

tion. It is therefore most conveniently represented in the hyper-stereogram by the projections of a set of five points equidistant from one another on the hypersphere at $2 \tan^{-1} (1/\sqrt{5})$ apart. The simplest orientation which gives rise to the standard form (Mackay & Pawley, 1963),

$$\frac{1}{4} \begin{pmatrix} 1 & 1 & 3 & \sqrt{5} \\ 1 & -3 & -1 & \sqrt{5} \\ -3 & 1 & -1 & \sqrt{5} \\ -\sqrt{5} & -\sqrt{5} & \sqrt{5} & -1 \end{pmatrix}$$

for the matrix, is a point at the centre of the hyper-stereogram together with four points tetrahedrally arranged around it in the centres of the positive wxy octants at $r = \sqrt{5}/\sqrt{3}$. The effect of the V operation in the hyper-stereogram is most simply envisaged as a combination of a $\bar{4}$ rotation axis and a reflexion in a hyper-plane making $\tan^{-1} (\sqrt{5}/\sqrt{3})$ with this axis. In the above case the $\bar{4}$ rotation axis would be the z axis, with its rotation component about the xz plane, and the

hyper-plane would be equally inclined to the w , x and y axes.

The X operation can similarly be represented by the same five points together with their opposites.

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Neutron-Diffraction Study of $\text{Tb}(\text{OH})_3$ – A Case of Severe Extinction*

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Neutron-diffraction experiments on a single crystal of $\text{Tb}(\text{OH})_3$ have indicated severe extinction effects. For some Bragg reflections the observed neutron cross section is attenuated by a factor of ten owing to extinction. A least-squares refinement (including extinction) of the structure factors deduced from integrated intensities measured at room temperature gives structural parameters in good agreement with a previous determination, and new information about the position and thermal vibrations of the hydrogen atom. The final residual of 0.036 indicates that extinction is well accounted for by the Zachariasen formulae, and the value of g , the extinction parameter, is $(6 \pm 1) \times 10^4$. The polarized-neutron technique has been used to measure the ratio between the magnetic and nuclear structure factors at 2.6°K, at which temperature $\text{Tb}(\text{OH})_3$ is ferromagnetic ($9 \mu_B/\text{Tb}$ atom). The effect of extinction is particularly dramatic in this experiment, but again the results may be explained with the simple Zachariasen correction and the same extinction parameter as used for the unpolarized data. The corrected magnetic scattering amplitudes deduced from the polarized-neutron experiment allow the magnetic form factor of the terbium atom to be found, and compared to that measured in terbium metal; this aspect of the investigation is discussed in a separate article.

Introduction

The problem of extinction in experiments concerned with measuring Bragg intensities in both X-ray and neutron diffraction has received much attention over the last few years. Recognized in the very early days of crystallography by Darwin (see James, 1958) extinction results in the stronger Bragg intensities appearing weaker than predicted by the kinematical theory. Experiments aimed at determining crystal structures are

somewhat independent of this problem, since the stronger reflections are often disregarded in the refinements, and the correlation between the extinction and the final positional parameters is usually small. The most thorough treatment of extinction has been formulated by Zachariasen (1967, 1968a, 1968b). Despite doubts about the mathematical treatment (Werner, 1969), and the physical significance of the final parameters (Lawrence, 1972; Killean, Lawrence & Sharma, 1972), the Zachariasen theory has found wide acceptance among experimentalists, and is now routinely included in least-squares refinements of the structural parameters. Second-order corrections in the form of

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anisotropic extinction (Coppens & Hamilton, 1970) and angular-dependent terms (Cooper & Rouse, 1970) have been applied in certain cases.

Extinction may also be a serious problem in experiments with polarized-neutron diffractometers. In these experiments the magnetic scattering amplitude M is arranged to interfere either constructively or destructively with the nuclear scattering amplitude N (see *e.g.* Nathans & Pickart, 1963). Thus for one neutron polarization state the intensity of the Bragg reflection is $I_+ \propto (N+M)^2$ and for the other state is $I_- \propto (N-M)^2$. The measurement of the ratio of these two intensities (the flipping ratio) leads to a determination of the ratio M/N . This ratio is relatively easy to measure, and the precision in determining M/N is usually much greater than in determinations of the crystal structure factors. Therein, of course, lies the power of the polarized-neutron technique, and it has been used to determine

the spatial extent (*i.e.* the magnetic form factor) of the unpaired electrons in metals, alloys, and a few compounds of both the 3d and 4f series. In all cases, the nuclear scattering amplitude has been known and, together with the measured flipping ratio, allows the magnetic scattering amplitude to be found. Our aim in the present experiment was to measure the magnetic form factor of the terbium ion in the compound $\text{Tb}(\text{OH})_3$ and compare it with that determined in terbium metal (Steinsvoll, Shirane, Nathans, Blume, Alperin & Pickart, 1967; Brun & Lander, 1971). At the outset, however, we encountered very large extinction effects. The present paper is concerned with these extinction effects in a single crystal of $\text{Tb}(\text{OH})_3$ as measured with both unpolarized and polarized neutrons. In particular, we wish to highlight some of the unique aspects of extinction that appear in the polarized-neutron experiment. Perhaps surprisingly, we find the simple Zachariasen formula completely adequate to correct the extinction, which in some strong reflections results in a decrease in the observed intensity by a factor of 10. As a result of being able to account for the extinction, we are able to complete the original aim of the experiment and determine the magnetic form factor of terbium in $\text{Tb}(\text{OH})_3$. A paper dealing with this aspect of the problem has been submitted to *Physical Review*.

