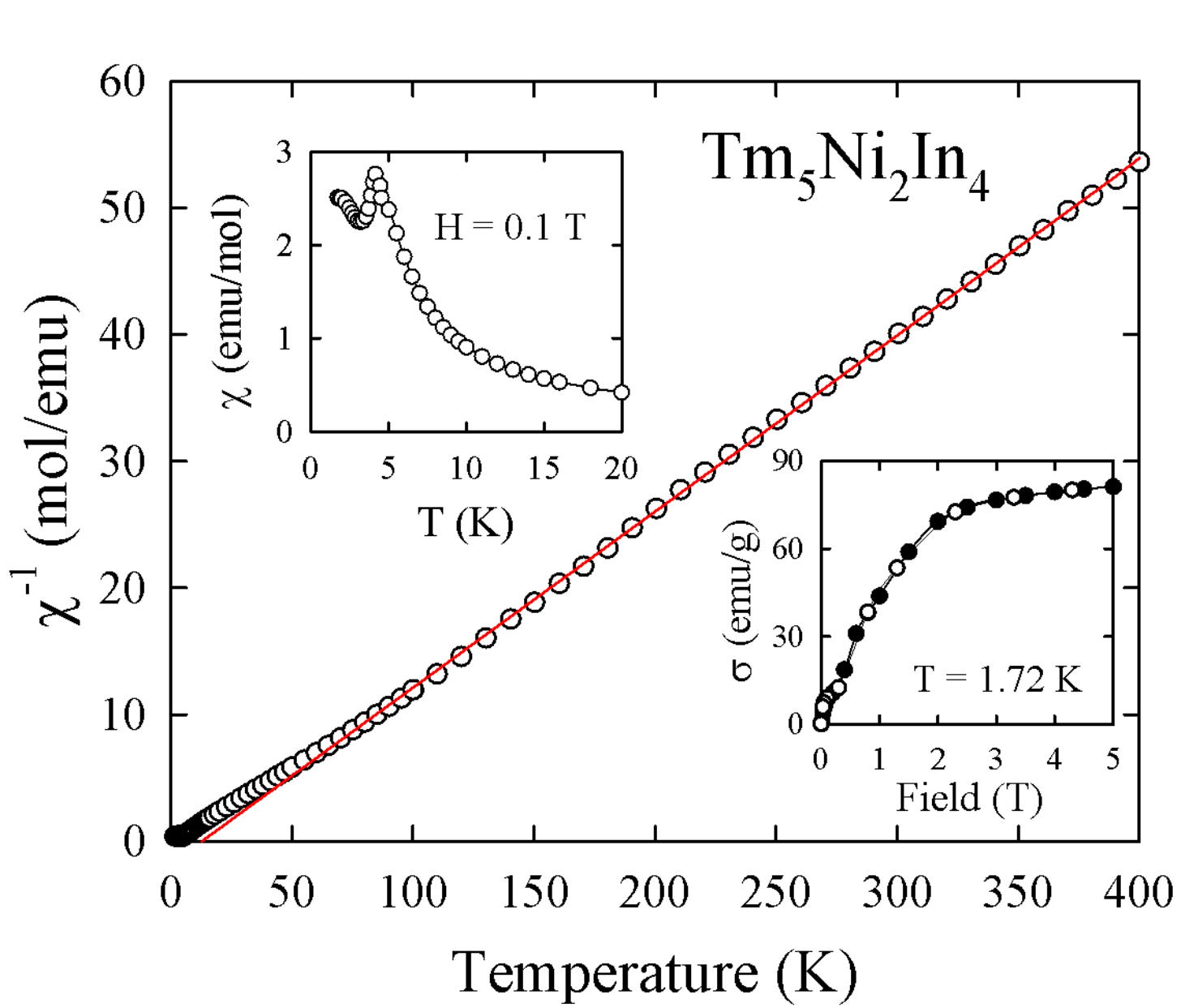
Unit cell parameters			
a[Å]	b[Å]	c[Å]	V[Å^3]
17.6404(27)	7.8093(16)	3.5412(5)	487.83(23)
Positional parameters (x, y, z)			
Tm (2a)	0	0	0
Tm' (4g)	0.2208(12)	0.2486(40)	0
Tm'' (4g)	0.4151(13)	0.1212(27)	0
Ni (4h)	0.3040(10)	0.0292(28)	0.5
In (4h)	0.5729(25)	0.2026(50)	0.5
In (4h)	0.8477(16)	0.0668(53)	0.5
Reliability factors			
R_{Bragg} [%]		7.41	
$R_{profile}$ [%]		2.78	
χ^2		1.26	

