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Magnetic structure of the $YbMn_2SbBi$ compound

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ABSTRACT

A neutron diffraction investigation has been carried out on the trigonal La_2O_2S-type (hP5, space group $P\bar{3}ml$, No. 164; also $CaAl_2Si_2$-type) $YbMn_2SbBi$ intermetallic compound. The $YbMn_2SbBi$ presents antiferromagnetic ordering below 138(3) K and ferrimagnetic ordering below 112(3) K. Between 138 and 112 K, the magnetic structure of $YbMn_2SbBi$ consists of antiferromagnetically coupled *ab*-plane magnetic moments of the manganese atoms ($\mathbf{D_{1d}}$ magnetic point group). Below 112(3) K, the ferromagnetic components of Yb and Mn begin to develop, and the magnetic structure of $YbMn_2SbBi$ becames the sum antiferromagnetic component with $\mathbf{D_{1d}}$ magnetic point group and ferromagnetic one with $\mathbf{C_2}$ magnetic point group. The magnitude of Yb and Mn magnetic moments in $YbMn_2SbBi$ at 2 K ($M_{Yb} = 3.6(2)\ \mu_B$, $M_{Mn} = 3.5(2)\ \mu_B$) correspond to the trivalent state of the Yb ions and tetravalent state of the Mn ions.

1. Introduction

The existence of the $YbMn_2Sb_2$ compound, adopting the La_2O_2S-type structure (also called $CaAl_2Si_2$-type; *hP*5, Space group $P\bar{3}ml$, No. 164, $\mathbf{D_{3d}}$ ($\bar{3}2/m$) point group) was earlier reported by Ruhl and Jeitschko [1]: in this structure prototype the Yb atoms occupy the *1a* (0, 0, 0) special position, manganese atoms occupy the *2d* site (1/3, 2/3, Z_{Mn}) and antimony atoms occupy the *2d* site (1/3, 2/3, Z_{Sb}). The magnetic ordering (with a magnetic transition at about 120 K) and magnetic structure have been found for this compound in works [2,3]. The commensurate magnetic structure of $YbMn_2Sb_2$ ($\mathbf{C_i}$ magnetic point group, $P\bar{1}$ magnetic space group) consists of antiferromagnetically coupled manganese magnetic moments in the Mn1 [1/3, 2/3, Z_{Mn}] and Mn2 [2/3, 1/3, $-Z_{Mn}$] positions, the ytterbium magnetic moment is zero. At 4 K, the magnetic moment of the Mn atom is $\mu_{Mn} = 3.6(1)\ \mu_B$ [3] that corresponds to the tetravalet state of manganese in $YbMn_2Sb_2$ ($M^{Mn4+} = 4\ \mu_B$ [4]).

The substitution of Sb for Bi in $YbMn_2Sb_2$ compound leads to the formation of the $YbMn_2SbBi$ solid solution with changes in interatomic distances and considerable changes in the magnetic parameters. Hence, to determine the type of magnetic ordering and the magnetic structure of $YbMn_2SbBi$, neutron diffraction study was carried out and the results are presented here.

2. Synthesis and experimental details

Commercial ytterbium (pieces cut from ingot, with purity 99.9 wt.%), manganese (small grains from a platelet previously surface-cleaned by conc. HNO_3, with purity 99.99 wt.%), antimony (grains, with 99.999 wt.% purity) and bismuth (grains, with 99.999 wt.% purity), were used as the starting components. After few preparations were firstly attempted in an arc-furnace, and due to the fact that preparation of such a kind of samples by arc melting leads to a non-negligible weight loss (i.e.: as it generally happens for melting and annealing high-melting compounds containing one or more volatile metals), a new synthesis method has also been attempted, also. Even being more laborious technique (since it is a two-step procedure), and requiring sealed containers, it has been successfully employed to prepare a large and single-phase sample (total weight of about 9 g) and utilised in the present work. As a first step, the equiatomic binary alloy Mn_2SbBi has been prepared by induction melting of the elements in outgassed Ta crucibles, closed by welding under pure Ar, by heating up to 1250–1300 °C; manganese antimonide forms by nearly congruent melting, besides, its formation temperature (840 °C) is relatively low: much lower than that of the melting point of Mn metal (1246 °C) [5]. In the second step, Yb and Mn_2SbBi have been mixed in the stoichiometric amounts, sealed again under Ar into an outgassed Ta crucible, and reacted by induction heating up to about 1300 °C. The crucibles were then sealed under vacuum in quartz tubes and annealed in a resistance furnace at 800 °C for 7 days; after annealing, they were air cooled. Preparation of Mn_2SbBi inside a Ta crucible has proved not to give rise to pollution contamination due to reaction towards the container material, as well as no Ta contamination in the final $YbMn_2SbBi$ was noticed.