Experimental results

Previous work

The rare-earth hydroxides crystallize in the yttrium hydroxide structure (Wyckoff, 1964, Vol. 2, p. 77). The space group is $P6_3/m$ (No. 176) with two molecular units per unit cell. The atomic positions are: rare earth in $2(d) \pm (\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and both oxygen and hydrogen in $6(h) \pm (x, y, \frac{1}{4}; -y, x-y, \frac{1}{4}; y-x, -x, \frac{1}{4})$. The unit-cell

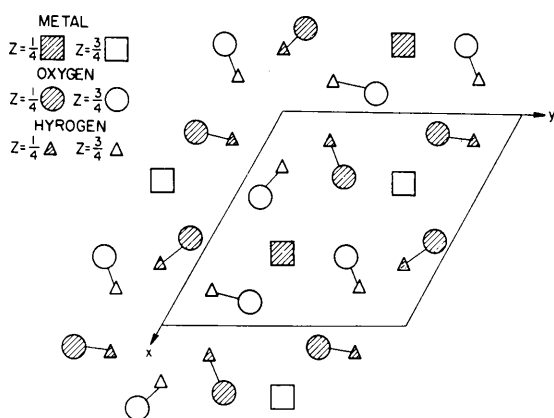


Fig. 1. The (00.1) projection of the structure of $\text{Tb}(\text{OH})_3$.

Table 1. Results of least-squares refinements of room-temperature single-crystal data on $\text{RE}(\text{OH})_3$ compounds

Standard deviations refer to the least significant digit. Coherent scattering lengths of $b_{\text{Tb}} = 0.76$, $b_{\text{O}} = 0.58$, and $b_{\text{H}} = -0.374$ (all $\times 10^{-12}$ cm) were used. In refinements with anisotropic thermal parameters (see Table 2) the effective temperature factor is defined as $B_{\text{eff}} = 8\pi^2 (r_1 \times r_2 \times r_3)^{2/3}$, where r_1 , r_2 , and r_3 are the radii of the thermal ellipsoid.

	Christensen <i>et al</i> (1967) X-rays $\text{Y}(\text{OH})_3$	Unpolarized neutrons $\text{Tb}(\text{OH})_3$		
		Isotropic, no extinction	Isotropic, with extinction	Anisotropic, with extinction
Metal				
x	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
y	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B (\AA^2)	0.64 (1)	Fixed 0.6	0.6 (1)	0.6 (1)
Oxygen				
x	0.3112 (7)	0.311 (2)	0.3091 (5)	0.3096 (4)
y	0.3957 (7)	0.396 (2)	0.3950 (5)	0.3952 (4)
z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B (\AA^2)	0.75 (6)	Fixed 0.75	0.8 (1)	$B_{\text{eff}} = 0.65$
Hydrogen				
x	0.142 (4)	0.147 (3)	0.143 (1)	0.143 (1)
y	0.279 (4)	0.285 (3)	0.279 (1)	0.278 (1)
z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
B (\AA^2)	D 0.9	Fixed 2.0	2.3 (2)	$B_{\text{eff}} = 2.4$
g ($\times 10^4$)	—	—	6.7 (1.0)	6.3 (1.1)
R	0.023	0.189	0.063	0.036

dimensions for all the hydroxides are approximately the same, and for Tb(OH)₃ $a=6.270$ and $c=3.560$ Å, each ± 0.005 Å. Christensen, Hazell & Nilsson (1967) determined the structural parameters for Y(OH)₃ using single-crystal X-ray diffraction. The position of the hydrogen atom was determined from a neutron-diffraction investigation of Y(OD)₃. The results of this investigation are given in Table 1. In their paper, Christensen, Hazell & Nilsson placed the rare-earth atom in the position $2(c)$, *i.e.* at $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. We prefer to follow Wyczkoff, and have interchanged the x and y coordinates as originally tabulated by the authors.

The projection of the structure onto the (00.1) plane is shown in Fig. 1.

Unpolarized neutrons

All experiments in the present study have been performed on the same single crystal of Tb(OH)₃, kindly sent to us by Professor W. P. Wolf of Yale University. The preparation of these crystals is described by Mroczkowski, Eckert, Meissner & Doran (1970, 1972). The crystal used was approximately circular in cross section (diameter 1.5 mm) and of length 4.5 mm. The c axis was parallel to the long axis.

Integrated intensities were measured with a standard four-circle diffractometer located at the CP-5 Research Reactor. The incident neutron wavelength was 1.05 Å. In examining half of reciprocal space with $\sin \theta/\lambda \leq 0.65$ Å⁻¹ 531 Bragg reflections were measured. After making absorption corrections ($\mu=4.3$ cm⁻¹) the data reduced to 93 inequivalent reflections. The standard deviations, as judged by counting statistics and the variation within an equivalent set (usually 6 reflections), were between 3 and 8%. The results of the first least-squares refinement with these data are given in the third column of Table 1. Although the positional parameters are in good agreement with the previous work, the residual is high (0.189), and the refinement required all the temperature factors to be negative. Positive temperature factors were obtained only after the twenty or so strongest reflections were excluded – a sure sign of severe extinction. Consequently the observed structure factors were refined with the *LINUS* least-squares routine (see Coppens & Hamilton, 1970) that includes the Zachariasen correction for extinction. An immediate improvement was observed in R (0.063), and the thermal parameters acquired reasonable values. The value for the extinction parameter itself, however, was exceedingly high, and indicated that in some strong reflections the diffracted intensity was attenuated by a factor of six due to extinction.