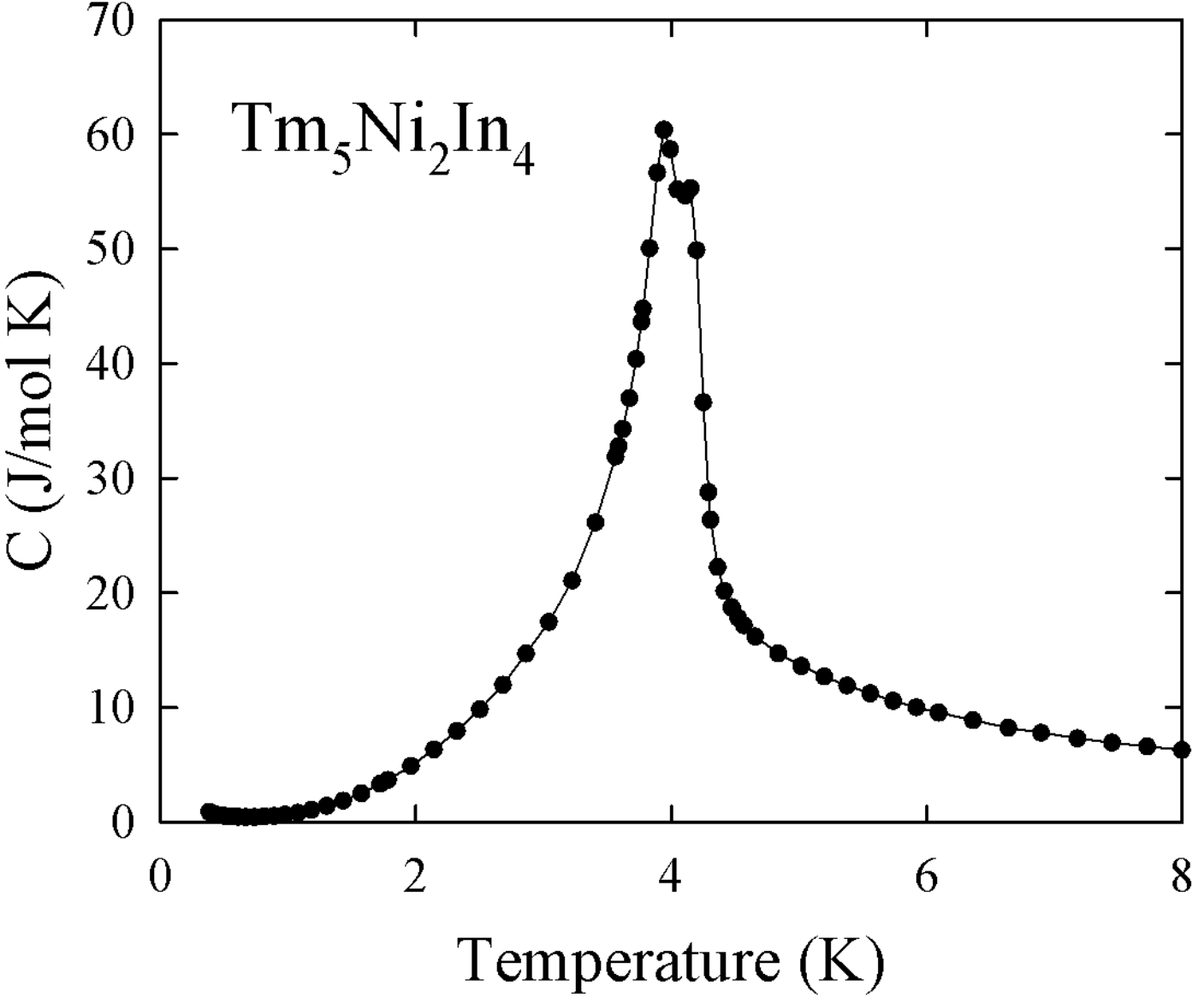
Table 2. Details of magnetic structure as refined from neutron diffraction pattern at 1.5 K. μ_i corresponds to the *i*-th component of magnetic moment while μ is a resultant moment. Thulium atoms indices corresponds with those used section 3.3. Standard deviations are given in parentheses.