X-ray powder patterns were obtained either by a Guinier–Stoe camera (Cu Kα radiation, pure Si as an internal standard: $a = 0.54308$ nm), or on a diffractometer DRON-3 (Cu Kα radiation, $2\Theta = 20$–$70°$, 0.05° step, 6 s/step). The Guinier patterns were indexed with the help of the Lazy-Pulverix program [6], the lattice parameters were calculated by least squares method.

The neutron diffraction investigation was carried out from 150 K to 2 K in zero applied field at the Institute Laue-Langevin, Grenoble, France (on the powder D1B diffractometer, wavelength $\lambda = 0.252$ nm) [7]. The diffraction patterns were indexed, and the calculations performed, by using the Fullprof-program [8].

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Table 1
Interatomic distances $D \pm 5 \times 10^{-4}$ nm and then ratio to sum of the atomic radii [9] of corresponding atom $\Delta = D/(R_{atom1} + R_{atom2})$ for atoms in La_2O_2S-type compounds at 300 K: $YbMn_2Sb_2$ ($a = 0.4528$ nm, $c = 0.7448$ nm, $Z_{Mn} = 0.629$, $Z_{Sb} = 0.251$) and $YbMn_2SbBi$ ($a = 0.45493$ nm, $c = 0.7475$ nm, $Z_{Mn} = 0.615$, $Z_X = 0.250$).

Atoms	D (nm)	Δ
(a) $YbMn_2Sb_2$		
Yb–6Sb	0.3214	1.01
–6Mn	0.3804[b]	1.24
–6Yb	0.4528	1.30
Mn–3Sb	0.2763	0.99
–1Sb	0.2815	1.01
–3Mn	0.3244[c]	1.22
–3Yb	0.3804[b]	1.24
–6Mn	0.4528[d]	1.70
Sb–3Mn	0.2763	0.99
–1Mn	0.2815	1.01
–3Yb	0.3214	1.01
(b) $YbMn_2SbBi$		
Yb–6X[a]	0.3223	1.00
–6Mn	0.3896[b]	1.27
–6Yb	0.4549	1.31
Mn–1X	0.2728	0.96
–3X	0.2814	1.00
–3Mn	0.3139[c]	1.18
–3Yb	0.3896[b]	1.27
–6Mn	0.4549[d]	1.70
X–1Mn	0.2728	0.96
–3Mn	0.2814	1.00
–3Yb	0.3223	1.00

[a] $X = Sb_{0.5}Bi_{0.5}$.
[b] Yb–$Mn_{1,2}$ distance.
[c] Mn_1–Mn_2 distance.
[d] Mn_1–Mn_1 (Mn_2–Mn_2) distance.

3. Results and discussion

The substitution of Sb for Bi in $YbMn_2Sb_2$ compound leads to changes in cell parameters and interatomic Yb–$Mn_{1,2}$, Mn_1–Mn_1 (Mn_2–Mn_2) and Mn_1–Mn_2 distances: $a = 0.4528$ nm, $c = 0.7448$ nm, $Z_{Mn} = 0.629$, $Z_{Sb} = 0.251$ in $YbMn_2Sb_2$ and $a = 0.45493$ nm, $c = 0.7475$ nm, $Z_{Mn} = 0.615$, $Z_X = 0.250$ in $YbMn_2SbBi$ (Table 1). The ratio of shortest interatomic distances to sum of the atomic radii of Yb, Mn, Sb and Bi atom $\Delta = D/(R_{atom1} + R_{atom2})$ corresponds to the metallic nature of bond and trivalet state of Yb in the $YbMn_2Sb_2$ and $YbMn_2SbBi$ ($R_{Yb}^{III} = 0.1740$ nm, $R_{Mn} = 0.1334$ nm, $R_{Sb} = 0.1451$ nm, $R_{Bi} = 0.1537$ nm [9]), The Mn_1–Mn_2 distances decreases from $YbMn_2Sb_2$ to $YbMn_2SbBi$ with distortion of Mn coordination polyhedron.