Following Zachariasen (1967)

$$\begin{aligned} N_{\text{obs}}^2 &= S^2 N_c^2 y \\ y &= (1 + 2x)^{-1/2} \\ x &= \frac{3}{2} Q_0 \lambda^{-1} r(r - r^*) + r^* Q \lambda^{-1} \bar{T} \\ r^* &= r/[1 + (r/\lambda g)^2]^{1/2}, \end{aligned} \quad (1)$$

where S is the scale factor, N_{obs} the observed nuclear structure factor, N_c the theoretical structure factor, Q the crystallographic quantity $N_c^2 V^{-2} \lambda^3 / \sin 2\theta$, where V is the volume of the unit cell and θ is the Bragg angle. We have introduced the term N for the nuclear structure factor, rather than the more familiar F , so as to distinguish between nuclear and magnetic structure factors, N and M respectively. The two terms for x in equation (1) correspond to primary and secondary extinction respectively. \bar{T} is the effective path length, defined by $\bar{T} = -\frac{1}{A} \frac{dA}{d\mu}$, where A is the absorption factor.

Historically the parameter g is associated with extinction in diffraction experiments and we prefer this to the r^*/λ of equation (1). If we assume secondary extinction of either Type I or II (but not a mixture), then,

$$y = (1 + 2gQ\bar{T})^{-1/2}. \quad (2)$$

In this experiment we find g values of $\sim 6 \times 10^4$, which are an order of magnitude greater than those reported for other crystals. For Type I (see Zachariasen, 1967, for an explanation of these terms) g is related to the half-width of the Gaussian function that describes the angular distribution of the mosaic blocks in the crystal. For Type II g is related to the average radius r of the perfect domains in the crystal. Zachariasen has noted that very large values of $gQ\bar{T}$, as observed in this experiment, suggest Type II extinction. If we assume primary extinction, then $3Q\lambda^{-1}r^2$ is substituted for $2gQ\bar{T}$ in equation (2). In this experiment the path lengths do not vary enough to distinguish between primary and secondary extinction. We have therefore used the conventional expression given in equation (2) in the data reduction.

The unpolarized-neutron data were also refined with anisotropic temperature factors. The metal atom is at a special position, and is constrained to vibrate isotropically in the xy plane (Waser, 1955; Levy, 1956). Two thermal parameters are therefore sufficient for the metal atom, one defining the radius in the xy plane, and the other the extent of the motion parallel to the z axis. Within experimental error the metal atom exhibits no thermal anisotropy, the root-mean-square thermal vibration being 0.09 ± 0.01 Å [$= (B/8)^{1/2}/\pi$, where B is the isotropic temperature factor]. This result is in excellent agreement with Christensen, Hazell & Nilsson. For oxygen and hydrogen, the thermal anisotropy is defined by four parameters, β_{11} , β_{22} , β_{12} , and β_{33} ($\beta_{13} = \beta_{23} = 0$). The first three define an ellipse in the xy plane, and following Waser (1955) we calculate the angle φ that the major axis of this ellipse makes with the O–H bond, see Fig. 1. From physical arguments we might expect the hydrogen atom to vibrate preferentially at right angles to the O–H bond, *i.e.* $\varphi_H \simeq 90^\circ$. On refining with anisotropic temperature factors for the hydrogen atom only, the residual dropped to 0.037, and the major axes of the hydrogen thermal ellipsoid are in the plane perpendicular to the O–H bond. A further refinement including anisotropic temperature factors for

the oxygen atom gave no significant improvement in the residual, and the thermal motion of the oxygen atom is essentially isotropic, again in good agreement with Christensen, Hazell & Nilsson. The values of the β_{ij} , and the root-mean-square axial lengths of the thermal ellipsoids are given in Table 2.

Table 2. *Anisotropic thermal parameters of oxygen and hydrogen in RE(OH)₃*

The angle ϕ is defined as that between the major axis (of length r_1 , Å) of the thermal ellipsoid and the O-H bond. (All parameters, except ϕ , are expressed $\times 10^3$).