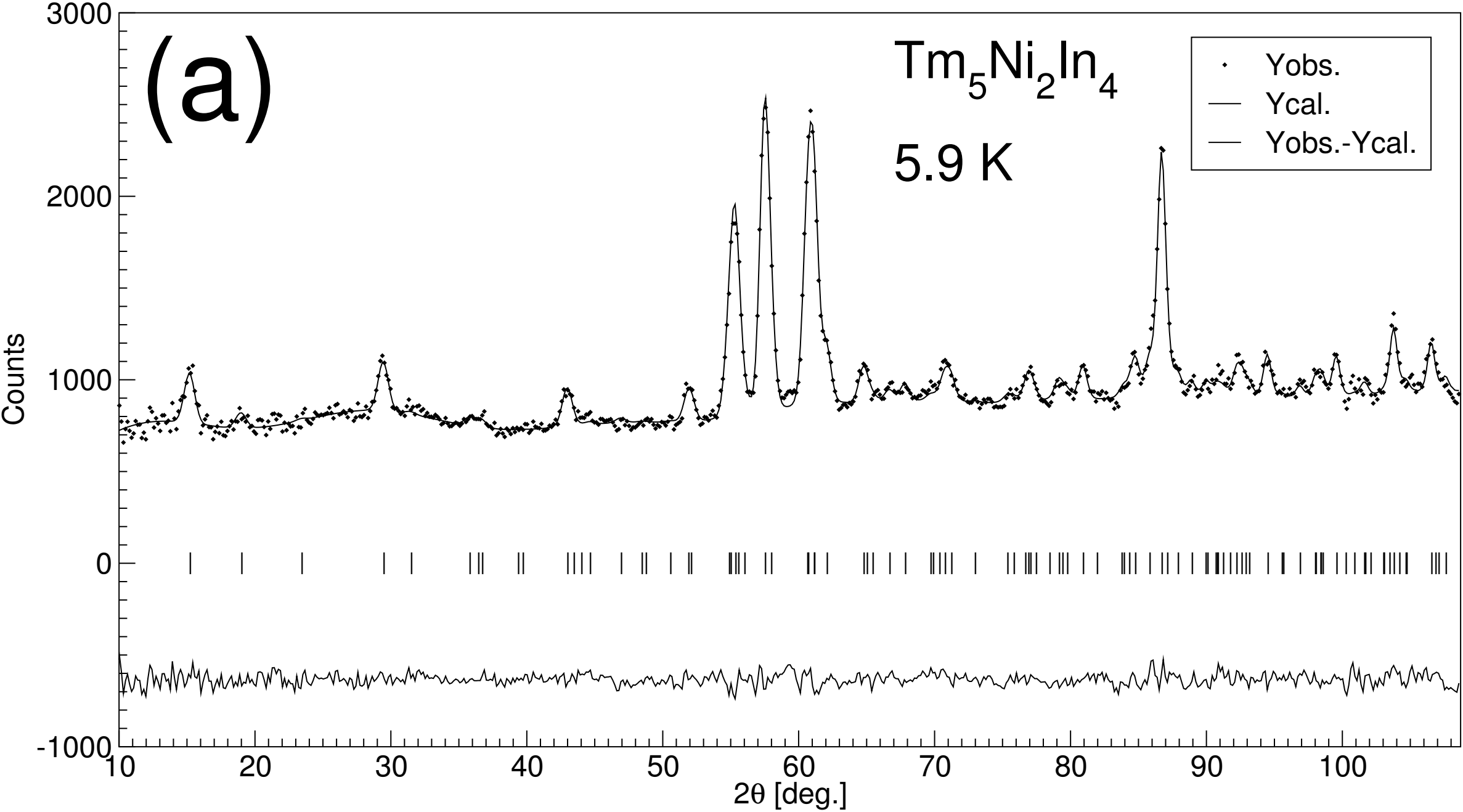
Temperature [K]	1.5			
Lattice parameters: a [Å]	17.6334(29)			
b[Å]	7.8027(18)			
c[Å]	3.5389(5)			
V[Å^3]	486.91(26)			
	μ_x [μ_B]	μ_y [μ_B]	μ_z [μ_B]	μ [μ_B]
Tm 2a: 1st sublattice				
Tm1	3.0(8)	6.7(4)	0	7.4(5)
Tm1	3.0(8)	6.7(4)	0	7.4(5)
Tm' 4g: 2nd sublattice				
Tm'1	6.7(5)	3.4(5)	0	7.5(5)
Tm'2	6.7(5)	3.4(5)	0	7.5(5)
Tm'3	-2.8(4)	1.6(4)	0	3.2(5)
Tm'4	-2.8(4)	1.6(4)	0	3.2(5)
Tm" 4g: 3rd sublattice				
Tm"1	-1.2(4)	2.8(4)	0	3.1(4)
Tm"2	-1.2(4)	2.8(4)	0	3.1(4)
Tm"3	-1.5(5)	-5.8(5)	0	6.0(4)
Tm"4	-1.5(5)	-5.8(5)	0	6.0(4)
R_{magn} [%]	7.38			
$R_{profile}$ [%]	4.23			
χ^2	2.97			

