

Crystal Structure and Magnetic Structure of TbOOH

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The monoclinic modification of terbium oxide hydroxide, TbOOH, was prepared using hydrothermal technique. The crystal structure was investigated by three-dimensional single-crystal X-ray analysis and was refined to a conventional *R*-value of 8.1%. The space group is $P2_1/m$, No. 11, with $a = 6.04 \text{ \AA}$, $b = 3.69 \text{ \AA}$, $c = 4.33 \text{ \AA}$, and $\beta = 109.0^\circ$. The terbium atom is seven coordinated with oxygen atoms, and the structure is not hydrogen bonded.

The compound is antiferromagnetic with a Néel temperature of 10°K . Neutron diffraction powder patterns were measured at 300°K and 4.2°K . The magnetic super lattice reflections were indexed on the basis of a monoclinic unit cell with the dimensions $a_M = 2a$, $b_M = b$, $c_M = c$, and $\beta_M = \beta$, where a , b , c , and β are the dimensions of the chemical unit cell. The structure contains two independent magnetic atoms. A noncolinear antiferromagnetic arrangement of the spins describes the magnetic structure. The spin at one atom has an angle of 43° with the ac plane and the projection of the spin on the ac plane has an angle of 59° with the a axis. The spin on the other atom has an angle of -43° with the ac plane, the projection having the same angle of 59° with the a axis.

The monoclinic modification of terbium oxide hydroxide, TbOOH, is antiferromagnetic with a Néel temperature of 10°K , and shows metamagnetic properties at 4.2°K (1). The compound has the yttrium oxide hydroxide structure with space group $P2_1/m$ and two formula units in the cell (2, 3). A single crystal X-ray diffraction investigation of the crystal structure and a neutron diffraction investigation of the magnetic structure is reported below.

Experimental

Chemistry

Terbium oxide hydroxide was prepared from Tb_4O_7 . Fifteen grams of Tb_4O_7 were placed in two platinum boats in a quartz tube and were treated with hydrogen at 800°C for 20 hr. A Guinier powder pattern of the white product showed only lines from the cubic modification of terbium

oxide, Tb_2O_3 . This compound was treated hydrothermally with 100 ml 2 *M* NaOH in a pressure bomb lined with pure gold at 615°C , 750 atm for 108 hr. A Guinier powder pattern of the product confirmed that it was pure monoclinic terbium oxide hydroxide.

X-Ray Technique

The crystal sample used in the X-ray investigation was from a previous preparation (1). A flat crystal with dimensions $0.0008 \times 0.031 \times 0.015 \text{ cm}$ was used. A total of 374 independent hkl reflections with $I > 2\sigma(I)$ were measured with a Picker diffractometer using $\text{MoK}\alpha$ radiation monochromated by reflection from a graphite crystal and using a scintillation counter in conjunction with a pulse height analyzer. Lorentz polarization corrections were applied and absorption correction was made using Well's method (4).

TABLE I
ATOMIC COORDINATES AND TEMPERATURE FACTOR
COEFFICIENTS^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²)
Tb	0.1899 (2)	1/4	0.3320 (3)	<i>b</i>
O (1)	0.048 (3)	1/4	0.771 (4)	0.1 (2)
O (2)	0.563 (4)	1/4	0.746 (5)	0.5 (3)
H	0.6 (1)	1/4	0.9 (1)	2 (1)

^a X-ray data, $R = 8.1\%$. Standard deviations in parentheses.

^b Anisotropic temperature factor parameters of the terbium atom with standard deviations ($\times 10^5$).

u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{13}	σu_{13}
184	46	122	65	160	52	-46	285

Neutron Technique

Neutron diffraction powder patterns were measured at 300°K and 4.2°K by a neutron diffractometer at Centre d'Études Nucleaires, Grenoble, using 1.11 Å neutrons. The sample was placed in a 15-mm diameter vanadium container. Lorentz correction was applied, $LP(\theta) = 1/\sin \theta \sin 2\theta$. The magnetic reflections were indexed

using a monoclinic cell with $a_M = 2a$, $b_M = b$, $c_M = c$, and $\beta_M = \beta$.

