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MAGNETIC STRUCTURES AND MAGNETIC SUSCEPTIBILITIES OF TERBIUM OXYSULFIDE AND OXYSELENIDE

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For the two isomorphous compounds Tb_2O_2S and Tb_2O_2Se, the magnetic susceptibility measurements on powder samples show an antiferromagnetic ordering with Néel temperatures of about 7.7 and 7K respectively. Differing in this respect from the other rare earth oxyselenides, the magnetic anisotropy of Tb_2O_2Se at low temperature is weaker than that of Tb_2O_2S.

We also determine the magnetic structures of these two compounds by neutron diffraction experiments at 1.5K. The magnetic cell is orthohexagonal and doubled along the c-axis; the magnetic moments make an angle, with the c-axis, of $47 \pm 10^\circ$ for Tb_2O_2S and $30 \pm 10^\circ$ for Tb_2O_2Se and the moment values at 1.5K are $8.14 \pm 0.2\mu_B$ and $6.5 \pm 0.2\mu_B$, respectively.

It is rather exceptional that in a rare earth uniaxial compound the magnetic moment makes an angle with the c-axis. However we interpret this situation by the fact that several levels exist very near to the ground state. The crystal field calculations are in good agreement with the experimental results.

1. INTRODUCTION

A SYSTEMATIC study of the paramagnetic properties of the rare earth oxysulfides R_2O_2S, using powdered samples, showed that only compounds with R = Gd, Tb, Dy, Ho and Yb have antiferromagnetic order;[1] the magnetic structures (except Gd) have been determined by neutron diffraction experiments.[2,3] However recent magnetic measurements on single crystals[4] showed, for Tb and Dy, an incompatibility between the obtained results and the magnetic moment direction given by reference 2. To remove this discrepancy we redetermined the magnetic structures of the terbium and dysprosium oxysulfides. For Dy_2O_2S the results are given elsewhere.[5]

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In this paper we give the magnetic structures and the magnetic properties of the rare earth oxysulfide Tb_2O_2S together with that of its isomorphous oxyselenide Tb_2O_2Se.

2. CRYSTALLOGRAPHIC STRUCTURE

The rare earth oxychalcogenides R_2O_2S and R_2O_2Se, from lanthanum to lutecium, form a series of compounds which have the same crystallographic structure.[6,7] They crystallize in the space group $P\bar{3}m - D^3_{3d}$ and in the hexagonal unit cell the atoms have the following positions (Fig. 1),

2R	in $\pm(\frac{1}{3}, \frac{2}{3}, u)$
2O	in $\pm(\frac{1}{3}, \frac{2}{3}, v)$
1S or 1Se	in $(0, 0, 0)$.

Table 1

	a(Å)	c(Å)	u	v	R
Tb_2O_2S	3.814	6.616	0.282 ± 0.002	0.630 ± 0.002	0.037
Tb_2O_2Se	3.876	6.859	0.291 ± 0.002	0.628 ± 0.002	0.027

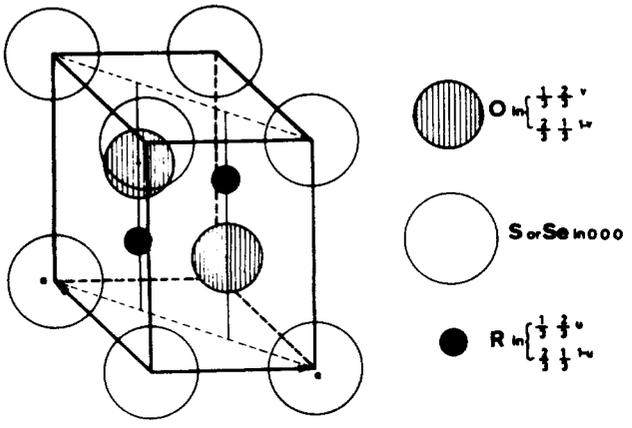

FIG. 1. Crystallographic structure of the rare earth oxychalcogenides R_2O_2S and R_2O_2Se.

For Tb_2O_2S and Tb_2O_2Se we determined the position parameters u and v by the aid of neutron diffraction diagrams obtained at room temperature. We used for the calculations, the following scattering lengths[8] in 10^{-12} cm/atom:

$b_{Tb} = 0.76$, $b_O = 0.577$, $b_S = 0.28$ and $b_{Se} = 0.78$.

The results are given in Table 1 with the reliability factor R defined as $R = \Sigma |I_{obs} - I_{calc}|/\Sigma I_{obs}$.