	Christensen <i>et al.</i> (1967)	Neutrons Tb(OH) ₃	
	X-rays Y(OH) ₃	Unpolarized 298°K	Polarized 2.6°K
Oxygen			
β_{11}	6 (1)	6 (1)	4 (2)
β_{22}	7 (1)	6 (1)	5 (1)
β_{12}	4 (1)	4 (1)	3 (2)
β_{33}	17 (3)	14 (3)	—
r_1	104 (10)	103 (10)	96 (12)
r_2	90 (10)	78 (8)	68 (10)
r_3	104 (9)	93 (12)	—
ϕ	$\sim 25^\circ$	$\sim 10^\circ$	$\sim 30^\circ$
Hydrogen			
β_{11}	—	16 (2)	6 (2)
β_{22}	—	14 (2)	10 (2)
β_{12}	—	6 (1)	0 (2)
β_{33}	—	72 (7)	—
r_1	—	170 (10)	159 (12)
r_2	—	142 (10)	93 (8)
r_3	—	215 (12)	—
ϕ	—	100° (15)	86° (15)

is the overall scale factor in the least-squares refinement, and y is the attenuation of the intensity due to extinction. In the refinements, the scale factor S is determined to $\pm 4\%$, and is strongly correlated ($+0.95$) with the overall extinction parameter. The errors for N_{corr} do not include any arising from uncertainty in the scale factor or in the extinction. Table 3 indicates that the agreement between $|N_c|$ and N_{corr} is good over the whole range of extinction, *i.e.* y values ranging from 1 to 0.18. We have found no evidence for anisotropic extinction in the Tb(OH)₃ data, nor evidence for angular effects such as observed by Cooper & Rouse (1970). In the latter case, however, we note that, in Tb(OH)₃, all the strong reflections occur at low scattering angles, a consequence of the oxygen and hydrogen atoms being at general positions and their large thermal vibrations. In conclusion the unpolarized neutron data provide excellent confirmation that the form of the extinction correction as given in equation (2) is valid for this material over a large range of extinction.

Polarized-neutron experiments

Polarized-neutron diffractometry provides a method of determining the ratio between the magnetic and nuclear structure factors M/N . The nuclear structure factor is determined by the positions and thermal motions of the atoms in the unit cell, and has been discussed in the previous section. For each reflection the magnetic structure factor is

$$M(hk.l) = 0.2696\mu f(\mathbf{k}) \times 2 \cos 2\pi(\frac{2}{3}h + \frac{1}{3}k + \frac{1}{4}l)e^{-W} 10^{-12} \text{ cm} \quad (3)$$

where μ is the magnetic moment per terbium atom, $f(\mathbf{k})$ is the magnetic form factor, \mathbf{k} is the scattering vector, and $W = B_{\text{Tb}} \sin^2 \theta / \lambda^2$ is the Debye-Waller factor for the terbium atom. The geometric factor reflects

In Table 3 the corrected and calculated nuclear structure factors have been tabulated for the $hk.0$ reflections with $\sin \theta / \lambda \leq 0.52 \text{ \AA}^{-1}$. $N_{\text{corr}} = N_{\text{obs}} / (S \times |y|)$, where N_{obs} is the observed nuclear structure factor, S

Table 3. *Observed nuclear structure factors corrected for extinction, N_{corr} , calculated structure factors N_c , and extinction factors y for neutron experiments*

$hk.0$	Unpolarized at 298°K $g = 6.3 \times 10^4$			Polarized at 2.6°K $g = 5 \times 10^4$			
	N_{corr}	$ N_c $	y	N_{corr}	N_c	y^+	y^-
10.0	1.95 (2)	1.918	0.20	-1.923 (3)	-1.937	0.106	0.776
11.0	0.72 (1)	0.756	0.55	0.730 (13)	0.781	0.112	0.159
20.0	0.17 (1)	0.151	0.96	0.194 (7)	0.187	0.337	0.283
12.0	1.54 (2)	1.486	0.38	-1.490 (7)	-1.531	0.211	0.930
21.0	2.39 (2)	2.302	0.26	2.321 (7)	2.342	0.792	0.171
30.0	3.76 (3)	3.592	0.18	3.697 (5)	3.702	0.109	0.877
22.0	0.65 (1)	0.668	0.72	-0.749 (12)	-0.737	0.351	0.217
13.0	2.06 (2)	2.018	0.33	-2.087 (8)	-2.075	0.231	0.778
31.0	0.66 (1)	0.684	0.72	-0.729 (10)	-0.751	0.353	0.765
40.0	1.53 (1)	1.512	0.44	-1.585 (6)	-1.531	0.299	0.944
23.0	0.43 (1)	0.505	0.84	-0.623 (7)	-0.619	0.452	0.861
32.0	3.74 (3)	3.560	0.21	-3.890 (37)	-3.835	0.177	0.315
14.0	3.01 (3)	2.950	0.26	3.122 (7)	3.156	0.168	0.687
41.0	1.17 (1)	1.218	0.54	1.397 (6)	1.391	0.249	0.767
50.0	0.83 (1)	0.824	0.70	-0.810 (6)	-0.838	0.459	0.988
33.0	0.23 (1)	0.211	0.97	0.161 (4)	0.194	0.392	0.457
24.0	1.42 (1)	1.386	0.52	1.468 (12)	1.433	0.854	0.387
42.0	0.19 (1)	0.156	0.98	0.091 (5)	0.063	0.858	0.809
15.0	0.86 (1)	0.813	0.74	-0.941 (10)	-0.870	0.457	0.988
51.0	2.22 (2)	2.201	0.36	2.197 (18)	2.269	0.559	0.300

the fact that the terbium atom is at the special positions $\pm(\frac{1}{3}, \frac{1}{3}, \frac{1}{4})$.