In general, the symmetry operation of $\mathbf{D_{3d}}$ ($\bar{3}2/m$) point group includes $\mathbf{S_6}$ ($\bar{3}$), $\mathbf{D_3}$ (**32**), $\mathbf{C_{3v}}$ (**3m**) subgroups of index 2, $\mathbf{D_{1d}}$ (**2/m**) subgroup of index 3, $\mathbf{C_3}$ (**3**) subgroup of index 4 and $\mathbf{C_{1v}}$ (**m**), $\mathbf{C_i}$ (**1′**) and $\mathbf{C_2}$ (**2**) subgroups of index 6 [10]. The possible magnetic point groups for the $\mathbf{D_{3d}}$ ($\bar{3}2/m$) point group are above-mentioned "colourless" point groups and "black–white" (Shubnikov) {$\mathbf{S_6}$, $2_x \times \mathbf{S_6} \times 1'$}, {$\mathbf{D_3}$, $m_x \times \mathbf{D_3} \times 1'$} and {$\mathbf{C_{3v}}$, $2_x \times \mathbf{C_{3v}} \times 1'$}. The magnetic structure of the La_2O_2S-type compound was determined in terms of the symmetry of above-mentioned magnetic point groups.

The evolution of the magnetic order upon cooling shows the development of commensurate magnetic reflections with wave vector $\mathbf{K_0} = [0, 0, 0]$ in the $YbMn_2SbBi$ neutron diffraction patterns (Fig. 1). Thermal variation of magnetic reflections shows the magnetic ordering below ~138 K (Fig. 2a). Analysis of the diffraction data shows that between 138 and 112 K, the magnetic structure of $YbMn_2SbBi$ consists of *ab*-plane antiferromagnetically coupled magnetic moments of the manganese atoms that normal to *a* axis ($\mathbf{D_{1d}}$ magnetic point group, **P2/m** magnetic space group, $\mathbf{AF}^{K0}$ ($\mathbf{D_{1d}}$) antiferromagnetic component) (Fig. 3a). Below

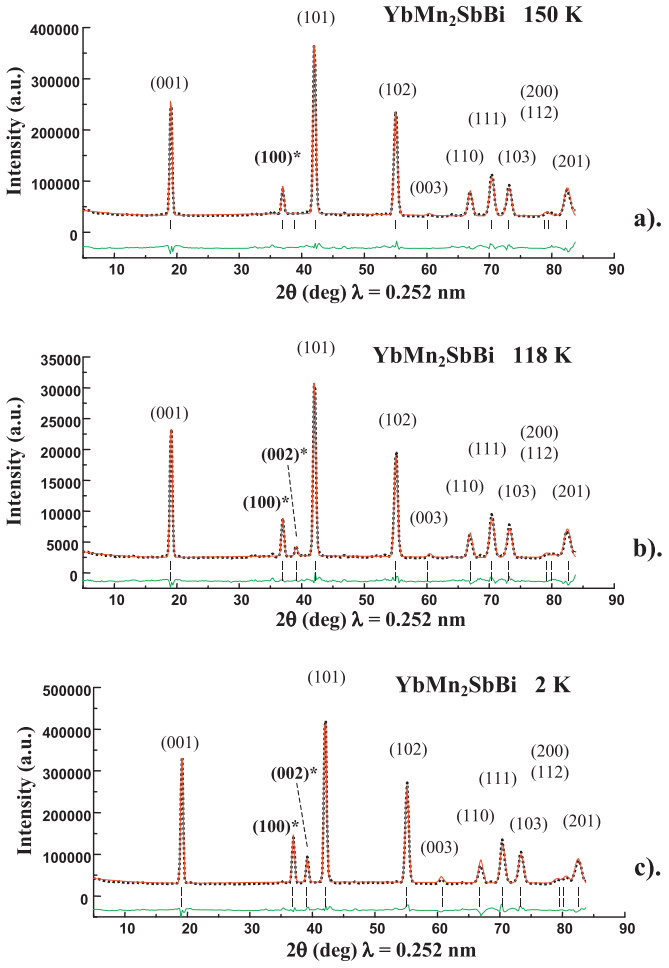

Fig. 1. Neutron diffraction pattern of $YbMn_2SbBi$ at 150 K (paramagnetic) (a), 118 K (antiferromagnet) (b) and 2 K (ferrimagnet) (c). *Thermal evaluation of reflection is given in Fig. 2a.