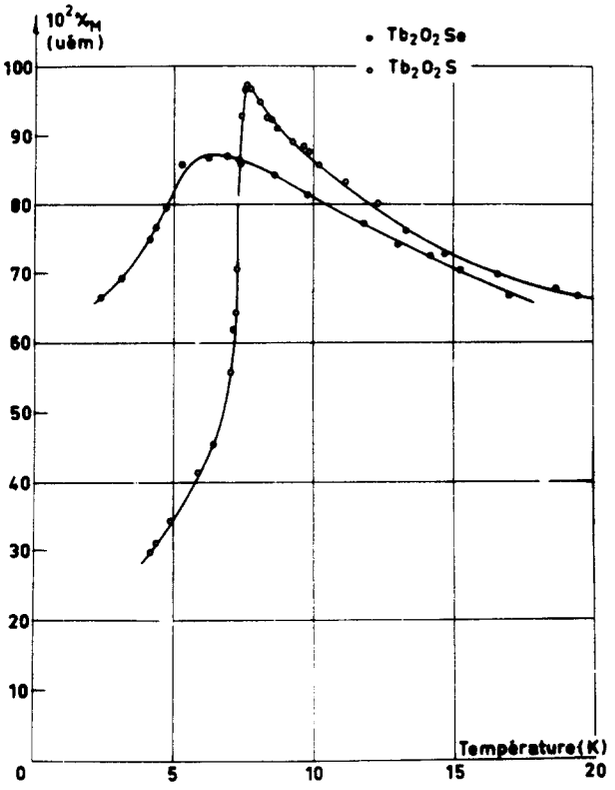

FIG. 2. Magnetic susceptibility of Tb_2O_2S and Tb_2O_2Se.

3. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility was measured, using a Faraday balance, between 2 and 300K on powdered samples.

For these two oxychalcogenides of terbium, the magnetic susceptibility above 20K is well represented by the Curie–Weiss law; the Curie constants are of the same order as the free Tb^{3+} ion value ($C_{Tb_2O_2S} = 11.8$, $C_{Tb_2O_2Se} = 12$ and $C_{free\ ion} = 11.82$ in e.m.u./ion). The paramagnetic Curie temperatures θ_p are also nearly the same: $\theta_p = -17$K for Tb_2O_2S and $\theta_p = -18$K for Tb_2O_2Se. This means that in the paramagnetic region there is no great difference in the crystal field splitting of the Tb^{3+} fundamental multiplet $^7F_6$ in the two compounds.

However at low temperature (below 20K) the molar susceptibility of Fig. 2 shows an important difference for the two compounds. From this figure we can see that terbium oxyselenide has a low magnetic anisotropy as compared with terbium oxysulfide, which leads to a lower Néel temperature ($T_N = 7$K for Tb_2O_2Se, $T_N = 7.7$K for Tb_2O_2S). This result is opposite to that obtained for the other rare earth oxychalcogenides (Gd, Dy, Ho) which show higher Néel temperatures for the oxyselenides.[9]