Crystal Data and Structure Refinement

X-Ray data. Terbium oxide hydroxide is monoclinic with space group $P2_1/m$, No. 11, with $a = 6.04 \text{ \AA}$, $b = 3.69 \text{ \AA}$, $c = 4.33 \text{ \AA}$, and $\beta = 109.0^\circ$. All atoms occupy site e , and the unit cell contains two formula units. The absorption coefficient for Mo-radiation is 391 cm^{-1} . Using the atomic coordinates and isotropic temperature factor coefficients from the crystal structure of YOOH (2, 3) as initial values of the parameters, the structure was refined to a conventional R -value of 8.1 %. The least squares program LINUS (5) was applied. Atomic scattering factors calculated from numerical Hartree-Fock wave functions by Cromer and Mann (6) were used in the structure factor calculations. Final atomic coordinates and temperature factor coefficients are listed in Table I, and observed and calculated structure factors are listed in Table II. Interatomic distances and bond angles are in Table III.

Neutron data. The intensities of the nuclear reflections listed in Table IV were used in a refinement of the atomic coordinates. The program D445 was applied (7). The atomic

TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS OF $TbOOH$

^a X-ray data, $R = 8.1\%$. Reading from left to right, the columns contain the values $h, k, l, 10 \times F_{\text{obs}}$, $10 \times F_{\text{calc}}$.

TABLE III

INTERATOMIC DISTANCES IN Å, BOND ANGLES IN DEGREES, STANDARD DEVIATIONS IN PARENTHESES

Tb—O (1)	2.33 (2)
Tb—O (1')	2.29 (1)
Tb—O (1'')	2.30 (2)
Tb—O (2)	2.38 (2)
Tb—O (2')	2.47 (2)
H—O (2)	0.96 (5)
O (1)—Tb—O (2)	84.0 (8)
O (2)—Tb—O (1')	137.1 (8)
O (1'')—Tb—O (1)	138.9 (6)
O (2)—Tb—O (2')	68.7 (6)
O (2')—Tb—O (2'')	96.9 (7)
O (2'')—Tb—O (1')	83.7 (6)
O (1)—Tb—O (1'')	77.5 (5)
O (1'')—Tb—O (1'')	107.4 (5)
O (1'')—Tb—O (1')	78.4 (5)

scattering lengths of Tb, O, and H were 0.76, 0.577, and $-0.378 (\times 10^{-12} \text{ cm})$, respectively (8). The resulting atomic coordinates are listed in Table V, and the calculated intensities are in Table IV. The *R*-value calculated from the intensities is 8.9%.

Magnetic Structure

Terbium oxide hydroxide is antiferromagnetic and the magnetic unit cell is twice the chemical unit cell. The magnetic structure is determined using the method developed by Bertaut (9). Magnetic reflections hkl are present for $h = 2n$ and for $h = 2n + 1$. The magnetic cell contains four magnetic atoms with the coordinates listed in Table VI. For one set of spins the combinations are:

$$\mathbf{F} = \mathbf{S}_1 + \mathbf{S}_2 \quad \text{and} \quad \mathbf{S}_3 + \mathbf{S}_4,$$

and

$$\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2 \quad \text{and} \quad \mathbf{S}_3 - \mathbf{S}_4,$$

\mathbf{S}_1 and \mathbf{S}_3 , \mathbf{S}_2 and \mathbf{S}_4 are

deducing each other by a $[\frac{1}{2}00]$ translation.

The irreducible representations Γ for the components of \mathbf{F} and \mathbf{A} are (10)

$$\begin{aligned} \Gamma_{1+} & \mathbf{F}_y \\ \Gamma_{2+} & \mathbf{A}_x \mathbf{A}_z \\ \Gamma_{1-} & \mathbf{F}_x \mathbf{F}_z \\ \Gamma_{2-} & \mathbf{A}_y \end{aligned}$$

and are the same for $\mathbf{k} = [000]$ and $\mathbf{k} = [\frac{1}{2}00]$.