Table 3. Difference between lattice parameters ($\Delta a = a_{LT} - a_{RT}$) and unit cell volumes ($\Delta V = V_{LT} - V_{RT}$) measured at low temperatures (1.5, 2.9 and 5.9 K) and those found at room temperature.

T [K]	Δa [Å]	Δb [Å]	Δc [Å]	ΔV [Å^3]
5.88	- 0.0141(32)	- 0.0244(18)	+ 0.0007(6)	- 1.82(27)
2.90	- 0.0186(27)	- 0.0291(19)	- 0.0015(5)	- 2.44(20)
1.53	- 0.0211(34)	- 0.0310(20)	- 0.0016 (4)	- 2.74(30)


Tm5Ni2In4
χ-1 (mol/emu)
Temperature (K)
0
10
20
30
40
50
60
0
50
100
150
200
250
300
350
400
χ (emu/mol)
H = 0.1 T
T (K)
0
1
2
3
0
5
10
15
20
σ (emu/g)
T = 1.72 K
Field (T)
0
30
60
90
0
1
2
3
4
5


Tm5Ni2In4
C (J/mol K)
Temperature (K)
0
10
20
30
40
50
60
70
0
2
4
6
8


(a)
$Tm_5Ni_2In_4$
5.9 K
Yobs.
Ycal.
Yobs.-Ycal.
Counts
3000
2000
1000
0
-1000
10
20
30
40
50
60
70
80
90
100
2θ [deg.]