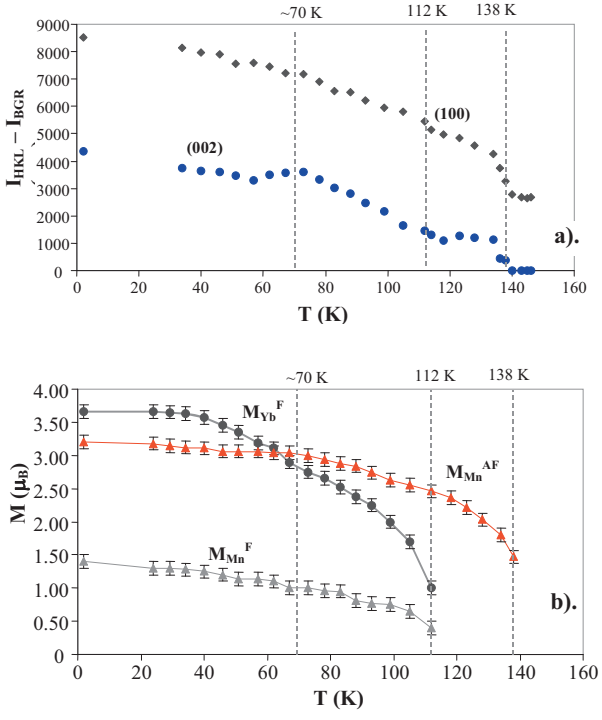

Fig. 2. Thermal evaluation of some reflections (a) and Yb and Mn magnetic components (b) of the $YbMn_2SbBi$.

Table 2
Crystallographic and magnetic parameters of La_2O_2S-type $YbMn_2SbBi$ compound at different temperatures T: the temperatures of magnetic ordering $T_{N,C}$, cell parameters a, c, atomic position parameters Z_{Mn} and Z_X, ferromagnetic and antiferromagnetic component M_j^F and M_j^{AF} of the j atom (Yb, Mn1[a] and Mn2), φ_j^{AF} and φ_j^F are the angles of corresponding magnetic component with a axis. The magnetic moments lie in the ab plane: the θ angle of all magnetic components with c axis is 90°. Reliability factors R_F (crystal structure) and R_F^m (magnetic structure) are given in percent (%).

$T_{N,C}$	Magnetic ordering	T (K)	Unit cell data	R_F	Atom	M_j^F (μ_B)	φ_j^F (°)	M_j^{AF} (μ_B)	φ_j^{AF} (°)	R_F^m
	Paramagnet	150	a = 0.45493(6) nm c = 0.7475(2) nm Z_{Mn} = 0.615(2) Z_X = 0.250(2)	5.2						
T_N^{ND} = 138(3) K	Antiferromagnet **AF^{K0} (D_{1d})**	118	a = 0.45493(6) nm c = 0.7464(2) nm Z_{Mn} = 0.615(2) Z_X = 0.249(2)	4.5	Yb Mn1 Mn2			0 2.2(1) 2.2(1)	 270 90	7.3
T_C^{ND} = 112(3) K	Ferrimagnet **AF^{K0} (D_{1d}) + F$_a^{K0}$ (C_2)**	2	a = 0.45490(5) nm c = 0.7448(2) nm Z_{Mn} = 0.597(4) Z_X = 0.236(2)	4.5	Yb Mn1 Mn2	3.6(3) 1.4(2) 1.4(2)	0 0 0	 3.2(2) 3.2(2)	 270 90	6.9

[a] Mn1 occupy (1/3, 2/3, X_{Mn}) site and Mn2 occupy (2/3, 1/3, $-X_{Mn}$) site in the La_2O_2S-type unit cell.