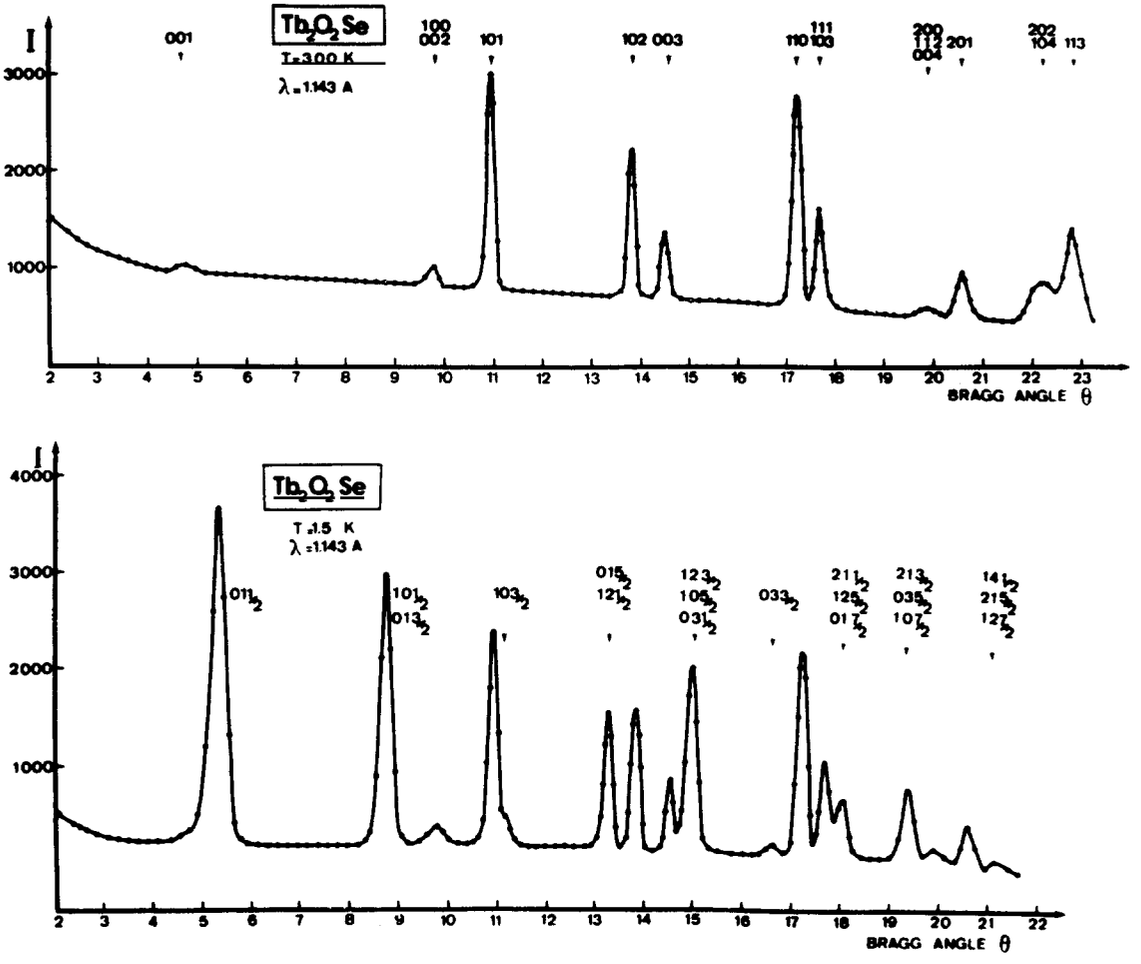

FIG. 3. Neutron diffraction pattern of Tb_2O_2Se.

4. MAGNETIC STRUCTURE

The magnetic neutron diffraction patterns obtained at 1.5K are identical for the two compounds Tb_2O_2S and Tb_2O_2Se, but the intensities are different. This means that for the two samples we have the same magnetic arrangement of the Tb^{3+} moments. The magnetic reflections can be indexed in a monoclinic cell $(a, 2a, 2c)$: the propagation vector is $k = (0, \frac{1}{2}, \frac{1}{2})$. Nevertheless we shall use the equivalent orthohexagonal cell $(a, b = a\sqrt{3}, c)$; here the magnetic unit cell can be described by an orthohexagonal one doubled along the c-axis; i.e. the propagation vector is $k = (0, 0, \frac{1}{2})$.

In Fig. 3, we represent the neutron diffraction diagrams for Tb_2O_2Se obtained at 300 and 1.5K.

In the orthohexagonal description with $l = (2n + 1)/2$ the magnetic structure factor can be written as:

$$\mathbf{F}_M = 2\eta f(\mathbf{m}_1 \cdot e^{2\pi i[(k/3)+lu]} - \mathbf{m}_2 \cdot e^{-2\pi i[(k/3)+lu]})$$

where

$$\eta = \frac{e\gamma^2}{mc^2} = 0.27 \cdot 10^{-12}\,\text{cm}.\mu_B^{-1}$$

f is the form factor,[10] $\mathbf{m}_1$ and $\mathbf{m}_2$ are the magnetic moments (in Bohr magneton) in the crystallographic cell at the coordinates u and $1 - u$ respectively.

The comparison of the intensities of the reflections $(01\frac{1}{2})$ and $(03\frac{3}{2})$ clearly indicates that $\mathbf{m}_1 = +\mathbf{m}_2$ for the two compounds; thus the magnetic structure factor is well determined.