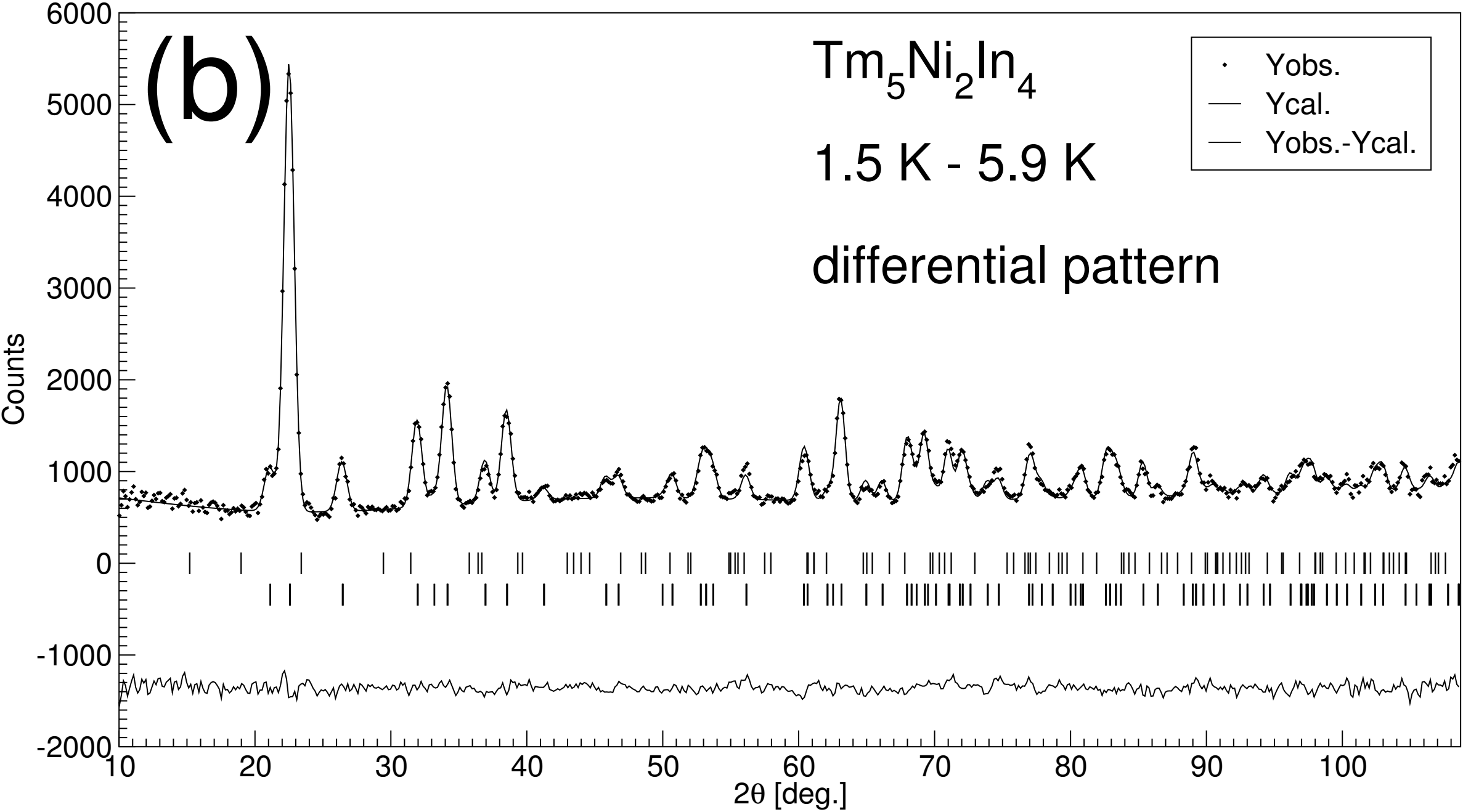
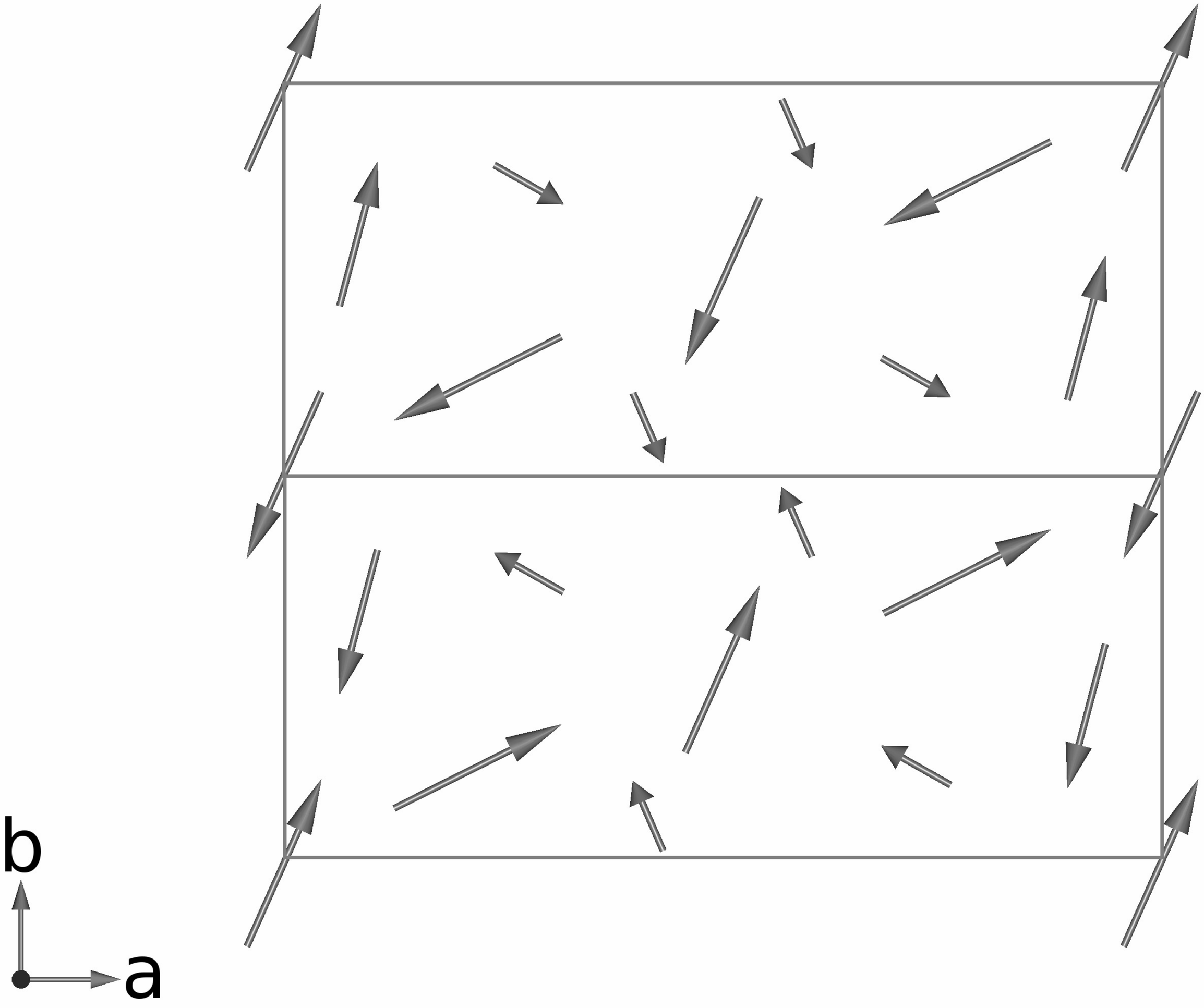
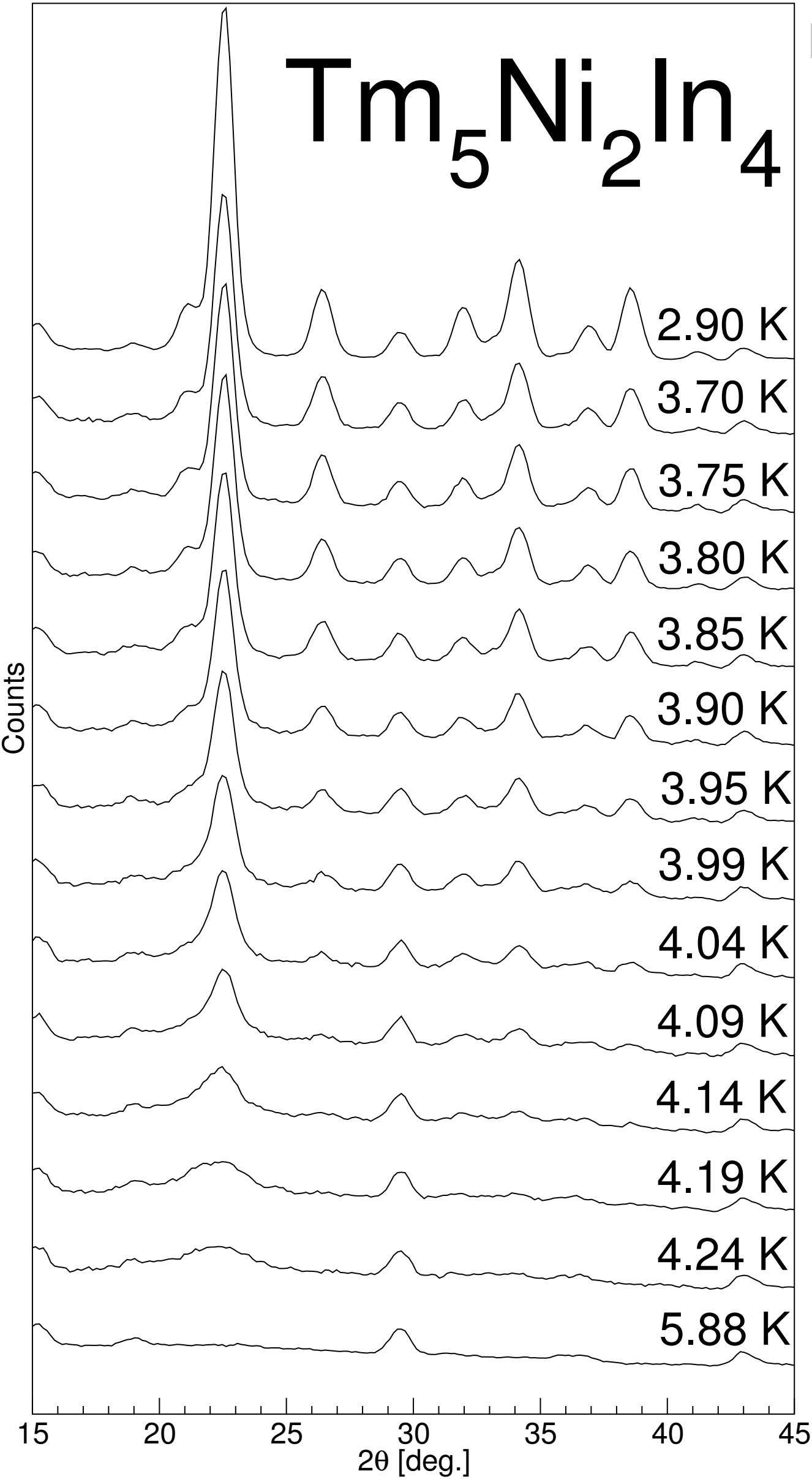

(b)
$Tm_5Ni_2In_4$
1.5 K - 5.9 K
differential pattern
Yobs.
Ycal.
Yobs.-Ycal.
Counts
2θ [deg.]
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10
20
30
40
50
60
70
80
90
100

Fig. 4




Tm5Ni2In4
2.90 K
3.70 K
3.75 K
3.80 K
3.85 K
3.90 K
3.95 K
3.99 K
4.04 K
4.09 K
4.14 K
4.19 K
4.24 K
5.88 K
Counts
15
20
25
30
35
40
45
2θ [deg.]

Highlights

[1] magnetic structure of $Tm_5Ni_2In_4$ is reported for the first time

[2] $Tm_5Ni_2In_4$ magnetic structure is verified by group theory symmetry analysis

[3] diffraction data are supported by magnetometric and calorimetric measurements