Using the polarized-neutron diffractometer at the CP-5 Research Reactor we have measured the flipping ratios of the first twenty Bragg reflections ($\sin \theta/\lambda \leq 0.52 \text{ \AA}^{-1}$). The incident neutron wavelength was 1.05 \AA . The sample was held in a field of 12.5 kOe applied parallel to the c axis, and the temperature of the sample was $2.6 \pm 0.2 \text{ }^\circ\text{K}$, at which temperature Tb(OH)₃ is ferromagnetic. Ideally the calculated flipping ratio is

$$R_c = (N + M)^2 / (N - M)^2 \quad (4)$$

for each reflection. Small corrections (usually less than 2%) have been made owing to incomplete neutron polarization and imperfect spin reversal (both 0.992 ± 0.003), but these are discussed elsewhere (*e.g.* Brown, 1970). Any possible half-wavelength contamination was reduced by a factor of 50 by using a ²³⁹Pu filter in the incident beam for all measurements.

The observed flipping ratios are given in Table 4. The errors quoted on R_{obs} are derived from a comparison of measurements on equivalent Bragg reflections, as well as from counting statistics. In contrast to measurements of integrated intensities the value of the flipping ratio can be obtained with very high precision (Nathans & Pickart, 1963; Nathans, Shull, Shirane & Andresen, 1959). Measurements on equivalent Bragg reflections agreed within the counting statistics in all cases. Furthermore, for several reflections the flipping ratio was measured as a function of the crystal rocking angle and was independent of the diffracted intensities. Multiple-scattering processes are often serious in polarized-neutron diffractometry (see *e.g.* Moon & Shull, 1964), but have not been observed in the present experiment.

On the basis of the results of the unpolarized-neutron data we anticipate that the correction for extinction will be very important in determining the structure factors from the observed flipping ratios given in Table 4. One approach is to use atomic and extinction parameters from the unpolarized-neutron experiment and determine the magnetic structure factor $M(hk.0)$. However, we will show that it is possible to obtain the atomic parameters, as well as the magnetic structure factors and the magnitude of the extinction correction, for each reflection from the polarized-neutron data alone. This method relies on the fact that $M(hk.0)$ is calculable, and that the differences between the observed and theoretical values of $M(hk.0)$ are likely to be small. A comparison between the atomic parameters determined independently from the two experiments provides a test of the analysis.

Magnetic measurements by Wolf, Meissner & Catanese (1968) have shown that Tb(OH)₃ becomes ferromagnetic at $3.7 \text{ }^\circ\text{K}$, with an ordered moment parallel to the c axis of $8.9 \pm 0.05 \mu_B$ per Tb atom, so the value of μ in equation (3) is known. As discussed in our companion paper, the magnetic scattering in this system is associated completely with the terbium atom. Under

Table 4. Flipping ratios for Tb(OH)₃ at $2.6 \text{ }^\circ\text{K}$

R_{obs} is the observed value. R_c is the calculated value based on the form factor of Fig. 2 and structural parameters in Table 1. R_{corr} is the observed value corrected for extinction with the Zachariasen formulae and $g = 5 \times 10^4$. To use the experimental numbers with equation (6) the instrumental corrections must be included, see Brown (1970).

$hk.0$	$\frac{\sin \theta}{\lambda}$	R_{obs}	R_c	R_{corr} ($g = 5 \times 10^4$)
10.0	0.092	16.0 (2)	67	64.8
11.0	0.159	1.427 (9)	2.1	2.01
20.0	0.184	0.810 (6)	0.69	0.68
12.0 } 21.0 } 30.0 }	0.244	25.2 (9)	77	66
22.0 } 13.0 } 31.0 }	0.276	0.087 (2)	0.024	0.022
23.0 } 32.0 } 14.0 }	0.319	27.1 (4)	84	86
40.0 } 24.0 } 33.0 }	0.332	0.573 (5)	0.36	0.356
42.0 } 15.0 } 51.0 }	0.332	7.62 (11)	24	22.4
44.0 } 25.0 } 34.0 }	0.368	4.43 (12)	9.7	9.21
46.0 } 26.0 } 35.0 }	0.401	21.9 (6)	59	50.3
48.0 } 27.0 } 36.0 }	0.422	5.62 (15)	10	10.3
50.0 } 28.0 } 37.0 }	0.422	1.894 (13)	3.4	3.33
52.0 } 29.0 } 38.0 }	0.460	7.13 (6)	23	24.8
54.0 } 30.0 } 39.0 }	0.460	6.66 (8)	19	18.5
56.0 } 31.0 } 40.0 }	0.478	45.8 (2.3)	81	69
58.0 } 32.0 } 41.0 }	0.478	1.243 (6)	1.5	1.45
60.0 } 33.0 } 42.0 }	0.487	0.150 (4)	0.07	0.07
62.0 } 34.0 } 43.0 }	0.487	0.724 (13)	0.75	0.68
64.0 } 35.0 } 44.0 }	0.513	45.3 (3.7)	94	69
66.0 } 36.0 } 45.0 }	0.513	0.409 (4)	0.24	0.22

these conditions the magnetic form factor is a smooth function of $\sin \theta/\lambda$, provided that measurements are confined to the plane perpendicular to the moment direction, *i.e.* $hk.0$ reflections. The form factor is given by

$$f(\mathbf{k}) = \langle j_0 \rangle + c_2 \langle j_2 \rangle + c_4 \langle j_4 \rangle + c_6 \langle j_6 \rangle,$$