In a spin Hamiltonian of order two approximation, one can have some coupling between

TABLE IV

OBSERVED AND CALCULATED NUCLEAR INTENSITIES ON ABSOLUTE SCALE, $\lambda = 1.11 \text{ \AA}$

h	k	l	θ	I_0	I_c	$\sum I_c$
1	0	0	5.57	2.10	1.76	1.76
0	0	1	7.78		3.97	
				9.70		8.64
1	0	-1	7.97		4.67	
1	1	0	10.31	9.79	13.48	13.48
1	0	1	10.99	0.62	1.94	1.94
0	1	1	11.67		4.70	
				5.54		6.03
1	1	-1	11.80		1.33	
2	1	0	14.21		11.18	
				18.68		20.32
2	1	-1	14.36		9.14	
1	0	-2	14.85	4.09	3.14	3.14
2	0	1	15.69		14.13	
				39.66 ^a		29.05
0	0	2	15.72		14.92	
2	0	-2	16.09		9.11	
				11.29		10.05
3	0	-1	16.16		0.97	
3	0	0	16.93	0.70	0.66	0.66
1	1	-2	17.28		6.18	
0	2	0	17.49		18.78	
2	1	1	18.03		34.72	
0	1	2	18.04		19.13	
				144.74		153.12
2	1	-2	18.38		39.31	
1	2	0	18.41		3.01	
1	0	2	18.43		6.53	
3	1	-1	18.44		25.45	
3	1	0	19.13		4.56	
0	2	1	19.25	21.10	6.97	19.81
1	2	-1	19.33		8.28	

^a Not included in the *R*-value calculation.

TABLE V

ATOMIC COORDINATES IN TERBIUM OXIDE HYDROXIDE, NEUTRON DATA

Atom	x	y	z
Tb	0.2195	1/4	0.3773
O (1)	0.0546	1/4	0.7804
O (2)	0.5978	1/4	0.7840
H	0.6413	1/4	0.9756

TABLE VI

ATOMIC COORDINATES AND SPINS OF THE FOUR TERBIUM ATOMS IN THE MAGNETIC CELL

Atom No.	<i>x</i>	<i>y</i>	<i>z</i>	Spin
1	0.0949	1/4	0.3322	S_1
2	-0.0949	3/4	-0.3322	$-S_1$
3	0.5949	1/4	0.3322	S_3
4	-0.5949	3/4	-0.3322	$-S_3$

modes only when they belong to the same representation. Two propagation vectors are necessary to explain the presence of all the magnetic reflections; the first vector $\mathbf{k} = [000]$ explains magnetic reflections hkl with $h = 2n$ and propagates the magnetic spin component in the ac plane: the (010) peak is very strong so a $A_x A_z$ mode is present belonging to Γ_{2+} .

In order to have spins of equal magnitude on equivalent atoms, it is necessary that the components of spins belonging to the two propagation vectors are perpendicular. Consequently,

TABLE VII

OBSERVED AND CALCULATED MAGNETIC INTENSITIES ON ABSOLUTE SCALE^a

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	f_{Tb}^{3+}	I_{obs}	I_{calc}	I_{calc}	I_{calc}
						$\psi = 39$	$\psi = 39$	$\psi = 43$
						$\phi = 53$	$\phi = 165$	$\phi = 59$
1	0	0	11.422	0.9683	16.20	18.12	18.22	21.30
2	0	0	5.711	0.9101	32.99	22.25	22.37	26.06
1	0	-1	4.327	0.8612	76.77	50.74	51.03	59.66
0	0	1	4.094	0.8450	21.07	29.43	54.57	13.68
2	0	-1	4.001	0.8391	44.01	65.08	14.05	36.92
3	0	0	3.807	0.8263	46.74	134.16	47.00	54.96
0	1	0	3.690	0.8172	73.97	120.71	74.38	65.58
1	1	0	3.511	0.7992	6.15	23.04	6.18	7.23
1	0	1	3.508	0.7992	9.47	9.47	19.44	11.13
3	0	-1	3.393	0.7700	3.82	13.82	3.84	4.49
2	1	0	3.099	0.7569	15.87	14.91	14.99	13.71
2	0	1	2.909	0.7300	0.02	0.02	1.10	0.00
4	0	0	2.855	0.7225	9.64	14.62	9.70	11.29
4	0	-1	2.810	0.7100	5.31	15.22	0.07	4.93
1	1	-1	2.808	0.7100	0.25	21.82	0.26	0.30
0	1	1	2.741	0.7048	66.28	49.34	29.81	18.17
2	1	-1	2.712	0.7006	49.34	73.01	34.40	66.08
3	1	0	2.650	0.6906	1.85	1.85	1.87	2.18
1	1	1	2.543	0.6692	33.38	39.13	33.56	39.25
3	1	-1	2.498	0.6642	102.19	89.54	39.35	90.04
3	0	1	2.422	0.6464	17.03	17.03	17.13	20.03
5	0	-1	2.346	0.6273	22.81	43.02	22.94	26.82
2	1	1	2.285	0.6115	43.02	194.39	105.53	37.02
5	0	0	2.284	0.6115	171.88	0.93	200.02	1.09
4	1	0	2.258	0.6060	33.07	33.07	33.26	32.55
4	1	-1	2.236	0.6006	94.56	94.56	37.56	86.30
						$R = 19.73\%$	$R = 20.30\%$	$R = 12.65\%$
						$\mu_B = 8.02$	$\mu_B = 8.04$	$\mu_B = 8.02$