112(3) K, the ferromagnetic components of Yb and Mn begin to develop, and the ferromagnetic transition occurs with resulting non-collinear arrangements of magnetic moments in the ab plane (Fig. 3b). The magnetic structure of $YbMn_2SbBi$ becames the sum antiferromagnetic component **AF^{K0} (D_{1d})** and ferromagnetic one with **C_2** magnetic point group (**F$_a^{K0}$ (C_2)**). The crystallographic data and magnetic parameters of $YbMn_2SbBi$ are given in Table 2. The maximum of the $I_{(002)}$ intensity near ~70 K (Fig. 2a) occurs when ferromagnetic component of $YbMn_2SbBi$ became bigger than antiferromagnetic one (Fig. 2b). The magnitude of Yb and Mn magnetic moments at 2 K (M_{Yb} = 3.6(2) μ_B, M_{Mn} = 3.5(2) μ_B) correspond to the trivalent state of the Yb ions (M_{Yb3+} = 4.0 μ_B) and tetravalent state of the Mn ions (M_{Mn4+} = 4.0 μ_B) [4].

In general, the evaluation of magnetic ordering of $YbMn_2SbBi$ is following: paramagnet (symmetry **D_{3d}** point group, **$P\bar{3}ml$** space group) → Antiferromagnet (symmetry **D_{1d}**, **P2/m**) → Ferrimagnet (symmetry **C_2**, **P2**). The $YbMn_2Sb_2$ shows evaluation of magnetic ordering: paramagnet (symmetry **D_{3d}** point group, **$P\bar{3}ml$** space group) → Antiferromagnet (symmetry **D_{1d}** ore **C_i** magnetic points group) [3]. So, the presence of Bi in the p-element mixed sublattice (Sb and Bi) facilitates the ferromagnetic ordering of La_2O_2S-type compound.

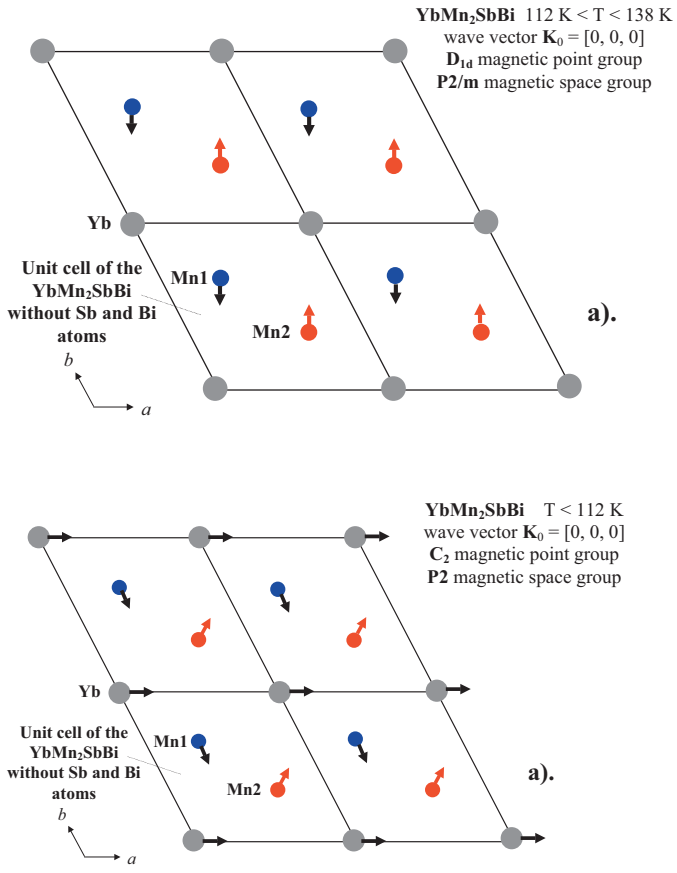

Fig. 3. Magnetic structure of the $YbMn_2SbBi$ compound between 138 and 112 K (a) and below 112 K (b).

4. Conclusion

The applied magnetic fields may play a role in shifting the magnetic transition temperature as it happens in the $YbMn_2Sb_2$ compound. In the known homologous compound $EuMn_2Sb_2$ [11], though the magnetic moments of the Mn-atoms sublattice might order antiferromagnetically, the overall magnetic structure could however be much more complicated, due to the possible ordering of the Eu-sublattice.

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