Table 2. Observed and calculated magnetic intensities of Tb_2O_2S at 1.5K

(*hkl*)	Observed intensities	Calculated intensities $\phi = 0$ $\theta = 30°$	$\phi = 0$ $\theta = 47.5°$	$\phi = 0$ $\theta = 60°$	$\phi = 0$ $\theta = 90°$	$\phi = 30°$ $\theta = 54°$	$\phi = 90°$ $\theta = 9°$
0 1 1/2	1793	1552	1653	1789	1794	1406	1418
1 0 1/2	2486	1474	1036	610	165	1163	1873
0 1 3/2		1062	1441	1861	2303	1622	679
		2536	2577	2471	2468	2785	2552
1 0 3/2	453	417	339	386	268	305	451
0 1 5/2	2169	305	483	711	791	494	129
1 2 1/2		2240	1977	1807	1481	1746	2419
		2545	2460	2518	2272	2240	2548
1 0 5/2	5023	909	1186	1312	1585	1426	723
0 3 1/2		1432	1497	1481	1515	1282	1367
1 2 3/2		2295	2321	2208	2194	2266	2293
		4636	5004	5001	5094	4974	4383
0 3 3/2	355	479	442	567	449	307	441
0 1 7/2	2577	457	857	1169	1523	974	131
1 2 5/2		731	774	925	876	722	653
2 1 1/2		1402	957	602	172	983	1778
		2590	2588	2696	2571	2679	2562
1 0 7/2	2626	17	5	43	1	3	12
0 3 5/2		1101	1354	1445	1692	1301	909
2 1 3/2		1554	1213	851	497	1336	1871
		2672	2572	2339	2190	2640	2792
R		7.2%	4.6%	5.8%	6.4%	6.3%	9.9%
m in μ_B		8.07	8.14	8.18	8.09	8.06	8.0

The magnetic intensity is given by:

$$I_M = p\langle\sin^2\alpha\rangle|\mathbf{F}_M|^2$$

where: p is the multiplicity of the reflection (hkl), and
α is the angle between the scattering vector and the antiferromagnetic direction.

The intensity of the $(01\frac{1}{2})$ reflection shows that the magnetic moment direction can be neither along the b axis nor in the (b, c) plan. A systematic calculation was performed with the magnetic moment in the (a, c) plane and in a plane which makes an angle of 30° with the (a, c) plane.

Tb_2O_2S

For Tb_2O_2S, the results are summarized in Table 2; θ is the angle of the antiferromagnetic direction Δ with the c axis and ϕ is the angle of the projection of Δ on the basal plane with the **a** axis. The direction, in the (a, c) plane, making an angle of 47° with the c axis, gives the best agreement between calculated and observed intensities (R = 4.6%). However we can see that the determination of the angle θ is not very accurate and moreover ϕ may be 0 or 30° with about the same intensity agreement.

The difficulty arises from the fact that the lattice parameters are, unfortunately, such that c is approximately equal to $b(b = a\sqrt{3})$. This means that most of

Table 3. Comparison of calculated and observed intensities Tb_2O_2Se at 1.5K

hkl	I_{obs}	I_{calc} $\phi = 0$ $\theta = 31°$	$\phi = 30°$ $\theta = 17.5°$	$\phi = 90°$ $\theta = 0$
0 1 1/2	2203	2005	1860	1808
1 0 1/2	3694	2176	2738	2837
0 1 3/2		1601	1222	1044
		3777	3960	3881
1 0 3/2	581	335	285	261
0 1 5/2	3257	362	205	138
1 2 1/2		2978	3141	3158
		3340	3346	3296
1 0 5/2	7242	1457	1296	1156
0 3 1/2		2195	2190	2188
1 2 3/2		3569	3715	3689
		7221	7201	7033
0 3 3/2	389	385	388	263
0 1 7/2	3131	641	301	154
1 2 5/2		862	782	739
2 1 1		1850	2226	2287
		3353	3309	3180
1 0 7/2	4318	18	37	36
0 3 5/2		1711	1534	1452
2 1 3/2		2340	2823	2894
		4069	4394	4382
R		4.6%	5.3%	5.3%
m in μ_B		6.50	6.50	6.42

the magnetic reflections are superimposed in such a manner that when we change the angle θ one Bragg intensity increases and the other one decreases, so that the total intensity is nearly unchanged (Table 2).

However we can conclude that the magnetic moments make an angle of about 47 ± 10° with the c-axis; for this direction we obtained a magnetic moment value of 8.14 ± 0.2 μ_B at 1.5K.

Tb_2O_2Se

The comparison between the calculated and observed intensities is given in Table 3. For this compound we have the same difficulties for the determination of the magnetic moment direction as for Tb_2O_2S.