^a The intensities are obtained as differences between diagrams taken at 4.2°K and 300°K. $\lambda = 1.11$ Å.

for the second wave vector $\mathbf{k} = [\frac{1}{2}00]$, the spins must be perpendicular to those of the first \mathbf{k} vector, either along the b axis, or in the ac plane (Γ_{2+}). In this way, two possibilities for the spins arrangement are possible: A_z , or A_xA_z . The A_xA_z mode can be ruled out by the intensity calculations and point symmetry considerations.

The intensities of the magnetic reflections are: for $h = 2n$ [$\mathbf{k} = 000$], $I_M = 0.27^2 pf^2 4aI^2 S^2 \cos^2 \psi \{1 - (d^2/\sin^2 \beta) [\sin(\beta - \phi)h/a + \sin \phi l/c]^2\}$, and for $h = 2n + 1$ [$\mathbf{k} = \frac{1}{2}00$], $I_M = 0.27^2 pf^2 4aI^2 S^2 \times \sin^2 \psi [1 - (d^2 k^2/b^2)]$, where p = the multiplicity of the reflection, f = the magnetic form factor of Tb^{3+} (II), $aI = 2i \sin 2\pi(hx + k/4 + lz)_1$ (coordinates of atom No. 1 of Table VI), ψ = the angle between the spin at atom No. 1 and the ac plane, ϕ = the angle between the projection of that spin on the ac plane and the a axis, d = the interplanar spacing in Å, and S = the magnetic moment in μ_B units.

For $\mathbf{k} = [000]$ the strong (200) reflection and the weak (001) reflection corresponds to a ϕ angle of approximately 60° .

For $\mathbf{k} = [\frac{1}{2}00]$ the magnitude of the intensity of the reflections (100), (300), and (10 \bar{l}) suggests that the spin has a large component along the b axis.

Using the observed intensities of the reflections (10 \bar{l}) or (300) and (010), $\psi = 39^\circ$ is calculated, and using the observed intensities of the reflections (200) and (10 \bar{l}), $\phi = 53^\circ$ or $\phi = 165^\circ$ is found. For the two models $\psi = 39^\circ$, $\phi = 53^\circ$, and $\psi = 39^\circ$, $\phi = 165^\circ$, only reflections with $h = 2n$ and $l \neq 0$ will be different. The intensities calculated for the two models are listed in Table VII. The model with $\phi = 165^\circ$ can be ruled out. The maximum of the powder line including the reflections (001) and (20 \bar{l}) is at the position of the (20 \bar{l}) reflection. Refinement of the model with $\psi = 39^\circ$ and $\phi = 53^\circ$ was made by changing the values of the angles in steps of 1° and calculating the R -value:

$$\sum_i |I_{\text{obs}} - \sum_j I_{\text{calc}}| / \sum_i I_{\text{obs}}$$

\sum_i is a summation over all reflections, \sum_j is a summation over a group of not resolved reflections.

A second neutron diffraction powder pattern has been measured recently at 300°K and 4.2°K with a 2.06 Å wavelength, in order to separate the (010), (300) and the (20 \bar{l}), (001) contributions; it confirmed absolutely the first diagram and showed that the observed intensity of (20 \bar{l})

was three times that of (001). The best agreement between observed and calculated intensities, $R = 12.6\%$ was obtained for $\psi = 43^\circ$ and $\phi = 59^\circ$, and from the scale factor used to bring the calculated magnetic reflections on an absolute scale a magnetic moment for Tb^{3+} of $8.02 \mu_B$ is obtained: this means a moment of $5.47 \mu_B$ along the b axis, and of $5.86 \mu_B$ in the ac plane.