where the coefficients c_2 , c_4 , and c_6 are determined from the magnetic ground state of the $4f$ -electron configuration. In Tb(OH)₃ the ground state of Tb³⁺ has been determined by Wolf, Meissner & Catanese (1968) as the nearly pure doublet $|{}^7F_6 J_z = \pm 6\rangle$. The coefficients c_2 , c_4 , and c_6 are 0.3704, -0.0833 , and 0.0116 respectively. The $\langle j_n \rangle$ integrals are spherical Bessel transforms of the $4f$ one-electron radial density, and theoretical values are tabulated by Blume, Freeman & Watson (1962, 1964). The difference between the theoretical form factor and that measured is expected to be small. As an illustration of this point, we have drawn in Fig. 2, the theoretical form factor, and two experimental ones for terbium, that for terbium metal in the fully ordered state, and (anticipating the conclusions of this study) that for Tb(OH)₃. The last quantity to be considered in evaluating equation (3) is the Debye-Waller factor for terbium below the Curie temperature (*i.e.* $T < 3.7 \text{ }^\circ\text{K}$). For terbium metal at $4.2 \text{ }^\circ\text{K}$ Steinsvoll *et al.* (1967) used a value of 0.12 \AA^2 . With the assumption that the $4f$ magnetization density moves rigidly with the terbium nucleus the effect of Debye-Waller factor for Tb partially cancels in the polarized-neutron experiment. Furthermore, the range of $\sin \theta/\lambda$ is small. We have therefore fixed B_{Tb} at 0.2 \AA^2 .

In column 4 of Table 4, we have tabulated R_c , the calculated flipping ratios, derived from our knowledge of N and M as discussed above. Clearly R_c and R_{obs} are in very poor agreement. The agreement is so bad, in fact, that R_c is never within 4σ of R_{obs} . Another way to illustrate the severity of the extinction is to derive $(M/N)_{\text{obs}}$ from R_{obs} , assuming no extinction, and then use equation (3) to solve for $(\mu f)_{\text{obs}}$. The results are plotted in Fig. 3. The solid curve is the same form factor as in Fig. 2, but normalized to $9\mu_B$. Recall that we expect the (μf) values to lie very close to this curve. The precision of the polarized-neutron method is demonstrated in this Figure since, in most cases, the error bars are smaller than the points drawn, but the absolute values of the $(\mu f)_{\text{obs}}$ are clearly nonsense. The discrepancies between the experimental points and the

smooth curve are due to extinction. Of particular interest is the scatter of the points both above and below the smooth curve. The effect of extinction is to give a smaller diffraction cross section than the true value. For the polarized-beam technique, this results, in the case of $M > N$, in a larger apparent M/N value, since, according to equation (4), R is decreasing as M/N increases. The reverse, of course, is true for $M < N$.

Using the Zachariasen formulae the expression for the flipping ratio in equation (4) may be corrected for extinction by

$$R_{\text{obs}} = \frac{(N+M)^2 y^+}{(N-M)^2 y^-} \quad (5)$$

where the factors y^+ and y^- refer to the attenuation of the intensity in the two spin states. In equation (2) y^+ requires $(N+M)^2$ substituted for N^2 in Q , and y^- requires $(N-M)^2$. The Zachariasen formula in principle refers to integrated intensities, whereas the measurements with the polarized-beam method are of peak intensities. However, as noted above, no variation of R_{obs} occurs across the diffraction profile and hence equation (5) is a valid use of the Zachariasen correction. Equation (5) leads to the concept of a flipping ratio R_{corr} , and a corresponding $(M/N)_{\text{corr}}$, that have been corrected for extinction, thus

$$R_{\text{corr}} = R_{\text{obs}} \times (y^-/y^+) \quad (6)$$

Equation (6) cannot be solved directly for $(M/N)_{\text{corr}}$, because the extinction corrections themselves contain these terms, but may be solved readily by an iterative procedure. To analyze the observed flipping ratios the following procedure was adopted. First, a theoretical magnetic form factor, and hence a set of $M(hk.0)$, was assumed. Second, an extinction parameter and a form for the extinction [e.g. equation (2)] was chosen. Using equation (6) values for $(M/N)_{\text{corr}}$ may be found, and hence values for N_{corr} , since we have assumed a set of M . The resulting set of nuclear structure factors may then be used in refining the structural parameters with

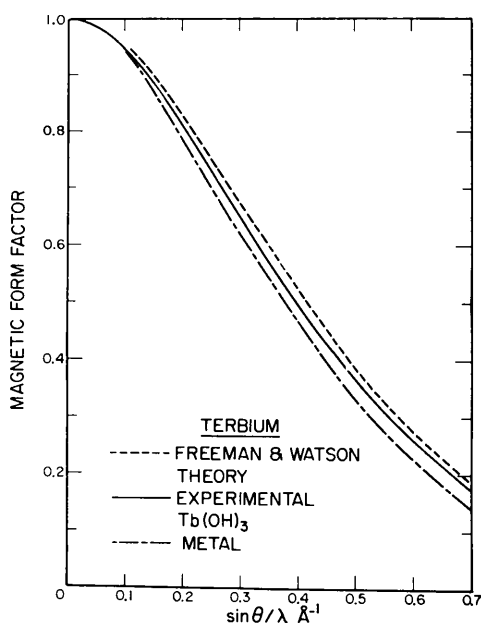


Fig. 2. Magnetic form factors of terbium in the ordered state.