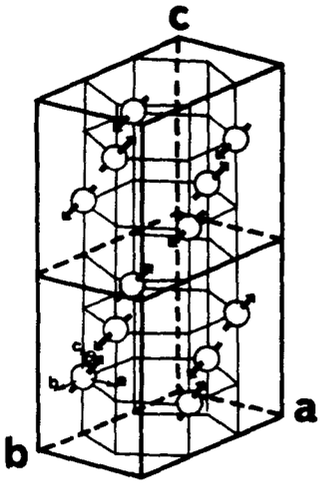

FIG. 4. Magnetic structure of Tb_2O_2S and Tb_2O_2Se.

The best agreement (R = 4.6 per cent) is obtained for a direction in the (a, c) plane making an angle $\theta = 30 \pm 10°$ with the c-axis and the magnetic moment value is found to be 6.5 ± 0.2 μ_B at 1.5K.

The magnetic structure of Tb_2O_2Se is very similar to that of Tb_2O_2S, Fig. 4, except for a change in the moment angle with the c-axis and in the magnetic moment value.

5. DISCUSSION

This type of magnetic structures is relatively exceptional in rare earth compounds, particularly in uniaxial ones like oxychalcogenides. Generally the antiferromagnetic direction lies either along the principal axis or perpendicular to this axis. This result is valid if the fundamental ground state is either a doublet or a pseudo-doublet (formed by two singlets near together) relatively well isolated, that is to say the magnetic interaction energy must be weaker than the distance to the first excited level. In Tb_2O_2S this is not the case.[11]

We determined the crystal field level of the Tb^{3+} ion, in a Y_2O_2S host lattice, by optical spectroscopy;[12] we obtained the result that the ground state of Tb^{3+} cannot be considered as a doublet or a pseudo-doublet but as a set of a doublet, two singlets and another doublet with energy separations: 0, 6, 15 and 26 cm^{-1} (the other excited levels lie 100 cm^{-1} above).

This situation gives rise to a magnetic anisotropy which depends on the magnetic field direction and on its value. From crystal field calculations we deduced that the easy magnetisation axis makes an angle of about 42° with the *c*-axis and that the magnetic moment value in this direction is about 8 μ_B; this value is in very good agreement with the experimental one: 8.14 ± 0.2 μ_B.

In the case of Tb_2O_2Se we did not determine experimentally the crystal field levels of the Tb^{3+} ion, but in the light of the preceding results we can consider that these levels are nearly the same as in the terbium oxysulfide.

However as several levels lie very near to the ground state, a small variation in the level positions and in the wave functions may give rise to an important change of the magnetic anisotropy and of the magnetic moment value. As we have a reduced magnetic moment value in the oxyselenide, the excited levels of the Tb^{3+} ion might be more separated from the ground state than in the oxysulfide. Indeed calculations performed on Tb_2O_2S show that an increase of the separation of the first excited level implies a decrease of the moment value and of its angle with the *c*-axis.

On the other hand the smaller Néel temperature value of Tb_2O_2Se is not due to a weakening of the superexchange interactions through the selenium compared to that of sulfur, but only to the different magnetic moment values. Indeed with equal magnetic moment values the Néel temperature of the rare earth oxyselenide is higher than the corresponding oxysulfide,[9] which confirms that the superexchange interaction at 180°, is greater for R–Se–R than for R–S–R.

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Les mesures de susceptibilité magnétique, sur des échantillons polycristallins, indiquent que les deux composés isomorphes Tb_2O_2S et Tb_2O_2Se s'ordonnent antiferromagnétiquement pour des température de Néel respectivement de 7,7 et 7K environ. A basse température, contrairement aux autres oxyséléniures de terres rares, l'anisotropie magnétique de Tb_2O_2Se est plus faible que celle de Tb_2O_2S.

Par des expériences de diffraction neutronique à 1,5K nous avons déterminé la structure magnétique de ces deux composés. La maille magnétique est orthohexagonale doublée selon l'axe c; les moments magnétiques font un angle avec l'axe c de $47 \pm 10^\circ$ pour Tb_2O_2S et de $30 \pm 10^\circ$ pour Tb_2O_2Se et la valeur du moment à 1,5K est respectivement de $8,14 \pm 0,2\ \mu_B$.

Le fait que dans un composé uniaxial de terre rare la direction des moments fasse un angle avec l'avec l'axe c est tout à fait exceptionnel. Toutefois nous avons interprété cette situation par la fait qu'il existe plusieurs niveaux de champ cristallin très proches du niveau fondamental; l'accord entre le calcul et l'expérience est très bon.