Discussion

The crystal used in the X-ray investigation was twinned in the same way as previously investigated crystals of YOOH (2). The reflections $hk0$ have intensity contributions from two crystals and are given a scale factor different from that of the $hk\ell$ reflections.

Some of the $hk\ell$ reflections from one of the two crystals are not sufficiently separated from reflections from the other crystal, resulting in an indeterminacy of the intensities of the reflections in question. Such reflections have been omitted in the refinements. Taking the twinning of the crystal and the unfavourable shape of the sample into consideration, a very low R -value should not be expected.

The single-crystal X-ray investigation confirmed that the monoclinic modification of $TbOOH$ has the yttrium oxide hydroxide structure. The atomic coordinates of the terbium atom does not deviate more than three standard deviations from the coordinates of the metal atom in YOOH, and the atomic coordinates of the oxygen atoms in the $TbOOH$ structure are the same within six standard deviations as the coordinates found in the YOOH structure (2). Two sets of terbium–oxygen distances are found. One set with an average value of 2.31 Å and a standard deviation of 0.02 Å, the other set with an average value of 2.44 Å and a standard deviation of 0.02 Å. The two sets are significantly different from each other. The oxygen atoms of type O (2) having the longest distances to the terbium atoms are the oxygen atoms of the OH^- ions.

Refinement of the atomic coordinates using the neutron diffraction powder pattern measured at 300°K gave the coordinates listed in Table V. The values giving the best agreement between observed and calculated neutron intensities are apparently different from the coordinates listed in Table I. This is possibly due to the fact that some of the reflections from the neutron diffrac-

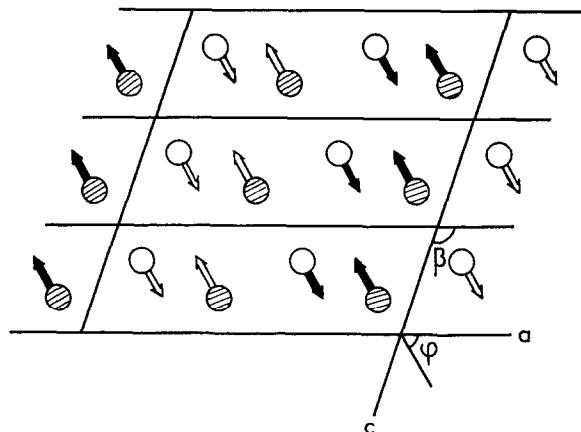


FIG. 1. Projection of the magnetic structure in the [010] direction. Terbium atoms at $y = 1/4$ and $y = 3/4$ are shown as open circles and shaded circles, respectively.

tion powder pattern have contributions in the intensities from an unidentified impurity.

The atomic coordinates of the terbium atom from Table I have been used in the calculation of the magnetic structure factors. Figure 1 is a projection of the magnetic structure in the [010] direction. The oxygen and hydrogen atoms have been omitted. Open arrows indicate a spin having an angle $\psi = 43^\circ$ with the ac plane and filled arrows are indicating a spin having an angle $\psi = -43^\circ$ with the ac plane. The magnetic structure of TbOOH is thus a noncolinear antiferromagnetic structure different from the colinear antiferromagnetic structure of DyOOH (10), and also different from the colinear antiferromagnetic structure of ErOOH (12). The magnetic moment of $8.02 \mu_B$ for the Tb^{3+} ion is in acceptable agreement with the magnetic susceptibility experiment (1).

Crystal field anisotropy and interaction is introduced in order to explain this noncolinear antiferromagnetic structure. The point symmetry of the rare earth ion in TbOOH is m . Tb^{3+} is a non-Kramers ion, and in a low symmetric crystalline field the energy levels will split into singlet states only. In this case, magnetic ordering requires at least two singlets not very much different in energy, and the spins are in the mirror planes or point in a direction perpendicular to these planes. If the ground state splits into more than two singlets, into four for instance, the spins may have other directions. The anisotropic directions are then not in the mirror planes but are in two directions arranged symmetrically with respect to the direction of the b axis, and

each of the two directions are forming an angle ψ with the ac plane. This is due to the symmetry of the group. Two propagation vectors are considered for the magnetic structure: \mathbf{k}_1 corresponding to the ac plane component, and \mathbf{k}_2