Table 5. Structural parameters for $\text{Tb}(\text{OH})_3$, deduced from polarized-neutron experiments at 2.6°K , with various values of the extinction parameter used to correct the data

All parameters, except B , R , and g expressed $\times 10^4$. The refinements have used the experimental form factor in Fig. 2 and a scale factor of unity.

g ($\times 10^4$)	$y = \frac{1}{(1+2x)^{1/2}}$	5	7	$y = \frac{\tan^{-1} \sqrt{3}x}{\sqrt{3}x}$	$y = \frac{1}{1+x}$
Oxygen					
x	3105 (7)	3107 (6)	3108 (7)	3106 (9)	3113 (31)
y	3960 (6)	3963 (6)	3965 (7)	3965 (8)	3962 (32)
B (\AA^2)	0.31 (6)	0.49 (6)	0.59 (7)	0.54 (11)	0.1 (4)
Hydrogen					
x	1417 (11)	1418 (10)	1420 (11)	1423 (13)	1402 (52)
y	2764 (10)	2773 (9)	2779 (10)	2772 (12)	2783 (54)
β_{11}	59 (17)	65 (15)	67 (17)	60 (23)	103 (100)
β_{22}	100 (20)	113 (18)	119 (21)	105 (25)	84 (96)
β_{12}	4 (16)	8 (15)	16 (17)	12 (21)	-30 (80)
R	0.022	0.022	0.025	0.025	0.070

a conventional least-squares routine. This refinement does not, of course, include the extinction as a parameter, since this aspect is dealt with in using equation (6) to derive the set of N_{corr} .

In the analysis sets of N_{corr} were calculated for several values of g using both the Freeman & Watson (FW) and the metal form factors in Fig. 2. A shallow minimum in the residual was found with $g = 5 \times 10^4$. Ideally the scale factor used in these refinements should be unity ($S = 1$), but the best fit between SN_{calc} and N_{corr} derived with the FW form factor was obtained with $S = 1.03$ (1). A similar analysis using the metal form factor gave $S = 0.93$ (1). The variation of S from unity reflects the scaling nature of the form factor; for example the FW form factor would result in a good fit with $S = 1$ if the magnetic moment was $8.6\mu_{\text{B}}$ ($= 8.90/1.03$). Since the correct magnetic moment is 8.90 (5) μ_{B} , the third form factor in Fig. 2 was constructed to give a scale factor of unity. The final parameters for a number of g values are given in Table 5. We have also tried the expressions $y = \tan^{-1} |3x|/3x$ and $y = (1+x)^{-1}$, where $x = gQT$, for the extinction. The arctan form is suggested as an alternate by Zachariassen (1967), and, as judged by the residual, is equally as good as $y = (1+2x)^{-1/2}$, provided g is increased to 12×10^4 . The form $y = (1+x)^{-1}$ is inadequate but the best fit is with $g = 0.8 \times 10^4$. With $y = (1+2x)^{-1/2}$, the best fit is with $g = (5 \pm 1) \times 10^4$, in good agreement with $(6 \pm 1) \times 10^4$ as found in the unpolarized-neutron experiment. The structural parameters at 2.6 K (Table 5) are also in excellent agreement with those at room temperature (Table 1). The results of including anisotropic temperature factors in the analysis of the polarized-neutron data are summarized in Table 2. For the hydrogen atom the inclusion of these effects is significant; indeed the thermal anisotropy is increased at 2.6 K compared to the values at room temperature. As expected, the direction of the major thermal motion of the hydrogen atom in the xy plane remains perpendicular to the O-H bond. The thermal vibrations of the oxygen atom are isotropic at 2.6 K. In Table 3, the N_{corr} values determined from the polarized-neutron experiment at 2.6 K are tabulated with the corresponding N_c values calculated with the structural parameters of Table 5. The values of y^+ and y^- are also given. When compared to the results from the unpolarized-neutron experiments, the N_{corr} values determined with the polarized-neutron technique have an increased precision, and have their sign determined. For most reflections knowing the sign is not important, but the additional information may be especially useful for weak Bragg reflections.

As a final step the structural parameters of Table 5 may be used to calculate the nuclear structure factors, and R_{obs} may be reprocessed to obtain R_{corr} , and hence M_{corr} . These values of R_{corr} are given in Table 4, and are in good agreement with R_c . Another way to represent the data is to plot $(\mu f)_{\text{corr}}$ versus $\sin \theta/\lambda$, and this is done in Fig. 4. The extent of our success in accounting

for extinction in $\text{Tb}(\text{OH})_3$ with the Zachariassen formulae may be measured by how close the $(\mu f)_{\text{corr}}$ points in Fig. 4 are to the smooth curve. The improvement over Fig. 3 is remarkable.

Small deviations of the experimental points from the curve in Fig. 4 occur for some of the reflections that have very small nuclear structure factors. In particular, the 42.0 reflection has $(M/N)_c = -13.8$, and N must be known accurately before $(\mu f)_{\text{corr}}$ can be calculated reliably. At this level of accuracy inadequacies in the description of the atomic structure (for example, the model used for the thermal vibrations of the hydrogen atom is probably inaccurate) become evident, but investigations of such effects should be made on crystals with less extinction.