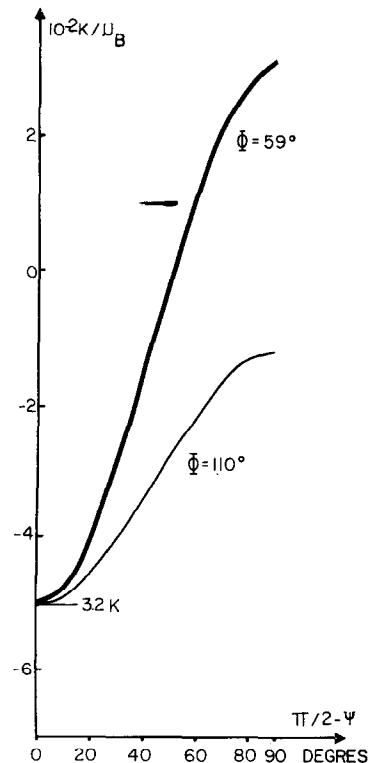


FIG. 2. The variation of the dipolar energy with the angle $(\pi/2 - \psi)$ between S_1 and the b axis.

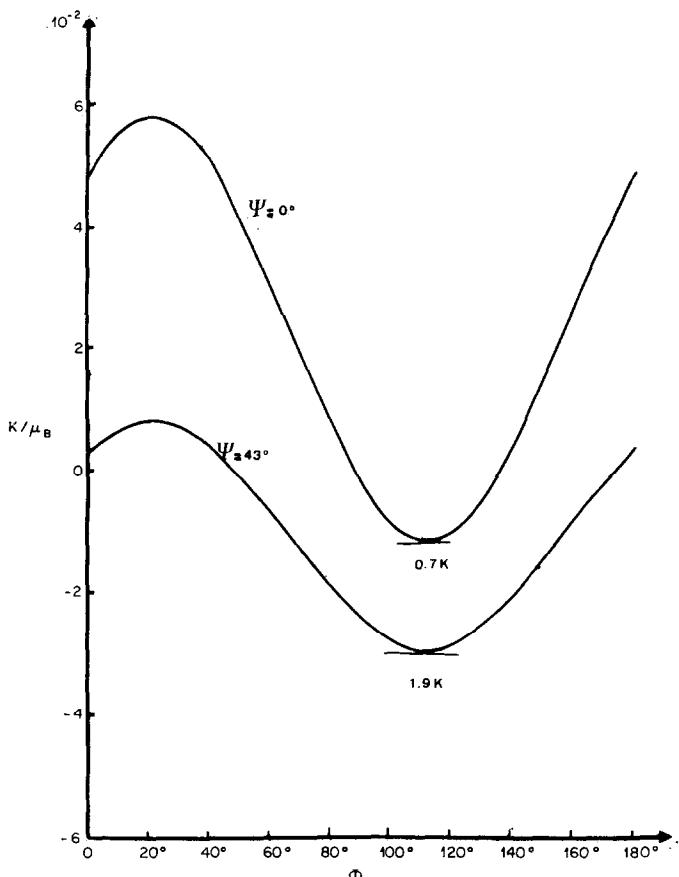


FIG. 3. The variation of the dipolar energy with the angle ϕ between S_1 and the a axis in the ac plane.

to the b axis component of the anisotropy directions.

If interactions are only isotropic, the magnetic structure is colinear, and this hypothesis can be ruled out in the case of TbOOH. The anisotropic interactions deriving from dipolar energy have been calculated. In a low symmetric structure as that of TbOOH the minimum of dipolar energy will be along the b axis or in the ac plane approximately along the direction of the c axis (see Figs. 2 and 3). The value of the energy which has an effect on the Tb^{3+} ion reaches a maximum at $3.2^\circ K$ and at $1.9^\circ K$ respectively, in the two directions mentioned above. This means that crystalline field anisotropy is dominating. Starting from a model where the spins are fixed in a direction in space ($\psi = 43^\circ$, $\phi = 59^\circ$) dipolar energies corresponding to a colinear and to a non-colinear arrangement of the magnetic spins S_1 and S_2 have been calculated. The energy is lowest in the case of a noncolinear model.

Considering the anisotropy fixed by the crystalline field it is concluded that the dipolar energy is in favour of a noncolinear structure.

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