Conclusions

In the present study we have found the simple Zachariassen formulae totally adequate in accounting for very severe extinction both in a conventional integrated-intensity measurement, and in a more demanding polarized-neutron experiment on $\text{Tb}(\text{OH})_3$. In the polarized-neutron experiment the precision of the measurements is extremely high, and the effects of extinction are very important (see Table 4). A further advantage of the polarized-neutron experiments is that the scale factor often may be eliminated in evaluating the extinction. Uncertainties in the overall scale factor are difficult to eliminate in integrated-intensity measurements, and in the final least-squares analyses the

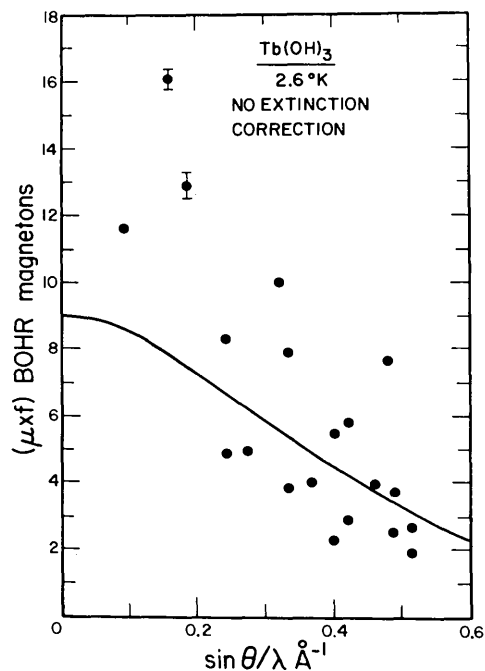


Fig. 3. Values of $(\mu f)_{\text{obs}}$ from polarized-neutron experiment on $\text{Tb}(\text{OH})_3$ at 2.6 K. No extinction correction has been applied. The solid curve is as in Fig. 2. The experimental uncertainty is the size of the point unless otherwise indicated.

scale factor is always highly correlated with the extinction parameter. The single parameter g that is used in accounting for the extinction [see equation (2)] is the same in both experiments.

A number of further experiments are suggested by the results reported here. X-ray integrated-intensity measurements should also reflect the large extinction in $\text{Tb}(\text{OH})_3$ crystals. The variation of extinction with incident neutron wavelength could be measured with either polarized or unpolarized neutrons. The use of the Zachariasen formula in equation (5) has an interesting consequence in measuring very small values of M/N , a situation frequently encountered in polarized-neutron experiments. If $M \ll N$ then equation (4) yields $R \approx 1 + 4M/N$. If the extinction is severe (e.g. when the crystal is large) all the forms suggested by Zachariasen give $y^+/y^- \approx 1 - 2M/N$. The result, therefore, is that $M_{\text{corr}} \approx 2M_{\text{obs}}$. The assumption is sometimes made that, if the magnetic scattering amplitude is small, the extinction cancels when measuring the ratio of two cross sections with polarized neutrons. The above consideration shows that such an assumption may lead to a value for the magnetic scattering amplitude that is wrong by a factor of two. Conversely this limit, and by implication the Zachariasen theory, could be tested by measuring the flipping ratio on a Bragg reflection with a known small value of M from a large single crystal (e.g. iron, cobalt, or nickel). The results would be of particular interest to experimentalists presently involved in measuring small magnetic cross sections in high-field superconducting magnets with polarized neutrons.

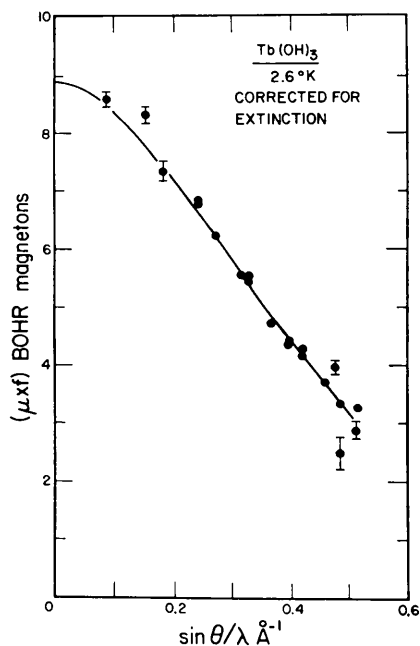


Fig. 4. Values of $(\mu f)_{\text{corr}}$ from polarized-neutron experiment on $\text{Tb}(\text{OH})_3$ at 2.6 °K. The data have been corrected for extinction as described in the text. The solid curve is the best fit to the data.

Finally, the physical origin of the extinction in the present experiment remains obscure. In both Types I and II, as discussed by Zachariasen (1967), the diffraction profiles should be sharp when the extinction is severe. However, for the $\text{Tb}(\text{OH})_3$ crystal the diffraction profiles are much broader than the instrumental resolution, and this suggests that the extinction is primary rather than secondary. Assuming spherical domains the domain radius is 0.008 cm. For primary extinction, no dependence on path length should be observed. Unfortunately in the present experiment the path lengths \bar{T} do not vary sufficiently to test this model.

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